

Folds in floating membranes: from elastic sheets to granular rafts

Etienne Jambon-Puillet

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présentée par

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Sujet de la thèse :

Membranes plissées à la surface de l'eau: des films élastiques aux radeaux granulaires

soutenue le 03 Octobre 2016

devant le jury composé de :

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Notations

Symbol	Description	
$\partial_X^n Y$	n^{th} derivative of the function Y with respect to the variable X, for	
	functional derivative standard notation will be used	
$\mathrm{d}X$	Infinitesimal variation of the variable X	
δX	Uncertainty on X	
\overline{X}	Complex conjugate of X	
\widehat{X}	Fourier transform of X	
\overrightarrow{V}	Vector V	
(x,y,z)	Cartesian coordinate, x is the main direction (along the length), y	
	is direction where buckling occurs (along the thickness), z is the	
	transverse direction (along the width)	
$(\overrightarrow{e_x}, \overrightarrow{e_y}, \overrightarrow{e_z})$	Unit vectors of the Cartesian coordinate	
(s, θ)	2d Curvilinear coordinate, s is the arc length, θ is the angle between	
	the local tangent and the x axis	

iv

Contents

Notations				
Introduction 1				
1	Cor	Compression of heavy floating elastic sheets		
	1.1	Introduction	13	
		1.1.1 State of the art: the first and only non linear experimental study	14	
		1.1.2 State of the art: following theoretical work	15	
		1.1.3 Our contribution	18	
	1.2	Results	18	
		1.2.1 Experiment and general results	18	
		1.2.2 Wrinkles	22	
		1.2.3 Wrinkle to fold transition and fold before self-contact	25	
		1.2.4 Evolution of the fold after self-contact	32	
		1.2.5 Reversibility of the folding process	38	
	1.3	Conclusion	40	
2	Cor	npression of granular rafts	43	
	2.1	Introduction	43	
		2.1.1 Buckling of particle laden interfaces	44	
		2.1.2 The granular rafts	47	
		2.1.3 Our contribution	49	
	2.2	Experiment and general results	50	
		2.2.1 Wrinkles	54	
		2.2.2 Fold before self-contact	59	
		2.2.3 Fold after self-contact	72	
		2.2.4 Limits of the elastic model and open questions	82	
	2.3	Conclusion	94	
3	Dro	ops floating on granular rafts	95	
	3.1	Coalescence vs flotation	95	
		3.1.1 Inhibiting coalescence	95	
		3.1.2 Experiment and results	98	
	3.2	Floating drop shape and raft deformation	102	
		3.2.1 Droplet shapes on various substrates	102	
		3.2.2 Experiment	104	

	$3.3 \\ 3.4$	3.2.3 Results 106 Potential applications 117 Conclusion 122	5 7 2	
Conclusion 123				
\mathbf{A}	She	et production and analysis 127	7	
	A.1	Sheet production	7	
	A.2	Sheet properties	3	
		A.2.1 Sheet thickness	3	
		A.2.2 Tensile test	3	
		A.2.3 Beam deflection $\ldots \ldots 130$)	
		A.2.4 Swelling and boundary condition	L	
в	Hea	vy Elastica model 133	ł	
Ľ	B 1	The Euler-Bernoulli beam theory		
	B.2	The heavy Elastica	5	
_	_			
С	Fou	rier transform profilometry 137		
	C.1	Principle	7	
	C.2	Limitations and adjustments for granular rafts)	
		C.2.1 Limitations \dots 139)	
	C a	C.2.2 Adjustments for granular rafts)	
	C.3	Practical application	2	
D	Part	ticle characterisation 147	7	
	D.1	Shape	7	
	D.2	Contact angle	3	
Bibliography 151			L	

comme tout commence dans le pli de la citation [...], le dedans du texte aura toujours été hors de lui, dans ce qui semble servir de « moyens » à l'« oeuvre »

Jacques Derrida, La Dissémination, p384

Introduction

Foreword

A fold is usually defined as the shape produced when a flexible and relatively flat object is bent over on itself, such that one part of it covers another. In the everyday language, wrinkles are numerous folds on a piece of fabric or on the skin and a crease is the mark left on an object that has been folded. These topological structures are familiar to all of us as we frequently see them in our daily lives. From the skin that forms on hot milk and folds up when we push it away, to the wrinkles that appear when you wrap your lunch with cling film, folded structures are unavoidable. They are present in a wide range of length scales both in Nature and in man-made products. We can see them on living systems like dry fruits, insect wings, brains, plant leaves or pollen grains as well as on inert objects like the buckling of train rails or geological strata (Fig 0.1), in metal oxide layers, carbon nanotubes or lava flows. In science fiction, even space-time itself can fold to form wormholes, allowing the characters to travel faster than light. Folds are also very common in arts to create complex structures (Fig 0.1) and textures and the word fold is associated to various concepts in contemporary philosophy, such as the identity or the inside and the outside.

In natural sciences, wrinkles and folds are usually associated with the buckling of a slender structure embedded in a matrix, under a compressive load. As soon as one exceeds a threshold load, the structure bends itself sinusoidally over its whole length. This deformation is called wrinkles and evolves as compression increases. It localises in regions of high curvature called folds. In the past, buckling usually meant the failure of mechanical structures and studies focused on the threshold loads to avoid it. More recently, there has been a renewed interest in taking control of elastic instabilities to obtain materials with unconventional properties. Moreover, many scientists are interested in the morphogenesis of landscapes and biological tissues where folds are naturally present. As a result, many fundamental and applied studies have looked at the wrinkling instability in the past decade, but much less work has been done on folds. The localisation of wrinkles into folds involves large deformations and non linear equations. Therefore, the literature on the subject usually considers simple geometries and only elastic materials. Nonetheless, folds are observed on all sorts of geometries and in complex materials such as biological membranes, foams, surfactant monolayers or particle covered interfaces. For such materials a simple elastic description is not straightforward, especially for discrete materials. What is the physical mechanism leading to wrinkles and folds?



Figure 0.1: Top left: Paint wrinkles on the surface of a dustbin. Photo: Jessica Rosenkrantz¹. Top right: Geological fold at Cap de Creus. Photo: I.E. van Gelder². Bottom: Forms in Succession #5, porcelain sculpture, Shegekazu Nagae³.

The objective of this thesis is to study experimentally and theoretically wrinkles, but also and above all folds in a model particle laden fluid interface that we call a "granular raft". Before this work, many properties of these granular rafts have been described by continuum mechanics models despite the evident discrete nature of these objects. Following this approach and the literature on wrinkles in particle rafts, we use the formalism developed for floating elastic plates to describe folds in granular raft. In particular we want to understand under which circumstances granular rafts can be described as elastic materials, and when this description fails. We expect our findings to provide a better understanding on the mechanical properties of all particle laden interfaces. As a result, this will contribute to the understanding of objects that consist in a collection of these interfaces such as "Pickering emulsions" or particle stabilised

¹http://n-e-r-v-o-u-s.com/blog/?p=6687

²http://geologicalnotes.weebly.com/photo-collection.html

 $^{^{3}}$ http://www.powerhousemuseum.com/insidethecollection/2015/05/japanese-folds-exhibition

BACKGROUND

foams. Moreover, we aim to improve the comprehension of folds in floating elastic plates by looking at effect that were neglected and regimes never explored experimentally.

In order to guide non expert readers, we first introduce some general concepts that are discussed throughout this thesis: buckling on foundations and the formation of wrinkles, and particles at liquid-fluid interfaces. We also give a brief literature overview to highlight the open questions that we address in the thesis, while the key articles are discussed in more details in the introduction of their corresponding chapter.

Background

Wrinkles

To observe wrinkles in a physical system, two basic ingredients are necessary: a slender structure (beam or plate) and a "foundation". In order to present the wrinkling instability gradually, we first look at the simpler case of a slender structure alone.

Buckling of slender structures

Under an external load a slender structure has two modes of deformation: bending and stretching. The first accommodates the load with an out of plane displacement of the structure, while the second accommodates it with an in plane displacement (Fig 0.2 a)) [1]. Let us consider a plate of length L_0 , width W and thickness t clamped on both ends. We impose a compressive displacement Δ on one end of the plate. To simplify the problem, let us assume the plate responds either with pure bending or pure stretching and its Poisson ration $\nu = 0$. The associated energies are:

$$U_{stretch} = \frac{Et}{2} \iint \left(\frac{\Delta}{L_0}\right)^2 dS \sim Et\Delta L_0 W$$
$$U_{bend} = \frac{Et^3}{24} \iint \mathscr{C}^2 dS \sim Et^3 \frac{\Delta}{L_0^2} W$$

Where E is the Young modulus and \mathscr{C} the curvature. If the plate is slender, *i.e.* $L_0 \sim W >> t$ then $U_{bend} << U_{stretch}$. In other words absorbing the imposed compression costs less energy through bending than stretching for slender structures. For a plate of given dimensions, the thinner it is the more favourable bending is. This leads to the description of slender structures as incompressible, because stretching is usually negligible. It greatly simplifies the description of slender structures and usually gives very good results. If the incompressible assumption does not hold (for very large deformations or moderately slender structures) one has to treat both bending and stretching. This leads to the complicated system of Föppl-von Kármán equations [1]. We now come back to our slender, thus incompressible, plate whom is subject to a compressive displacement Δ . The only possible response being bending, the plate will have an out of plane displacement to accommodate the in plane compression. This is called "buckling" and was first studied by Leonhard Euler in the 18th century for the buckling of columns. The buckling of incompressible slender structures under compressive forces is nowadays called the Euler's Elastica theory.



Figure 0.2: a) Schematic of the two modes of deformation for a compressed beam: stretching and bending. b) Schematic of the Euler's Elastica. The Cartesian (x, y) and the intrinsic coordinates (s, θ) are drawn.

Let us look briefly at the main results of the Elastica theory. To do so we use the Euler-Bernoulli beam theory (see appendix B). We consider a plate of dimensions (L_0, W, t) subject to an external load P (Fig 0.2 b)). We introduce the Cartesian coordinates (x, y) and the intrinsic coordinates (s, θ) where $\theta(s)$ is the local angle between the beam and the x axis and s is the arc-length. The equilibrium equation of the beam is obtained through a force and moment balance (appendix B) or an energy minimisation under the inextensibility constraint.

$BW\partial_s^2\theta + P\sin\theta = 0$

Remark (Pendulum analogy). If we replace the arc-length s by time, the equilibrium equation of the Elastica becomes exactly the classical pendulum equation. Many features are thus common in both systems [2], and knowledge of the pendulum can help to solve Elastica on foundation problems [3, 4].

Here B is the bending stiffness per unit width (for a plate): $B = \frac{Et^3}{12(1-\nu^2)}$. To find the critical buckling load, we can linearise this equation for small deformations, *i.e.* $\sin \theta \approx \theta$. The solutions of the linearised equation are a combination of sine and cosine of wavenumber $\sqrt{\frac{P}{BW}}$. Accounting for the boundary conditions gives the buckling threshold. For the clamped-free boundary conditions in Fig 0.2 b): $(\theta(0) = 0, \partial_s \theta(L_0) = 0)$, we obtain $P_c = BW \left(\frac{\pi}{L_0}(n+\frac{1}{2})\right)^2$ where n is a natural number that selects the mode. Below the buckling load, the only possible solution that satisfies the boundary conditions is $\theta(s) = 0$, *i.e.* the plate remains undeformed (flat). This odd situation comes from the inextensibility hypothesis, in a real structure this load is absorbed through pure stretching, but as soon as one goes above $P_c(n = 0)$ the plate buckles out of plane over its entire length and absorbs the load via pure bending. Everyone has done this experiment, for instance with a sheet of paper or a ruler, and observed the shape taken by the object. The wavelength is selected by the system size, and the structure always buckles in the first mode (n = 0), *i.e.* with a wavelength $\lambda = 2L_0$ and an out of plane displacement A of very large amplitude like in Fig 0.2 a). Although higher order modes are theoretically possible, they are not seen in static experiments because they require higher loads. As a result, we cannot produce wrinkles with a slender structure alone.

To see wrinkles, *i.e.* a buckling of higher order (smaller wavelength and amplitude) which is not governed by the system size alone, a slender structure must be associated

with a "foundation". The term foundation here should not be taken too literally as it describes anything that restrains the slender structure and prevents the formation of low order modes.

Buckling on a foundation

The simplest theoretical foundation we can consider is a purely elastic foundation or Winkler foundation [1, 5, 6]. It consists of a series of infinitesimal springs of stiffness Kthat connect the beam to another object which is usually undeformable (Fig 0.3). The energy has now two contributions: the bending energy of the beam and the stretching energy of the foundation. If we come back to our slender structure under compression, minimising the energy will lead to a competition between the two terms. The beam wants to bend with the largest possible amplitude while the elastic foundation wants to make the smallest possible amplitude. The system has to make a compromise and select an intermediate deformation.



Figure 0.3: Schematic of a beam resting on an elastic foundation. The foundation is modelled as a bed of infinitesimal springs.

About a decade ago Cerda and Mahadevan [7] generalised the notion of elastic foundation and applied it to qualitatively explain all sorts of wrinkling pattern. Any energy term that scales as $U \sim \frac{1}{2} \iint Ky^2 \, dS$ at the linear order will produce wrinkles of wavelength and amplitude:

$$\lambda \sim \left(\frac{B}{K}\right)^{1/4} \qquad A \sim \lambda \left(\frac{\Delta}{L_0}\right)^{1/2}$$

Here K is the effective stiffness of the effective "foundation". In their paper they stretched thin elastic plates in the z direction and wrinkles appeared in the x direction. Their effective foundation comes from the stretching energy in the z direction. But physical foundations also have similar energetic terms. It is straightforward for a bed of spring like Fig 0.3 but it can also be applied to more realistic foundations. In the general case we have [8]:

$$U_s = \frac{1}{2} \int W K u_s \mathrm{d}s$$

Where Ku_s is the deformation energy of an infinitesimal part of the substrate that has to be determined. In the case of Cerda and Mahadevan [7] $Ku_s = T(\partial_x y)^2$ which gives a wavelength $\lambda \sim \left(\frac{BL_0^2}{T}\right)^{1/4}$. If the plate lies on a liquid foundation then the restoring force comes from the fluid gravitational energy. For every element ds of the plate the

fluid energy will be:

$$KWu_s ds \equiv dU_{fluid} = \int d(mg) dy' = \int (\rho g W dxy') dy'$$
$$= \frac{1}{2} W \rho g y^2 dx = \frac{1}{2} W \rho g y^2 \cos \theta ds$$

Hence $K_{fluid} = \rho g$ and the wavelength is $\lambda_{fluid} \sim \left(\frac{B}{\rho g}\right)^{1/4}$. If the foundation is an elastic solid, then the energy is more complicated [9]. But if you assume the elastic foundation is stretched only over a distance λ below the beam then $K_{elastic} \sim E_s/\lambda$ with E_s the substrate's Young's modulus [7]. This gives a wavelength $\lambda_{elastic} \sim t \left(\frac{E}{E_s}\right)^{1/3}$. This formalism is very powerful and gives us a very general understanding of the wrinkling phenomenon. It is worth mentioning the case of a viscous layer sandwiched by another viscous fluid [10]. The equilibrium equations are similar and predict a wrinkling instability of wavelength $\lambda \sim t \left(\frac{\eta}{\eta_s}\right)^{1/3}$ where η and t denote the viscosity and the thickness of the layer and η_s denote the viscosity of the surrounding fluid. This relationship is useful in geology to explain the folding of geological strata [11–13].

Literature overview

As described above, there are three classical methods to produce wrinkles. One can put a thin elastic sheet under tension, one can compress a stiff and thin elastic sheet glued on a soft elastic solid or inserted inside a soft elastic matrix; finally, one can compress a thin elastic sheet floating at a fluid-liquid interface. Although there is a literature on wrinkles induced by tension (*e.g.* [7, 14, 15]), we focus on soft elastic substrates. We also mention studies on liquid substrates, but we keep the key articles for the introduction of chapter 1.

To produce stiff and thin sheets on elastic substrates, the surface of an elastomer can be stiffened with chemical modifications [16] or a thin stiff elastomer can be glued to a softer compatible elastomer [17]. The procedure is usually done while the bulk elastomer is under tension, such that releasing this tension produces wrinkles. Depending on the applied stress and geometry the surface wrinkles in various modes: stripes, hexagonal, herringbones, labyrinth, ... [18–20] (Fig 0.4). Wrinkles on elastic substrates have found many applications (see [21] (2006) for a review). To cite a few examples, wrinkles can make adhesives surfaces [22], hydrophobic antibacterial surfaces [23], microlenses [24] or enhance light harvesting [25]. Similar models have been used by the morphogenesis community as the differentiated growth of biological tissues induces stresses that produce wrinkles. The most striking example being the formation of the brain structure [26], but it can also be applied to the gut formation [27] or simply on skin wrinkles [7]. More recently people started to look at the behaviour of these systems under large strains and discovered a rich variety of phenomena: period doubling [9], folding/creasing [28, 29] and delamination [30, 31]. These non linear behaviours are more complex. A unified description is still lacking as most studies focus on particular cases and the control of these non linear structures remains difficult.

BACKGROUND



Figure 0.4: **a)-d)** Pictures of the different wrinkling mode observed for elastic supported sheets. Source: [18, 19]. **e)-g)** Picture showing the period doubling at high compression. Compression increases from e) to g). Source: [8].

We now turn to the liquid substrate literature. In a typical experiment an elastic sheet is deposited on a liquid (usually water) and the sheet is compressed to trigger the instability. Various modes of compression have been studied: direct uniaxial compression [32, 33], capillary induced compression with a drop [34–36] or with surfactants [37], indentation [38, 39], viscous [40] or pressure [41] induced stresses. Even though folds are regularly observed, most of these studies focus on small strains and analyse only the wrinkling pattern. An interesting thing to note is that wrinkles and folds can also be observed in other type of fluid supported materials such as biofilms [42], capsules [43, 44], foams [45], surfactants [46-48] and particle covered interfaces [32, 49, 50] (Fig 0.5). But again the analysis (if there is one) is usually restricted to the wrinkling pattern. The experimental limitation of many of these studies is that they only look from above, under a microscope for instance. By doing so they can measure a wavelength and try to predict it, but to study folds, which are isolated objects, they need to measure either the fold size, its shape or the loads associated with it. These measurements are difficult on small or complex objects and typically requires profilometers or custom force sensors. Moreover, folds are highly non linear structures and their theoretical analysis is difficult. As a result, the literature on folds in fluid supported objects is limited to the very simple case of a rectangular elastic sheet floating on water compressed uniaxially (see chapter 1). Before we conclude this section, it is worth mentioning the case of thick sheets where delamination occurs at large strains [52]. On the other hand for ultrathin sheets [53], a different class of folding independent from the material properties occurs. the bending rigidity being negligible, the sheet folds itself to minimise the surface energy under the inextensibility constraint.



Figure 0.5: Top left: Biofilms produced by different bacteria floating on a culture medium after ~ 67 h, we can clearly see wrinkles (on A and B) and folds (B). Scale bar 1 cm. Source: [42]. Bottom left: Compressed monolayer of 2.6 μ m polystyrene particles at the octane-water interface. The first picture shows the initial corrugations which evolve into folds in the second picture as compression increases. Scale bar 100 μ m. Source: [51]. Right: Monolayer of surfactants at the air-water interface, compression increases from a) to c). The white dots are 1 μ m fluorescent particles added to visualize the fold. Scale bar 300 μ m. Source: [48]

Particles at interfaces

Particles laden interfaces are not as easy to see in everyday life. Nonetheless, they are present in our homes: in our shaving foam, in the "crema" of our espressos [54] or in our skin care products. They are also involved in the petroleum industry, during crude oil extraction. A century ago Ramsden [55] and Pickering [56] have been the firsts to think about using particles to stabilise emulsions and foams. Particles spontaneously migrate to liquid-fluid interfaces and modify their properties like surfactants [57, 58]. Nowadays an emulsion stabilised by solid particles is called a "Pickering Emulsion". Before describing the complex properties of particles covered interfaces, let us first see how they adsorb and aggregate to interfaces.

Particles adsorb to interfaces

Surfactants are amphiphilic molecules, *i.e.* they contain both a hydrophilic group (the "head" usually a polar/ionic group) and an hydrophobic group (the "tail" usually

BACKGROUND



Figure 0.6: Schematic of a solid spherical particle or diameter d and contact angle θ_y at a liquid-fluid interface.

a carbon chain). These molecules spontaneously adsorb to interfaces to minimise their energy. Solid particles have a similar behaviour, they adsorb to interfaces to minimise the system energy. Let us consider a solid spherical particle of diameter d and contact angle θ_y placed at a liquid-fluid interface. For the sake of simplicity we neglect line tension, contact angle hysteresis and gravity (Fig 0.6). The energy necessary to attach this particle to the interface is the surface energy of the particle wetted spherical caps, minus the surface energy of the particle in the upper (or lower) phase, minus the energy of the removed liquid-fluid interface. With some elementary geometry and trigonometry all the surfaces can be expressed with d and θ_y :

$$\Delta U_{adsorb} = \pi \frac{d^2}{2} (1 + \cos \theta_y) \gamma_{s/low} + \left(\pi d^2 - \pi \frac{d^2}{2} (1 + \cos \theta_y) \right) \gamma_{s/up}$$
$$- \pi d^2 \gamma_{s/up \ or \ low} - \pi \frac{d^2}{4} \sin^2(\theta_y) \gamma_{up/low}$$

Where $\gamma_{a/b}$ is the surface energy between compound a and b: s denote solid, up the upper fluid, low the lower fluid. If we now use the Young-Dupré relationship: $\cos \theta_y = \frac{\gamma_{s/up} - \gamma_{s/low}}{\gamma_{up/low}}$ we can simplify the energy to:

$$\Delta U_{adsorb} = -\pi \frac{d^2}{4} \gamma_{up/low} (1 \pm \cos \theta_y)^2$$

The sign in the brackets depends on whether you attach the particle from the upper or lower phase. We can immediately see that the energy variation is always negative, which means that whatever the contact angle, the particle will prefer to stay at the interface ΔU_{adsorb} depends on d and θ_y , if the particle prefers to be wet by the upper (respectively lower) phase the adsorption energy from the upper (respectively lower) phase will be weaker. However, outside of the range $0 < \theta_y$ (°) < 20 and $160 < \theta_y$ (°) < 180 the energy is very large and particles can be thought as irreversibly adsorbed. If we consider a colloidal particle of diameter $d = 1 \ \mu m$ and contact angle $\theta_y = 90^\circ$ at an air-water interface $\gamma = 72 \ mN.m^{-1}$ then $|\Delta U_{adsorb}| \sim 10^7 \ kT$, even nanoparticles of diameter $d = 10 \ nm$ are irremediably adsorbed. This shows that particles cannot be removed from the interface by thermal fluctuations. However, in this thesis we work with dense and large particles and in that case we cannot neglect gravity any longer. The surface energies still want to maintain the particle at the interface but now they have to overcome gravity instead of thermal fluctuations. The calculation to determine whether a particle will stay at the interface or sink is more complicated in that case because we must compute the deformation of the interface (see [59]). Nonetheless, the adsorption energy is very strong, such that millimetre sized object can stay at the interface despite a high density mismatch. The typical example being a metallic paper clip floating on water.

Particles aggregate at interfaces

When several macroscopic particles $(d \gtrsim 10 \mu m)$ are placed at a liquid interface, they will experience an attractive or repulsive force. Gravity being no longer negligible, the liquid interface around the particles is deformed. As soon as these deformations overlap, the system will try to minimise its energy and induce an attractive or repulsive force on the particles. This effect has been named the "Cheerios effect" by Vella and Mahadevan in their comprehensive paper on the subject [60]. More generally anything that deform the liquid interface, such as a wall creates a "capillary" force on a floating particle. The sign of this force (attraction or repulsion) depends on both the wetting properties and the density of the two interacting objects. Usually for identical particles this capillary force is attractive and this leads to particle aggregation. For two spherical particles at a planar interface, the force decays exponentially for small interfacial deformations: $F_{cap}(r) \sim -\sqrt{\frac{r}{\ell_c}} \exp\left(-\frac{r}{\ell_c}\right)$ where r is the distance between the particles and $\ell_c = \sqrt{\frac{\gamma}{\rho g}}$ is the capillary length ([61-63]). Once well controlled, this interaction can be used to self-assemble two dimensional complex structures (e.q. [64-66]). However, in specific cases several large and dense particles aggregated together may sink even if they all float individually [67, 68].

At the colloidal scale ($d \leq 10 \ \mu m$), the magnitude of this capillary force becomes negligible (it depends on the particle size and density). Nevertheless, colloidal particles can still aggregate as new physical phenomena arise like thermal fluctuation or van der Waals and electrostatic forces At this scale, particles mainly aggregate via collisions. A particle in the bulk is brought to the interface by thermal fluctuations, where it remains stuck. Then it diffuses, comes in contact with another particle and remains trapped in a potential well close to the other particle. This usually results in beautiful fractal clusters [69, 70].

Modification of the interface properties

With the help of these attractive forces, it is easy to cover completely an interface with particles. Once covered the interface behaves as a shell; it prevents coalescence between droplets (see chapter 3), and in the case of an emulsion, slows down Oswald ripening [71–73]. An interesting thing to note is that just like the Bancroft rule for surfactant stabilized emulsions, one can choose which phase will be dispersed in the other by tuning the particle hydrophobicity (via the contact angle) [74, 75]. This shell can also be used to encapsulate liquids. Indeed, a droplet covered with particles, the so-called "liquid marble" [76], can be manipulated like a solid bead. It provides a convenient way to transport small volumes of liquids [77, 78] and have found many applications as sensors, micro reactors or capsule templates (see [79] for a recent review).

Yet, the modifications of the interface does not boil down to steric effects. The effective surface tension γ_{eff} of particle covered interfaces has been measured both

for flat interfaces (e.g. [80]) and liquid marbles with various methods (summary here [81]). It seems that hydrophobic particles decrease the surface tension $(\gamma_{eff} < \gamma)$ while hydrophilic particles do not modify it. Particles also modify the rheology of the interface. Like a 3d suspension, as the particle surface fraction ϕ increases, the interface mechanical properties transition from liquid-like to solid-like. At low coverage the interface behaves like a liquid with an effective surface viscosity. This viscosity increases with ϕ and diverges as we approach jamming. Upon further increase of ϕ the rheology of the interface becomes solid-like [82, 83]. This transition is similar to the glass transition in polymers, except here the concentration plays the role of the temperature. In 2003, Cicuta et al. [82] have demonstrated this analogy. They have measured the rheological properties of particle covered interfaces (storage and loss moduli) as a function of the shearing frequency and packing fraction. They have shown that their data could be superposed in a master curve with a time-concentration superposition similar to the time-temperature superposition for polymers around the glass transition. This shows that particles at interfaces are soft glassy materials, with stress relaxation time scales that diverge as we approach jamming. Finally, there are striking evidences that particles at interfaces behave like elastic solids around the jamming transition. They can sustain anisotropic stresses [84], fracture under tension [85, 86] and they buckle/wrinkle under compression [49, 51, 81, 87–92] (Fig 0.7).



Figure 0.7: **a**) Picture of a bubble covered with polyamide particles. Thanks to the shell of particles, the bubble can sustain an elongated shape. Source [84]. **b**) Top and side view of an evaporating liquid marble. Compression increases from left to right. The interface buckles like a dented ping-pong ball. Source [81]

Nowadays, after the experimental evidences of solid like properties, it is rather standard to describe jammed particle covered interfaces as elastic materials (see chapter 2). However, other studies have shown phenomena that could not be explained by continuum mechanics models like Janssen effect [93], particle expulsion [87, 91, 94] or non elastic buckling [95–98]. It is not so clear under which circumstances continuum mechanics models are valid and when they are not. Moreover, all of theses studies look at the onset of buckling and do not explore large deformations. Several authors have reported folds in particle laden interfaces but to the best of our knowledge, no one has studied them. How they form and evolve with compression is still unknown.

Thesis organisation

The objective of this thesis is to study wrinkles and folds in granular rafts. The first challenge is to construct a buckling experiment that produces wrinkles and folds in a controlled manner and measures their characteristics (size, shape). Then we model the raft as an elastic sheet and confront this description to our data. By doing so we assess and enhance the continuum mechanics approach and determine its limits.

To understand wrinkles and folds in granular rafts, we first focus on the simple case of a dense floating elastic sheet in chapter one. In particular we experimentally study the influence of the sheet's own weight on the shape of the fold and include it in the floating elastic sheet model to understand these changes. We then compress the film beyond the point of self-contact and observe a new behaviour dependent on the film density: the single fold that forms after the wrinkle to fold transition forms a loop which encapsulates a cylindrical droplet of the upper fluid after self-contact. The encapsulated drop either causes the loop to bend upward or to sink deeper as compression is increased, depending on the relative buoyancy of the drop-film combination. We propose a model to qualitatively explain this behaviour.

In the second chapter we investigate the buckling of granular rafts. We start by presenting the experimental observations. Under compression the raft exhibits two distinct wrinkling patterns, then the deformation localises in a unique folds with a very peculiar shape until at some point it destabilises and sinks at the bottom of the tank. We analyse these results with the floating elastic plate model and show that it fails to describe the non linear regime. Then we introduce an alternative version of the heavy floating elastic plate model developed in the first chapter and discuss it in detail. We show that it can capture many features of the buckling instability. In particular the shape of the fold and the evolution of the fold size with compression is well reproduced by the model. This model is not suitable to study the shape of the fold after self-contact, but we show that it can describe the shape of rest of the raft away from the fold. Finally, we highlight the phenomena that we are not able to explain with the elastic description and show its limits. Further study of these phenomena could pave the way to enhance the mechanical description of granular rafts.

The third and last chapter deals with the interaction of a granular raft with a water drop. We show that when we deposit a water drop on top of a granular raft, depending on the particle size and contact angle, the drop either coalesces with the water bath below the raft or floats on it indefinitely. Then we vary the volume of floating drops and observe an interaction between the drop and the raft that produce unusual shapes. Finally, we discuss the possible applications of these floating drops.

There are four appendixes. The first describes how we produce and characterise our heavy elastic sheets. The second presents the Euler-Bernoulli beam theory and the derivation of the heavy Elastica model used in chapter one. The third is a review of Fourier transform profilometry and describes the technical challenges we have overcome to use it on granular rafts. The fourth deals with particle characterisation.

Chapter 1

Compression of heavy floating elastic sheets

Contents

1.1 Intr	oduction
1.1.1	State of the art: the first and only non linear experimental study 14
1.1.2	State of the art: following theoretical work
1.1.3	Our contribution
1.2 Res	ults
1.2.1	Experiment and general results
1.2.2	Wrinkles
1.2.3	Wrinkle to fold transition and fold before self-contact $\ldots 25$
1.2.4	Evolution of the fold after self-contact $\ldots \ldots \ldots \ldots 32$
1.2.5	Reversibility of the folding process
1.3 Con	clusion

This chapter studies the effect of the sheet density on the uniaxial compression of thin elastic sheets at a liquid-fluid interface. We first present the literature on weightless sheets that provide the basis for our analysis. Then we highlight the influence of the sheet's own weight experimentally and theoretically on all the phases of the experiment in their order of appearance: wrinkling phase, wrinkle to fold transition and fold phase up to very high compressions. We also briefly discuss the effects of surface tension acting on the edges of the sheet and the reversibility of the experiment.

1.1 Introduction

In the Introduction, we have seen how wrinkles form when a floating sheet is put under compression. Here we will discuss how wrinkles evolve into folds at high compressions.

1.1.1 State of the art: the first and only non linear experimental study

We start with the first study that explored the non linear behaviour of compressed fluid supported elastic sheets. Pocivavsek et al. [32] have shown with a simple system that the deformation spreads across the whole sheet at low compression (wrinkles) and then localises as compression increases (fold). This is the wrinkle to fold transition, a general process in buckling on foundation problems. They have also observed it in compressed floating gold nanoparticles and elastic sheets bound to gels and they suggested that it could be relevant in biological systems. The experiment is the following: they fill a tank with liquid (water, glycerol or mercury), they place an elastic sheet on the liquid surface (latex or polyester, the upper side is greased to make it hydrophobic), they clamp it on two opposite ends at 90° to the moving barriers, they move the barriers to compress uniaxially the sheet and image the deformation (schematic Fig 1.1 b)). Let us call L_0 , W and t the sheet initial length, width and thickness. By moving the barriers they impose a distance L between the two clamped edges: we call $\Delta = L_0 - L_0$ the compression. Fig 1.1 a) shows pictures of that experiment. As soon as Δ is positive, the sheet wrinkles along its whole surface with a wavelength λ (top picture). When the compression gradually increases, at first all the wrinkles grow uniformly, then one of them continues to grow while all the other shrink (middle picture). At high compression only one fold subsists while the rest of the sheet is flat (bottom picture). This is the wrinkle to fold transition.



Figure 1.1: Figure adapted from [32]. a) Polyester sheet on water, $(t = 10 \ \mu m, \lambda \approx 1.6 \ cm)$. b) Schematic defining the fold amplitude A_0 and its neighbouring wrinkle amplitude A_1 . c) Amplitude as a function of the compression for polyester on water sheets of different dimensionless sizes $(3.5 < N = L_0/\lambda < 8)$. Circles represent A_1 while squares represent A_0 , solid lines show numerical results for a sheet of length N = 3.5. Grey symbols show sheets that went through an antisymmetric configuration, black symbols are for sheets that stayed symmetric during the whole compression. Everything was made dimensionless by dividing lengths by λ .

In their study they completely solve the wrinkling regime with a linearised version of the model presented in section 1.1.2. They recover the scaling laws of Cerda and Mahadevan [7] on the wavelength of the wrinkles $\lambda = 2\pi \left(\frac{B}{\rho g}\right)^{1/4}$ and their amplitude $A = \frac{\sqrt{2}}{\pi} \lambda \sqrt{\frac{\Delta}{L_0}}$. The transition and the folding regime observed experimentally are anal-

ysed with numerical simulations (energy minimisation). Fig 1.1 c) show the amplitude measured experimentally as a function of the compression as well as the results of the numerical simulations. Once rescaled by the wavelength λ , all the data collapse on a master curve. Around $\Delta_c/\lambda \approx 0.3$, the amplitude of the main wrinkle becomes significantly higher than the amplitude of its neighbours. Moreover, the amplitude starts to deviate notably from the linear analysis prediction, this is the wrinkle to fold transition. For $\Delta_c/\lambda > 0.3$ the amplitude of the fold becomes linear $A_0 \sim 0.5\Delta/\lambda$ and is captured by the numerical simulations. Finally, they propose a scaling analysis to derive the energy of the sheet and the pressure needed on the side to compress it.

The experimental study from Pocivavsek *et al.* [32] gives very good insights in the floating Elastica problem but many questions remains unanswered. Firstly, a theoretical description of the transition and the fold regime is still lacking. Moreover, they numerically see two configurations depending on the dimensionless sheet length $N = L_0/\lambda$, upward and downward symmetric configuration when N is a half integer, two anti symmetric configurations when N is an integer (see Fig 1.2 a)). But experimentally they see antisymmetric solutions only at low compressions, the sheet always evolves toward a symmetric solution (mainly downward) at higher compressions. They also do not look at very high compressions, after both sides of the fold touch each other and reach self-contact. Finally, they neglect in their analysis (in agreement with their experimental system) the sheet weight and the liquid surface tension.

1.1.2 State of the art: following theoretical work

A few years later Diamant and Witten [3] have derived the complete equation for a floating incompressible elastic sheet of infinite length (without weight and surface tension). The model is the following: they consider an incompressible elastic sheet of infinite length, width W and bending modulus BW lying on a liquid of density ρ . The sheet is uniaxially compressed in the x direction. They introduce the intrinsic coordinates (s,θ) , where θ is the angle between the sheet and the horizontal axis and s is the arc-length; the sheet centreline is then parametrized in terms of arc-length, [x(s), y(s)] (Fig 1.5). The energy U of the sheet contains contributions from bending $U_b = \frac{BW}{2} \int_{-\infty}^{\infty} (\partial_s \theta)^2 \, ds$ and from the underlying fluid substrate $U_s = \frac{\rho g W}{2} \int_{-\infty}^{\infty} y(s)^2 \cos \theta \, ds$. They perform an energy minimization under the inextensibility constraint with the boundary conditions $\theta(\pm \infty) = \partial_s \theta(\pm \infty) = y(\pm \infty) = 0$. This yields a single equation for the intrinsic angle $\theta(s)$ that completely define the profile (See section 1.2.3 or [3] for the detailed procedure):

$$\partial_s^4 \theta + \left(\frac{3}{2} \left(\partial_s \theta\right)^2 + P\right) \partial_s^2 \theta + \sin \theta = 0$$

Everything was made dimensionless by dividing all lengths by $\ell_{eh} = \left(\frac{B}{\rho g}\right)^{\frac{1}{4}} = \frac{\lambda}{2\pi}$ and energies by $\frac{WB}{\ell_{eh}}$. Here *P* is the Lagrange multiplier associated with the inextensibility constraint, and corresponds physically to the dimensionless horizontal force (rescaled by $W\sqrt{B\rho g}$) applied on the elastic sheet by the compression. By analogy with the pendulum equation, they have found two analytical solutions represented on Fig 1.2 a). It has been shown in 2013 that this equation has a family of analytical solutions distinguished by the parameter φ which selects the symmetry of the profile $(0 \le \varphi \le \frac{\pi}{k})$



Figure 1.2: Figure adapted from [3, 4]. a) Dimensionless symmetric and antisymmetric solutions (respectively $\varphi = 0$ and $\varphi = \pi/2k$) as compression is increased down to self-contact. The curves are vertically shifted for clarity. b) Dimensionless profiles of a folded sheet (P = 1) as $k\varphi$ is varied from 0 (black) to $\pi/2$ (red).

[4, 99]:

$$\theta(s) = 4 \arctan\left(\frac{\kappa \sin(k(s+\varphi))}{k \cosh(\kappa s)}\right)$$

$$k = \frac{1}{2}\sqrt{2+P}, \quad \kappa = \frac{1}{2}\sqrt{2-P}, \quad P = 2 - \frac{\Delta^2}{16}$$
(1.1.1)

Fig 1.2 b) shows the solutions (1.1.1) as φ is varied while P = 1. The solutions (1.1.1) describe the wrinkle and fold regime observed experimentally in [32]. They recover analytically: the amplitude of the fold $A_0 = y(0) = \frac{\Delta}{2}$, the dimensionless pressure $P = 2 - \frac{\Delta^2}{16}$ (and thus the energy), the compression at self-contact ($\Delta_{sym} \approx 0.89\lambda$, $\Delta_{antisym} \approx 1.05\lambda$) and the complete shape of the sheet. Moreover, Diamant and Witten's results suggest that the wrinkle to fold transition is not a phase transition. The deformation is always localised, but the localisation length diverges at small compressions.

Nevertheless, a few questions still remain unanswered. For a given pressure all the configurations have the same energy and the same displacement. So why experimentally only the symmetric and antisymmetric configurations are reported and why at high compressions only the symmetric fold remains ? Is the finite length of the sheet important as suggested in [32] ? Very recently a few theoretical studies tackled some of theses questions.

Oshri *et al.* [100] have looked at the wrinkle to fold transition for finite length sheets. They have looked at the same problem as in [3] but with a sheet of finite length L_0 . They have derived an exact solution for the wrinkling regime and an asymptotic solution (valid for long sheets: $L_0 >> \ell_{eh}$) for the fold regime. They have found a critical compression at which there is a cross over between the wrinkling regime and the fold regime. This suggests that for finite sheets the wrinkle to fold transition is a second order phase transition. Finally, the critical compression depends on the sheet length: $\Delta_c = \lambda^2/L_0$.

Rivetti and Neukirch [101] have investigated the stability of the different symmetries for finite length sheets. They have computed numerically the possible shapes of the sheet



Figure 1.3: Figure adapted from [101]. Bifurcation diagram representing the sheet vertical deflection in the middle of the sheet y(s = 0) as a function of the horizontal displacement Δ/ℓ_{eh} for a sheet of length $L_0 = 22\ell_{eh}$. Continuous (respectively dashed) curves correspond to stable (respectively unstable) solutions. Red (respectively blue) curves correspond to symmetric (respectively antisymmetric) solutions. Green curves correspond to connection paths, where the solutions have no symmetry. Shaded parts correspond to solution where self-crossing occurs. The beam shapes correspond to the black dots in the bifurcation diagrams.

and performed a stability analysis to determine the equilibrium solution as the length and compression are varied. In a numerical experiment where the compression is increased gradually, the sheet can go from antisymmetric to symmetric configurations (and vice versa) several times via non symmetric modes. They have called this phenomenon the mode branching route to localisation. Fig 1.3 shows this branching route through a bifurcation diagram for a sheet of length $L_0 = 22\ell_{eh}$. They have also derived an asymptotic solution (valid for long sheets, different from [100]) that recovers the numerical results.

Démery et al. [102] have studied large folds, *i.e.* for very high compression after the self-contact $\Delta >> \lambda$. With numerical simulations (energy minimisation on a discretized sheet, with a high energetic cost for self crossing) and scaling arguments they have shown that the antisymmetric fold is energetically favourable over the symmetric fold after the self-contact. Fig 1.4 a) shows the energy of the two configuration as the compression increases. At sufficiently high compression (not shown in Fig 1.4 a)) the antisymmetric fold can even absorb excess length at zero pressure.

Another experimental study is of particular interest to us. Huang *et al.* [33] have compressed uniaxially ultrathin elastic sheets on water and looked at the wrinkling regime. In their experiment the bending rigidity is very low and surface tension is no longer negligible. The invariance along the width is broken by surface tension, the wavelength smoothly increases on the sheet edges, where surface tension comes into play. This is called a smooth cascade of wrinkles and it is shown in Fig 1.4 b). Qualitatively the surface tension acts like the foundation. To minimise the liquid bridge's surface it is favourable to minimise the amplitude, the sheet being incompressible it has to buckle in a higher order mode (smaller wavelength) to do so. The typical penetration length of the edge effect is the capillary length $\ell_c = \sqrt{\frac{\gamma}{\rho_g}}$. To understand their results they have included the surface tension in a 3d linear model similar to the one from



Figure 1.4: **a)** Figure adapted from [102]. Fold energy as a function of the imposed displacement for symmetric (red squares) and antisymmetric (blue circles). The black line is the exact solution (1.1.1). The sheet profiles are displayed before and after self-contact (solutions from (1.1.1) are shown as thick dashed lines). **b)** Source: [33]. Top view of the smooth cascade of wrinkles at the edges of the sheet. In their system of coordinates, the sheet is compressed in the Y direction.

[32]. A dimensionless number ϵ which represent the stress ratio of compression along the length (x) to tension along the width (z) governs the smooth cascade of wrinkles: $\epsilon = \frac{P}{W\gamma} \sim \frac{\sqrt{B\rho g}}{\gamma} = \left(\frac{\ell_{eh}}{\ell_c}\right)^2$. If $\epsilon >> 1$ surface tension is negligible like in [32], if $\epsilon << 1$ surface tension is dominant, the smooth cascade of wrinkle is observed and the value of ϵ dictates its overall morphology.

1.1.3 Our contribution

All these studies provide interesting theoretical results, but an experimental validation is still lacking. In particular a lot of assumptions have been used to simplify the problem. Surface tension, sheet weight, adhesion and friction of the sheet in self-contact are effects present in real systems but neglected here. Along with possible dynamical effects, they could have a significant impact on the sheet profile.

Our main ambition is to understand the impact of the sheet weight on the wrinkle to fold transition and on the fold evolution beyond self-contact. This is motivated by granular rafts, were the weight of the raft is crucial to understand its shape and destabilisation (chapter 2). But we believe it could be relevant for other systems where a significant density mismatch between the sheet and the foundation exists such as geology, glaciology or metal oxide layers on elastomers. Finally, it is also an opportunity to look experimentally at some of the theoretical results presented above.

1.2 Results

1.2.1 Experiment and general results

To produce heavy elastic sheets we mix a silicone based polymer with iron powder and spin coat the mixture. We obtain sheets of density $1.2 < \rho_s (g.cm^{-3}) < 2.6$ and

1.2. Results

thickness $50 < t (\mu m) < 120$ with two sets of sizes: $L'_0 = 90 mm$, W = 60 mm and $L'_0 = 75 mm$, W = 50 mm (see appendix A for details).



Figure 1.5: Schematic of the experimental set-up defining the length between the boundaries L, the wrinkle's wavelength λ and the wrinkle's amplitude A as well as the Cartesian and intrinsic coordinates used in the model: (x, y) and (s, θ) .

We conduct the experiments in a custom glass tank $(12 \times 11 \times 6.5 \, cm)$ with two parallel polymethylmethacrylate (PMMA) plates with horizontal protruding ends (Fig **1.5**). We fill the tank with tap water to a level higher than the protruding ends. Then we carefully place the elastic sheet at the air-water interface between the plates. We lower the water level (using a syringe) until the edges of the sheet come into contact with the protruding ends of the PMMA plates. The sheet naturally adheres strongly to the PMMA achieving a clamped boundary condition at the protruding ends. We adjust the water level with the syringe so that the sheet is completely flat. We slowly poor light mineral oil ($\rho_o = 0.838 \ g.cm^{-3}$, Sigma Aldricht) on top of the sheet (so that no oil invades the lower surface of the sheet, in contact with water). One of the PMMA plates is mounted on two perpendicular manual translation stages for alignment in the (y, z) direction and connected to a stepper motor (NRT150/M from Thorlabs) of micrometer precision in the x direction. In order for the fold to nucleate near the centre of the elastic sheet, at $L_0/2$, we make sure that the alignment is done very carefully at its clamped edges. The fold has to appear at least one wavelength λ away from the clamp to avoid any boundary effects. When we do not manage to have a central fold, we compare the results to a fold generated by applying a small pressure at the centre of the sheet to force its position. The compression is quasi-static: the stepper motor displaces the plate in small increments at a constant speed. The motor stops for 5 s between each step allowing the system to relax to its equilibrium shape. After the compression phase, we unload the sheet following the same procedure to look for any hysteresis. We image the elastic sheet from the side and/or the top with two Nikon D800-E cameras mounted with macro objectives (105 mm). We use either ImageJ or Matlab to analyse the images.

The general behaviour of the sheet as we increase the imposed displacement is the following. At zero compression, $L = L_0$ (L_0 is the size of the sheet minus the dimensions

of the protruding ends: $L_0 \approx L'_0 - 40 \text{ mm}$), the sheet lies flat at the interface. As soon as we start compressing the sheet $(\Delta = L_0 - L > 0)$, it buckles out of plane with a characteristic wavelength λ that develops along the sheet length (Fig 1.6 a)). This is the wrinkling state. As Δ increases, the wrinkles' amplitude A grows uniformly (Fig 1.6 b)) until rapidly only one of the wrinkles continues to grow while the others vanish progressively. The deformation then slowly localizes into one large fold (Fig. 1.6 c)). We observe a transition between the wrinkled state, where the deformation is distributed along the whole sheet, and a fold state where all the deformation is localized in a narrow region of high curvature, *i.e.*: the fold. After the wrinkle to fold transition, as Δ increases the fold continues to grow in amplitude while its curvature increases. Finally, the deformation is only concentrated in the single fold where the sheet comes into contact with itself (self-contact) and forms a loop as the rest of the elastic sheet recovers its initial flat state. At this point a column of the upper fluid is encapsulated in this "teardrop" shape (Fig. 1.6 d)). If we continue to increase Δ , depending on the sheet density the teardrop either goes down toward the bottom of the tank (Fig 1.6 e)) or tilts back up toward the interface (Fig 1.14 b)-c)).

In the following we will study the role of the elastic sheet density as we increase compression: during the wrinkling phase, the transition and the fold evolution, before and after self-contact. Finally, we will discuss the reversibility of the experiment.



Figure 1.6: Side images of an elastic sheet of density $\rho_s = 1.8 \ g.cm^{-3}$ at the oil-water interface. Compression Δ increases from **a**) to **e**), scale bar 5 mm. **a**)-**b**) The sheet displays a quasi-periodic out of plane displacement of amplitude A and wavelength λ called wrinkles. **c**) The deformation localizes in a single fold. **d**) The fold reaches self-contact. **e**) A column of oil is encapsulated in the fold which grows deeper towards the bottom of the tank.

1.2.2 Wrinkles

The wrinkles appear as soon as the compression Δ is positive. They develop along the sheet length, with a wavelength λ and an amplitude A defined in Fig. 1.5. We first want to know if the theoretical values for λ and A from [32] still hold for two fluids and different sheet densities.

Great care must be taken when measuring the wavelength. To satisfy the boundary conditions the sheet profile cannot be a pure sinusoid, it is a modulated one [32]: $y(s) = A \sin\left(\frac{2\pi s}{\lambda}\right) \sin\left(\frac{\pi s}{L_0}\right)$. Thus, for short sheets like ours (2.4 < N < 6.1) the horizontal distance between two adjacent maxima (or minima) around $s \approx L_0/2$ and $s \approx 0$ is notably different. To get a consistent measurement that represents the "true" wavelength, we measure λ (or $\lambda/2$) where the amplitude is maximal. By doing this measurement a few times we deduce the wavelength (mean value) and its uncertainty (standard deviation $\sim 3\%$). Another problem is that the wavelength is measured on the side, where surface tension may deforms the sheet. At first sight we do not see the cascade of wrinkles at the edges like in [33] but a careful examination reveals a shorter wavelength on the side than in the middle. In order to highlight the effect of surface tension at the edges, we take rather transparent sheets (thin pure vinyl polysiloxane (VPS) sheets and polydimethylsiloxane (PDMS) sheets) and physically draw lines with a marker pen in the middle. We then focus the camera on the line, the sheet being rather transparent we can see the line through it (Fig 1.12). We find a reduction of the wavelength on the side of the order of $\sim 10-15\%$. Assuming the middle wavelength is the undisturbed one, our side measurement should be slightly below $\lambda = 2\pi \left(\frac{B}{\Delta \rho g}\right)^{1/4} (\Delta \rho = \rho_{low} - \rho_{up}$ is the density difference between the lower and upper fluid, see 1.2.3). On Fig 1.7 a) we plot the wavelength for all our sheets as a function of its theoretical value $\lambda = 2\pi \left(\frac{B}{\Delta \rho g}\right)^{1/4}$. If we take into account the perturbation from surface tension, the agreement is correct and the sheet density has no impact on the wavelength. If we now turn to the maximum amplitude A (which is equivalent to A_0) from [32], we essentially recover the results of [32]. Fig 1.7 b) shows the dimensionless maximum amplitude as a function of the compression on the wrinkling regime for sheets of different size and density. The linear model describes well the experimental data up to $\Delta/\lambda \approx 0.2$, which sets the boundary for the wrinkling regime. Within our uncertainties and range of parameters, we experimentally do not see any effect of the sheet density ρ_s or dimensionless length N in this regime (even though [32] predicts a weak effect of the length). The infinite length, fully non linear, model from [3] performs worse than the finite length linear model. It shows that the finite length of the sheet is important in the wrinkling regime.

Remark (Uncertainties). Unless stated otherwise, we compute the error bars with regular uncertainty propagation. If the variable X depends on several variables y_i , *i.e.* $X = f(y_1, ..., y_n)$, then X uncertainty is $\delta X = \sum_{i=1}^{n} (\partial_{y_i} f) \, \delta y_i$. We evaluate the direct uncertainties δy_i either with the device resolution, or by repeating the measurement and taking the standard deviation.

We observe one thing that was not reported in [32], the wavelength is not a constant. Let us call λ_x the wavelength for $\Delta > 0$ and λ its value as $\Delta \to 0$. Fig 1.8 shows the normalised wavelength λ_x/λ (measured from the side) as a function of the compression



Figure 1.7: **a)** Experimental wavelength as a function of the theoretical wavelength (in mm) for all our sheets. Open circles are oil-water experiments while closed circles are air-water experiments. Red symbols represent the theoretical value obtained with the thickness deduced from weighing while blue symbols represent the theoretical value obtained with the thickness deduced from the laser line method (see appendix **A**). The solid line has a slope 1, while the dashed solid line has a slope 0.85. The wavelength on the edge falls within the grey area. **b**) Dimensionless maximum amplitude as a function of the compression. Open circles are oil-water experiments while closed circles are air-water experiments. Densities are colour coded and are in the range $1.2 < \rho_s (g.cm^{-3}) < 2.6$, red is the lightest and yellow the heaviest. Dimensionless lengths are in the range 2.8 < N < 6.1. The solid line is the prediction from [3] for a symmetric fold $A = \Delta/2$, the dashed lines are the predictions from the linearised model [32]: $\frac{A}{\lambda} = \frac{\sqrt{2}}{\pi\sqrt{N}} \sqrt{\frac{\Delta}{\lambda}}$ for N = 2.8 and 6.1, the shaded area represents the intermediate values of N.

rescaled by the sheet length Δ/L_0 . As we increase the compression, λ_x decreases in the wrinkling regime. Brau *et al.* [9] have seen a similar behaviour in the case of a solid elastic foundation. The explanation is pretty simple, the distance conserved during compression is the arc length distance and not the horizontal distance between two maxima. At the linear order they are the same $(\partial_s y = \sin \theta \approx \theta, \partial_s x = \cos \theta \approx 1$ thus $x \approx s$), but not in the non linear regime. To explain our results we keep the linear solution but we expand at the first non linear order the wavelength like in [9]:

$$\lambda_x = \int_{\frac{L_0 + \lambda}{2}}^{\frac{L_0 + \lambda}{2}} \mathrm{d}s \partial_s x \approx \int_{\frac{L_0 - \lambda}{2}}^{\frac{L_0 + \lambda}{2}} \mathrm{d}s \left(1 - \frac{\theta^2}{2} \right) \approx \int_{\frac{L_0 - \lambda}{2}}^{\frac{L_0 + \lambda}{2}} \mathrm{d}s \left(1 - \frac{(\partial_s y)^2}{2} \right)$$

If we inject $y(s) = A \sin\left(\frac{2\pi s}{\lambda}\right) \sin\left(\frac{\pi s}{L_0}\right)$, the linear solution (derived for $L_0 >> \lambda$) and make the assumption $L_0 >> \lambda$ we get:

$$\frac{\lambda_x}{\lambda} \approx 1 - 2\frac{\Delta}{L_0} \tag{1.2.1}$$

We choose the interval of integration to mimic the experimental measurement (around $s \approx L_0/2$). Integrating between 0 and λ gives a different result due to the modulation. Equation (1.2.1) is plotted on Fig 1.8, it predicts the linear variation observed experimentally, the slope is in good agreement with oil-water experiments while the air-water experiments tends to deviate from it. The approximation $L_0 >> \lambda_0$ cannot explain this deviation since $N = \frac{L_0}{\lambda} \sim 3.4$ for oil-water while $N \sim 4.5$ for air-water. Varying the density does not change the behaviour so we suspect an effect from surface tension ($\gamma_{a/w} = 72 \ mN.m^{-1}$ while $\gamma_{o/w} = 46 \ mN.m^{-1}$). We have seen that surface tension has an effect on λ on the edges, it could have an effect on the evolution of λ_x as well. To test this hypothesis we lower the air-water surface tension to $\gamma_{a/w_{SDS}} = 58 \ mN.m^{-1}$ using sodium dodecyl sulfate (SDS) and repeat the experiment with the sheet of density $\rho_s = 1.2 \ g.cm^{-3}$. The wavelength evolution with SDS is similar to oil-water and closer to equation (1.2.1). If we follow Huang's work and compute $\epsilon \sim \left(\frac{\ell_{eh}}{\ell_c}\right)^2$ [33] we find $\epsilon_{o/w} \sim 0.2$ and $\epsilon_{a/w} \sim 0.4$. It is rather intriguing because it predicts a stronger perturbation due to surface tension for oil-water interfaces than air-water interfaces and we see the opposite in Fig 1.8. Nonetheless, their scaling for the reduction of λ on the edge is consistent with our data. They predict $\lambda_{edge} \sim \epsilon^{1/6} \lambda$ which in our case gives a wavelength reduction of $\sim 15-20\%$ on the edges. Our primary objective is not to look at the effects of surface tension and a good control over it is tedious so we did not study it in details, but we should keep in mind that it has a small but visible effect in our experiments.

In summary, the sheet density has no influence in the wrinkling regime. We recover the main results from [32], except in our case surface tension is not completely negligible. Adding the sheet weight in the linear model gives similar results, it just adds a constant term to the equilibrium equation that can be cancelled with a shift in the y coordinate. This shifted position corresponds to the altitude where the sheet weight is balanced by the hydrostatic pressures of the liquids (see the model in section 2.2.2). However, we observe that the wavelength decreases as compression increases. We predict this decline by performing a weakly non linear analysis.

1.2. Results



Figure 1.8: Normalised wavelength as a function of the compression. Open circles are for oil-water experiments, closed circles for air-water and closed squares for air-(water+SDS). Densities are colour coded and are in the range $1.2 < \rho_s (g.cm^{-3}) < 1.8$, red is the lightest and yellow the heaviest. Lengths are in the range 2.8 < N < 4.5. The dashed line is the prediction from the linear theory and the solid line is the prediction of equation (1.2.1).

1.2.3 Wrinkle to fold transition and fold before self-contact

The wrinkle to fold transition occurs between $0.2 < \Delta_c/\lambda < 0.4$. It is in fact difficult to experimentally determine accurately when the transition occurs. Pocivavsek *et al.* [32] have looked at the deviation from the linear prediction and the ratio of amplitude between the two biggest wrinkles and were only able to give an approximate value of $\Delta_c \approx 0.3$. Oshri *et al.* [100] predict an abrupt change in the amplitude at the transition but we do not see it in our experiments. It is rather difficult to confirm or infirm their prediction, *i.e.* $\Delta_c = \lambda^2/L_0$. When we try to measure Δ_c our data are very scattered, we cannot see any trend and we recover the approximate value $\Delta_c \approx 0.3$.

In our experiments we see the branching route to localisation predicted by Rivetti and Neukirch [101] (Fig 1.3). It typically happens during the wrinkle to fold transition. Two possible routes are observed: the wrinkles start symmetric and the fold remain symmetric until self-contact or the wrinkles start antisymmetric (or non symmetric) and the sheet goes through a succession of non symmetric modes until it reaches a downward symmetric fold (Fig 1.9), then it stays downward symmetric until self-contact. The two routes are responsible for the two different trends in the amplitude (air-water vs oil-water for $\Delta/\lambda < 0.4$ in Fig 1.10). We never see more than one transition even though Rivetti and Neukirch predicted multiple ones. We believe it is because at high compression the sheet weight (neglected in their work) stabilises the downward symmetric configuration (see bellow). Another problem is that the initial state of the sheet is very sensitive to the boundary conditions, a slight misalignment can modify the symmetry of the profile and/or the fold position. We also suspect that small defects (in thickness or material property) can modify the selected buckling mode and make its prediction difficult for any practical application. Again we could not make quantitative comparisons with [101].



Figure 1.9: Side pictures of a sheet at the oil-water interface to illustrate the buckling route ($\rho_s = 1.4 \ g.cm^{-3}$, M = 0.10, \circ in Fig 1.10). Top picture is antisymmetric (point reflection drawn), middle picture posses no symmetry and bottom picture is symmetric (reflection axis drawn). Compression increases from top to bottom: $\Delta/\lambda = 0.20, 0.33, 0.49$. Scale bar, $5 \ mm$.

Fig 1.10 shows the dimensionless amplitude as a function of the dimensionless compression up to the self-contact as we vary the sheet densities, for clarity we only plot representative data for four sheets. After the transition $(\Delta/\lambda > 0.4)$, the behaviour still does not depend on sheet length: the deformation always localizes in a downward symmetric fold and the amplitude grows linearly with compression as in [3, 32]. However, as we vary the sheet density we find that the amplitude of the fold increases slightly with the sheet mass for air-water and oil-water experiments. To explain this dependence we first turn to the model by Diamant and Witten [3] which presents an exact analytical solution for a floating, weightless, incompressible elastic sheet of infinite length without surface tension. We will extend this model to account for the sheet weight.



Figure 1.10: Dimensionless wrinkle/fold amplitude as a function of the dimensionless compression up to self-contact. (\circ , \circ) represent oil/water experiments, (\bullet , \bullet) air/water experiments. Three sheet densities are presented (with different lengths/widths/thicknesses), giving rise to the four dimensionless weights presented in the legend. The black curve corresponds to the symmetric solution [3] (M = 0), the orange and purple curves correspond to the symmetric numerical solution of equation (1.2.6) for M = 0.10 and M = 0.18. Inset: Top view of the compressed sheet. The fold reaches self-contact at the edges of the sheet but is still open in the centre. Scale bar: 5 mm.

Model

Let us consider an incompressible sheet of length L_0 , width W, thickness t and density ρ_s lying between a fluid of density ρ_{up} (for the upper fluid) and a lower liquid of density $\rho_{low} > \rho_{up}$. The sheet is compressed uniaxially in the x direction (see Fig 1.5). We introduce the intrinsic coordinates (s, θ) in which s is the arc-length and $\theta(s)$ is the local angle between the tangent and the horizontal axis x; we parametrise the sheet centreline in terms of arc-length, [x(s), y(s)].

Neglecting surface tension, the energy of this system is: $U = U_b + U_{low} + U_{up} + U_g$ with U_b the bending energy, U_{low} and U_{up} the gravitational potential energies of the
liquid/fluids that are displaced by the sheet and U_g the gravitational energy of the sheet itself. In our system of coordinates we have:

$$U_b = \frac{BW}{2} \int_{-L_0/2}^{L_0/2} (\partial_s \theta)^2 \, \mathrm{d}s$$
$$U_{low} + U_{up} = \frac{\Delta \rho g W}{2} \int_{-L_0/2}^{L_0/2} y(s)^2 \cos \theta \, \mathrm{d}s$$
$$U_g = (\rho_s - \rho_{low}) g W t \int_{-L_0/2}^{L_0/2} y(s) \, \mathrm{d}s$$

with g the gravitational acceleration, $\Delta \rho = \rho_{low} - \rho_{up}$ the density difference between the fluids, B the bending modulus (per unit width) of the sheet, $B = Et^3/[12(1-\nu^2)]$, E is the Young's modulus and ν the Poisson ratio. Assuming the sheet is inextensible, we have a global constraint on the end displacement:

$$\Delta = L_0 - L = \int_{-L_0/2}^{L_0/2} (1 - \cos \theta) \, \mathrm{d}s$$

We also have a local constraint due to the use of intrinsic coordinates $\partial_s y(s) = \sin \theta(s)$.

To determine the equilibrium profile of the compressed sheet, we first minimise the total energy accounting for the two constraints mentioned above. This adds two Lagrange multipliers: P for the end displacement (which corresponds physically to the compressive force applied, $P = \partial_{\Delta} U$) and Q(s) for the relation between $\partial_s y$ and θ . To facilitate the calculation, we rescale lengths by $\ell_{eh} = (B/\Delta\rho g)^{1/4}$, energy by WB/ℓ_{eh} and P by $W(B\Delta\rho g)^{1/2}$ and only use dimensionless quantities in the following of this section. We find that the energies are

$$U_b = \frac{1}{2} \int_{-L_0/2}^{L_0/2} (\partial_s \theta)^2 \,\mathrm{d}s, \quad U_{low} + U_{up} = \frac{1}{2} \int_{-L_0/2}^{L_0/2} y(s)^2 \cos\theta \,\mathrm{d}s, \quad U_g = M \int_{-L_0/2}^{L_0/2} y(s) \,\mathrm{d}s$$

In this process a dimensionless number appears,

$$M = \frac{(\rho_s - \rho_{low})t}{\Delta\rho\ell_{eh}},\tag{1.2.2}$$

which measures the weight of the sheet relative to the restoring force provided by Archimedes' buoyancy over the horizontal length ℓ_{eh} . The action to minimize is therefore $\mathcal{S} = \int_{-L_0/2}^{L_0/2} \mathrm{d}s \, \mathcal{L}(\theta, \, \partial_s \theta, \, y, \, \partial_s y)$ with

$$\mathcal{L} = \frac{1}{2} \left(\partial_s \theta\right)^2 + \frac{1}{2} y^2 \cos \theta + My - P(1 - \cos \theta) - Q(s)(\sin \theta - \partial_s y)$$

We use Hamiltonian mechanics, following Diamant & Witten [3], to perform the minimization. The conjugate momenta and the Hamiltonian are:

$$p_{\theta} = \frac{\partial \mathcal{L}}{\partial(\partial_{s}\theta)} = \partial_{s}\theta, \quad p_{y} = \frac{\partial \mathcal{L}}{\partial(\partial_{s}y)} = Q$$
$$\mathcal{H} = p_{\theta}\partial_{s}\theta + p_{y}\partial_{s}y - \mathcal{L}$$

1.2. Results

Since \mathcal{L} has no explicit dependence on s, \mathcal{H} is a constant of motion, thus $\mathcal{H}(s) = \mathcal{H}(\pm L_0/2)$. Here we focus on localized deformations and therefore choose the boundary conditions

$$y(\pm L_0/2) = \theta(\pm L_0/2) = \partial_s \theta(\pm L_0/2) = 0,$$

which immediately gives that $\mathcal{H}(s) = 0$, i.e.

$$\mathcal{H} = \frac{1}{2} \left(\partial_s \theta\right)^2 + Q \sin \theta - \frac{1}{2} y^2 \cos \theta - My + P(1 - \cos \theta) = 0 \qquad (1.2.3)$$

Hamilton's equations $\partial_s p_{\theta} = -\partial \mathcal{H} / \partial \theta$ and $\partial_s p_y = -\partial \mathcal{H} / \partial y$ then give:

$$\partial_s^2 \theta + \left(\frac{1}{2}y^2 + P\right)\sin\theta + Q\cos\theta = 0 \tag{1.2.4a}$$

$$\partial_s Q - y \cos \theta - M = 0 \tag{1.2.4b}$$

If we differentiate (1.2.4a) with respect to s and eliminate $Q \sin \theta$ with (1.2.3) and $\partial_s Q$ with (1.2.4b) we get:

$$\partial_s^3 \theta + \left[\frac{1}{2} \left(\partial_s \theta\right)^2 + P\right] \partial_s \theta + y(1 - M\partial_s \theta) + M\cos\theta = 0 \qquad (1.2.5)$$

This equation can be solved numerically to obtain the profile of the sheet.

To compare (1.2.5) with the final equation of Diamant & Witten [3], we differentiate with respect to s:

$$\partial_s^4 \theta + \partial_s^2 \theta \left[\frac{3}{2} \left(\partial_s \theta \right)^2 + P - My \right] + \sin \theta (1 - 2M \partial_s \theta) = 0$$
 (1.2.6)

When M = 0, equation (1.2.6) reduces to that derived by Diamant & Witten [3]. We solve numerically the system of equations (1.2.6) for very large sheets using the MATLAB routine bvp5c with the analytical solution (1.1.1) as an initial guess and a continuation algorithm to follow the solutions as we vary the parameters. Fig 1.11 shows the profiles obtained with this procedure as we increase M. As M increases, the wrinkles localise sooner, the fold amplitude increases and it is thinner.



Figure 1.11: Dimensionless sheet profiles for different values of M at two fixed dimensionless compressions: $\Delta = 0.4\pi$ and $\Delta = 1.3\pi$. M increases from blue to green. The numerical dimensionless sheet length is $L_0 = 100$.

Remark (Boundary conditions). To model our experiments, the appropriate boundary conditions are $y(\pm L_0/2) = 0$. However, for an idealized, infinite sheet the boundary condition $y(\pm \infty) = -M$ might be more appropriate (so that it is freely floating far from the localization). This modification would change one term in the final equation, however this term can be absorbed through a shift in the load (see [100]) to recover equation (1.2.6).

Comparison with experiments

Adding the weight in the model gives us a new dimensionless quantity M (1.2.2). In the following we come back to dimensional quantities, except for the length N and weight M. If M << 1 the sheet weight is negligible, if M >> 1 it is significant. Despite our efforts to produce heavy sheets, we only reach M = 0.18 experimentally. It explains why we do not see qualitative differences in the profiles with the previous work (see Fig 1.11). Nevertheless, we can see in Fig 1.10 that the amplitude deviation due to weight is a function of this number M and is quantitatively captured by the model without any adjustable parameters for $\Delta/\lambda > 0.4$. We see that during the wrinkling regime ($\Delta/\lambda < 0.2$), our model predicts no influence of the weight and like the Diamant and Witten model is quite off from the data. Solving numerically equation (1.2.6) with small length sheets recover the linearised model result: $\frac{A}{\lambda} \sim \sqrt{\frac{\Delta}{\lambda N}}$.

Taking the sheet weight into account also explains why the fold always ends up in a downward symmetric configuration. Indeed, with our continuation algorithm as soon as we set $M \neq 0$ we are no longer able to converge to an antisymmetric solution. Even if an antisymmetric solution still exists for equation (1.2.6) with M > 0 (respectively M < 0), the downward (respectively upward) symmetric solution has a lower energy due to the contribution of the gravitational term U_g . In previous works [3, 4, 8, 99] all the elastic sheet configurations have the same energy. In our model the sheet weight lifts this degeneracy. The difference of energy increases with M, but also with Δ/λ . This explains why in experiments we may observe antisymmetric configurations for low compressions ($\Delta/\lambda < 0.25$) but as we increase the compression the sheet configuration will always evolve to a downward symmetric configuration. Conversely, the upward symmetric configuration should be observed when M < 0 (sheet density lower than water density) even though surface tension effects could also play a small role to determine the symmetry, as suggested in [32].

The last point of each curve corresponds to the point where the downward symmetric fold reaches self-contact and forms a loop, *i.e*: the teardrop shape. Experimentally we find that this point is reached for $\Delta_{sc}/\lambda \approx 0.8$ whereas using equation (1.2.6), this transition is found at a slightly higher value ($\Delta_{sc}/\lambda \approx 0.89$ for symmetric folds). The reason for this discrepancy is not immediately clear. Some insight into the shift of the compression required for self-contact is obtained by examining a top view of the fold. Inset Fig 1.10 shows a top picture of a fold when we see the self-contact on the side. The fold shape is not the same at the edges of the sheet and at its centre. Capillary forces pull the elastic sheet on its sides closing the fold tighter at its edges than at its centre. The small discrepancy between the theoretical and experimental Δ_{sc} can be attributed to the surface tension effect at the edges of the sheet. But if we now turn to the profiles, they are also perturbed by surface tension on the side. By using the

1.2. Results

technique described in section 1.2.2 (focusing the camera on a line in the middle of transparent sheets) we can compare our experimental profile to the model (equation (1.1.1) since for those sheets $M \sim 0$). Fig 1.12 a) shows a picture of a fold in the centre of the sheet (red line). If we calculate the theoretical sheet profile using equation (1.1.1), we obtain the overlaid blue dashed curve. The agreement is very good. Fig 1.12 b) shows the same fold at one edge of the sheet. The overlaid blue dashed line is the solution from equation (1.1.1). The agreement is not as good as in a). The profile undisturbed by surface tension can be accurately predicted by the solution (1.1.1) [4, 99] but the profile on the side cannot.



Figure 1.12: Side picture of a VPS sheet compressed at the air-water interface viewed in the centre and on the side at the same compression. **a**) focuses in the middle of the sheet. The red line is physically drawn, the overlaid blue dashed line is the solution (1.1.1) with the experimental parameters (Δ , λ) and $k\varphi = 0.60$. **b**) focuses on the side, the overlaid blue dashed line is the theoretical solution with the experimental parameters and $k\varphi = 0.35$.

In summary, we do see a difference in the fold amplitude due to the sheet weight. This difference is accurately predicted by an extension to the Diamant and Witten model [3] to account for the sheet gravitational energy. We also observe all the theoretically predicted symmetries. Our folds always ends up downward symmetric at high compression and this is also explained by taking the sheet density into account. We also see an effect of surface tension: to minimise its surface area the liquid interface pulls on the side of the fold modifying its shape on the edges. Surface tension also closes the fold faster on the edge than in the middle, but away from the edges the profile is well described by the

model.

1.2.4 Evolution of the fold after self-contact

The solutions (1.1.1) and equation (1.2.6) cease to be relevant beyond self-contact $(\Delta > \Delta_{sc})$ since the theoretical profiles overlap. Fig 1.13 a) shows the last valid numerical profiles at self-contact for M = 0 and M = 0.18. A loop is formed as both sides touch each other. We experimentally measure its width w and height h on our sheets. Fig 1.13 b) shows w and h as a function of λ . The loop size grows linearly with λ , all the other parameters are found irrelevant. Inset Fig 1.13 b) shows the evolution of the loop size with compression for a representative sheet. Once the loop is formed, its shape does not vary with compression. It corresponds to the shape predicted by equations (1.1.1) and (1.2.6) when the profile reaches self-contact (Fig 1.13 a)). However, the



Figure 1.13: a) Comparison of symmetric profiles at self-contact given by equation (1.1.1) in black and equation (1.2.6) for M = 0.18 in red. The arrows define the height h and the width w of the teardrop. b) Teardrop height h (red circles) and width w (blue squares) as a function of the wavelength. Closed symbols represent air-water experiments, open symbols oil-water experiments, solid line is given by the black profile of a) (equation (1.1.1)) and dashed line is given by the red profile of a) (equation (1.2.6) for M = 0.18). All other experimental parameters are found irrelevant and vary across the data. Inset Experimental teardrop height and width in one experiment (M = 0.14, $\rho_s = 1.8 \ g.cm^{-3}$) as a function of the compression. c) Side picture of a PDMS sheet compressed at the air-water interface viewed at a ~ 8 mm away from the side and on the side at self-contact (different Δ). Top picture focuses far from the edge. The black line is physically drawn, the overlaid red dashed line is the theoretical solution with the experimental parameters and $k\varphi = 0.45$. Bottom picture focuses on the edge, the overlaid red dashed line is the theoretical solution with the experimental parameters and $k\varphi = 0.45$. Scale bar, 5 mm.

1.2. Results

model slightly overestimate w and h since we measure the shape at the sheet edges, where surface tension effects come into play, and not at the centre of the sheet. Using the same technique as in Fig 1.12, we compare the loop in the centre and on the edge of a sheet in Fig 1.13 c). The experimental loop is the black line while the theoretical one is the overlaid red dashed line. The shape of the loop is again accurately predicted by solutions (1.1.1) away from the edges but not at the edge, where the experimental loop is smaller. Equation (1.2.6) predicts that the loop shrinks as M increases but we are not able to observe it experimentally. This effect is smaller than the role of surface tension at the sheet edges since we do not see any change in this teardrop shape when we increase M. Moreover, adhesion forces at the point of self-contact might come into play which, we believe, prevent the teardrop shape to evolve with the compression.

If we increase the compression beyond self-contact, we observe two different behaviours depending on the dimensionless mass M (Fig 1.14 a)-f)). Heavy sheets (M > 0.14) keep a symmetric configuration and encapsulate a column of the upper fluid in a teardrop shape fold (Fig 1.14 d)-e)) that grows deeper as the compression increases (Fig. 1.14 (f)). Lighter sheets (M < 0.14) start symmetric with the same teardrop shape but, as the compression increases, the loop starts to tilt and grows back up towards the interface (Fig 1.14 a)-b)) until it finally reaches an obstacle such as the clamp or the sheet (Fig 1.14 c)). Here we define the amplitude after self-contact, A^* , as the depth of the centre of the loop (see inset Fig 1.15). The amplitude $A = A^*$ before self-contact is reached. We measure A^* as we increase the compression beyond Δ_{sc} . Fig 1.15 represents the experimental amplitude as a function of the compression before and after self-contact. We vary the sheets densities and lengths and present our results using the dimensionless mass M described previously. When self-contact is reached the amplitude keeps growing linearly $(A^*/\lambda \approx 0.5\Delta/\lambda)$. At the scale of Fig 1.15 the variation of amplitude due to the mass M is not visible before self-contact; however, we find that this difference becomes more apparent after self-contact. The amplitude A^* increases linearly until it reaches a critical compression Δ_b at which the fold starts tilting slowly back up towards the interface *i.e.*: $\partial_{\Delta}A^*$ decreases. Fig 1.15 shows that as M increases, the transition from a straight to a tilted fold is found at a higher Δ_b . Finally, when the elastic sheet is sufficiently dense (M = 0.18 in Fig 1.15), the fold grows linearly downward and never bends back up.

We compare our results to the numerical work by Demery *et al.* [102] where they study a compressed sheet without mass after self-contact. They find two possible configurations for the shape of the sheet: a symmetric one which we also observe experimentally and an antisymmetric one which we never find. They show that the antisymmetric configuration has a lower energy but in our case the added weight of the sheet may explain why we only find the symmetric configuration (its energy is lowered by $U_g \sim -M\Delta^2$). Another discrepancy is that they predict for the symmetric configuration a teardrop that shrinks as the compression increases ($h \sim \Delta^{-1/3}$), the increase in hydrostatic pressure would push outside the fluid inside the teardrop as it sinks deeper. Experimentally the teardrop size is constant, we believe the main reason is that it would need the fluid to separate the two part of the sheet in self-contact, which is prevented in our experiment. We have experimental evidences of strong adhesion in the case of air-water experiments where there is a hysteresis at self-contact but not for oil-water experiments (see Fig 1.19). One could argue that the bending of the fold



Figure 1.14: Pictures of two folds as compression is increased. The two sets of pictures have the same dimensionless compression, from left to right $\Delta/\lambda \approx 0.93$, 1.19, 1.44. Scalebars, 5 mm. **a)-c)** sheet with a low mass M = 0.03, $\rho_s = 1.2 \ g.cm^{-3}$. **d)-e)** sheet with a high mass M = 0.18, $\rho_s = 1.8 \ g.cm^{-3}$. Colours have been inverted to enhance contrast.



Figure 1.15: Dimensionless wrinkle/fold amplitude A^* as a function of the dimensionless compression after self-contact. (\circ , \circ , \circ) represent oil/water experiments, (\bullet , \bullet) air/water experiments. \bullet show the data corresponding to the pictures in Fig 1.14. *Inset*: Schematic presenting the post buckling fold amplitude A^* (fold centre in red).

1.2. Results

Model

We need a new mathematical model to describe the evolution of the fold when $\Delta > \Delta_{sc}$. We neglect surface tension again so that the sheet behaviour is invariant along its width and the problem can be treated as two dimensional. The elastic sheet after self-contact can be modelled using the schematic Fig 1.16 a) where we break the system in two parts: a heavy beam corresponding to the part of the sheet in self-contact and a force acting at its tip (which is the teardrop shape encapsulating buoyant fluid).

$$F = \Delta \rho g \mathscr{A} - (\rho_s - \rho_w) g t \mathscr{L}$$
(1.2.7)

 \mathscr{A} and \mathscr{L} are respectively the half-area and half the perimeter of upper fluid encapsulated in the teardrop (Fig 1.16 a)). Considering these half quantities means that we are considering each half of the two that are in contact separately, and assuming they do not exert force on one another. While this reduction suggests that the problem is equivalent to that of a beam subject to a constant load at one end, we emphasize that the self-weight of the beam is important and so instead we must consider a heavy beam, subject to a constant force pushing at the tip (since we found the teardrop size to be constant experimentally). We assume a clamped boundary condition at the top for simplicity (Fig. 1.16 a)). At each compression step the portion in self-contact L^* grows, increasing the length of the effective beam.

We introduce again the intrinsic coordinates (s,θ) , with s the arc-length and θ the angle between the heavy beam and the x axis (for consistency of notation, the Cartesian coordinate have been rotated clockwise by 90 degrees compared to the model presented in the previous section). We parametrise the sheet centreline as [x(s), y(s)] which are given in terms of the intrinsic coordinates by $(\partial_s x = -\cos\theta, \partial_s y = -\sin\theta)$. In this system, the equation for the heavy Elastica is given by a balance of internal moments [103, 104] (see appendix B for full derivation):

$$\partial_s m = B \partial_s^2 \theta = -(F - (\rho_s - \rho_w)gts)\sin\theta$$

B is the beam bending modulus and *t* its thickness. ρ_s is the beam density and ρ_w the lower liquid (water) density. The boundary conditions are free-end in s = 0 and clamped in $s = L^*$:

$$\partial_s \theta(s=0) = 0, \quad \theta(s=L^*) = 0$$

The system is made dimensionless by dividing s by L^* :

$$\partial_s^2 \theta + \left[\tilde{F} - \left(\frac{L^*}{\ell_g} \right)^3 s \right] \sin \theta = 0$$

$$\partial_s \theta(s=0) = 0, \quad \theta(s=1) = 0$$
(1.2.8)



Figure 1.16: **a)** Schematic of a perfectly symmetric fold post self-contact. The fold is split in two parts: the portion in self-contact is treated as a heavy hanging column of length L^* and thickness t and the teardrop is modelled as a constant point force (upward gravitational force). The upper part is not taken into account here and a clamped boundary condition is assumed on the top of the beam. The Cartesian (x,y) and intrinsic coordinates (s,θ) are drawn. **b)** Dimensionless horizontal end displacement of the beam as a function of its length for a dimensionless force $F\ell_g^2/B = 2$. The orange curve is with an initial angle of 10° and the blue curve is without an initial angle. The horizontal dashed line show our criterion to determine the critical buckling length L_c^* . Inset Schematic of the tilted heavy hanging column defining the horizontal end displacement y_0 , all lengths are divided by L^* .

Here, $\tilde{F} = FL^{*2}/B$ is the dimensionless force applied by the buoyancy of the teardrop and $\ell_g = (B/[(\rho_s - \rho_w)gt])^{1/3}$ is the elasto-gravitational length comparing elastic and gravitational forces. Note that this elasto-gravitational length is closely related to the parameter M defined in equation (1.2.2) since $M = (\ell_{eh}/\ell_g)^3$. For small deformations, equation (1.2.8) can be linearised and we can determine analytically the buckling threshold [103]: This analysis gives the critical force \tilde{F}_c needed for the beam to buckle as a function of $(L^*/\ell_g)^3$. We thus obtain $\tilde{F}_c = \frac{F_c L^{*2}}{B} = f\left((\frac{L^*}{\ell_g})^3\right)$. Since the control parameter corresponds to the beam length L^* (the force is kept constant) we can rewrite this expression:

$$\frac{F\ell_g^2}{B} = \left(\frac{\ell_g}{L_c^*}\right)^2 f\left(\frac{L_c^*}{\ell_g}\right)$$
(1.2.9)

Equation (1.2.9) gives us the critical length (for a given force) needed for the beam to bend. However, in most experiments the fold is not perfectly aligned with the vertical axis when it reaches self-contact (Fig 1.14 a)). The average angle α between the fold and the vertical axis is $|\alpha| = 10^{\circ}$ (maximum value 26°). To account for this angle we can add an initial angle to the heavy Elastica model by changing the boundary condition at the top of the beam. We now solve equation (1.2.8) with the new boundary condition $\theta(s = 1) = \alpha$ (using the MATLAB routine bvp5c) to get the beam shape. With

1.2. Results

an initial angle the transition from straight to buckled becomes smooth. We thus need to define a criterion to get the critical buckling length L_c^*/ℓ_g . We look at the free end dimensionless horizontal displacement: $y/L^*(s = 0)$ (denoted as y_0 next). When the beam is straight $y_0 = \sin(\alpha)$ and when the beam starts to bend y_0 increases (Fig 1.16 b)). We take for critical length L_c^* , the length for which $y_0 - \sin(\alpha) > 0.1$. This choice of threshold comes from the experiments, the threshold needs to be much higher than the measurement uncertainty and the pictures of "buckled" beams need to be visually identifiable as buckled.

Comparison with experiments

To compare our model with the experiments, we use side pictures to measure \mathscr{A} , \mathscr{L} and L_c^* (using the buckling criterion described above). From these measurements we calculate the force (equation (1.2.7)) and we extract B from the wrinkles' wavelength $(B = \Delta \rho g \left(\frac{\lambda}{2\pi}\right)^4)$. We now have everything to test our model.



Figure 1.17: **a)** Phase diagram of the post self-contact fold buckling where \mathscr{A} and \mathscr{L} have been measured on side pictures. Green filled circles gives the critical length L_c^* before buckling for each experiment. Black open circles represent experiments where the fold never buckled. The data here represent all our experiments with all parameters varied. The black dashed curve and background colours are guides for the eye to distinguish experimental phases. The red solid curve is the analytical result of the model without an initial angle (equation (1.2.9)), the blue (respectively orange) solid curve is the numerical result of the model with an initial angle of 10° (respectively 20°). **b)** Phase diagram of the post self-contact fold buckling, but this time \mathscr{A} and \mathscr{L} are calculated with equation (1.1.1) to evaluate the force F.

In Fig 1.17 a) we plot the experimental phase diagram presenting the transition at which the fold starts to bend upwards. The analytical solution of our model without an initial angle (equation (1.2.9), red curve Fig 1.17 a)) captures qualitatively the fold's behaviour: there is a critical force below which the fold never buckles whatever the

length of the sheet may be. Our experimental data points lie well below the red curve describing equation (1.2.9) but have the right trend. If we now include the initial angle in our model (blue curve: $\alpha = 10^{\circ}$, orange curve: $\alpha = 20^{\circ}$), the model comes closer to the experimental values but is still not quantitative. We have made many assumptions in the model that could be wrong. By treating half of the system in our model we implicitly make the hypothesis that both sides of the fold (in the part in self-contact) can slide past each other. But if we consider them glued together, it "toughen" our beam (the force is multiplied by 2 while the rigidity is multiplied by 2^3) while our experimental beam seems "softer". Another problem is that we do not know the forces and/or moments acting on the top of our beam. The top is definitely neither free nor pinned. But the clamp boundary condition seems too strong as the top of the fold can move and rotate slightly as compression is varied.

But there is also a problem in our measurements: we measure the shape from the side where surface tension plays a role. We have seen in Fig 1.13 b) that our measurements of the teardrop shape are smaller than what we expect from equations (1.1.1) or (1.2.6). Then we have shown in Fig 1.13 c) that away from the side, we recover the shape of the fold predicted by the model. The width averaged force F due to the encapsulated fluid we have estimated from the side is smaller than its true value. If we use equation (1.1.1) to estimate the shape of the teardrop, we get a more precise estimation of the force acting on the beam. We plot the phase diagram for the fold bending using the calculated values for the teardrop shape instead of the one measured on the side in Fig 1.17 b). We can see that we almost reach a quantitative agreement with the model despite its numerous approximations.

1.2.5 Reversibility of the folding process

In the description of the experiment, we mentioned that after every loading, we unload the sheet to see if the buckling is reversible. We expect the elastic buckling to be reversible, but nothing is mentioned in the literature so far. We find some discrepancies between loading and unloading experiments, especially at the air-water interface. Fig 1.18 shows the amplitude as a function of the compression for the loading and the unloading of a representative sheet. We identify three non reversible behaviours:

- The buckling route during the wrinkling regime and the wrinkle to fold transition is sometimes different between loading and unloading. In Fig 1.18 the sheet goes trough an antisymmetric toward symmetric transition for $\Delta < 0.4\lambda$ during loading, but stays symmetric during the whole unloading process. This can happen for both air-water or oil-water experiments. It shows once more how energetically close all those configurations are at low compression.
- In Fig 1.18, we see a difference between the loading and unloading amplitude around Δ_{sc} . Fig 1.19 a)-d) shows pictures taken at the same compression before and after Δ_{sc} during loading and unloading at the air-water interface. For all air-water experiments, the self-contact stops at a lower critical compression during the unloading. To quantify this process we measure the length of the part in self-contact L^* as a function of compression Δ in Fig 1.19 e). We see a hysteresis at

1.2. Results

the air-water interface but not at the oil-water interface. As the gap between both sides of the fold becomes extremely narrow, a small amount of water infiltrates the gap (Inset 1.18). During unloading, the capillary forces of the trapped water prevent the unfolding, modifying completely the shape of the fold. At some point the forces in the sheet are high enough to chase the water. The loop abruptly unfolds and recovers its regular shape. This infiltration does not occur in oil-water experiments. Treating the surface to make it more hydrophobic might be able to prevent the infiltration.

• The fold bending is slightly different during loading and unloading. The fold recovers its symmetric shape at a lower compression during unloading. Again the effect is much more pronounced during air-water experiments suggesting that adhesion and/or the trapped water generate frictional forces during the unloading.



Figure 1.18: Amplitude as a function of the compression for a sheet of density $\rho_s = 2.0 \, g.cm^{-3}$ at the air water interface (M = 0.05, N = 3.4). Red circles represent loading while blue circles represent unloading. The three kinds of discrepancies between loading and unloading are highlighted. *Inset* Schematic of the water invasion process. The gap in the self-contact region is exaggerated.



Figure 1.19: **a)-d)** Side pictures of a sheet at the air-water interface ($\rho_s = 1.2 \ g.cm^{-3}$) during loading and unloading at the same compression ($\Delta/\lambda = 0.65$ and 0.99). Pictures **a)-b)** show the loading while **c)-d)** show the unloading. The shape between **a)** and **d)** is completely different. **e)** Dimensionless length in self-contact L^* as a function of the dimensionless compression Δ for the same sheet. Red circles represent loading while blue circles represent unloading. Closed circles represent air-water while opens circles represent oil-water. Dotted lines and arrows are guide to the eye. The sheet at the air-water interface exhibits a hysteretic behaviour between loading and unloading due to adhesion, the self-contact appears for a compression of $\Delta_{sc}/\lambda = 0.83$ during loading but disappears only at $\Delta_{sc}/\lambda = 0.47$. The sheet at the oil-water interface does not display hysteresis, the oil prevents the invasion of water and thus the adhesion.

1.3 Conclusion

We have studied experimentally and theoretically heavy thin elastic sheets compressed uniaxially at a liquid-fluid interface. As previously observed by Pocivavsek etal. [32], when confinement increases the sheet undergoes a transition from a uniform wrinkling state to a localized configuration in which a single fold is observed. During the wrinkling regime the sheet weight has no influence. However, we show that the wavelength decreases as we increase compression. We adapt the argument of Brau etal. 9 to explain this phenomenon. Then we show that all the symmetries predicted theoretically [4, 99] exist in our experiments. Our sheet follows different buckling routes to localisation qualitatively similar to the ones predicted [101]. However, in our case the fold always end up in a downward symmetric configuration at high compression. Adding the weight of the sheet in the model allows us to understand why. During the fold regime the weight of the sheet has an effect on the fold shape. Its amplitude at a given compression increases with the sheet weight. We include the sheet weight in the previous model from Diamant and Witten [4]. A new dimensionless number Mquantifies the importance of the sheet weight and the modified model predicts accurately the shift in amplitude. We also discuss the effect of surface tension, usually neglected theoretically. For our sheet surface tension is neither dominant nor negligible. The features predicted by the models (in the absence of surface tension) are quantitatively correct away from the edges but only qualitatively correct on the edges of the sheet.

1.3. Conclusion

The liquid meniscus wants to minimise its surface area and pulls on the sheet. It reduces the wavelength and tends to close the fold on the edges. The fold shape is slightly different and the self-contact occurs much faster on the edges. We then for the first time look experimentally at very high compressions, past the self-contact. We see that the sheet weight plays a major role in that regime. The fold can either buckle back toward the fluid interface or grow deeper as compression is increased. We use a simple idealised model to predict the two possible outcomes in a phase diagram. Finally, we discuss the reversibility of the experiment. Adhesion, either due to the sheet itself or water trapped in the region in self-contact makes the unfolding not exactly reversible for air-water experiments. However, with oil the sheet is lubricated and water invasion is prevented, making the experiment almost reversible.

Chapter 2 Compression of granular rafts

Contents

2.1 Intro	oduction	43
2.1.1	Buckling of particle laden interfaces $\ldots \ldots \ldots \ldots \ldots$	44
2.1.2	The granular rafts	47
2.1.3	Our contribution	49
2.2 Experiment and general results		50
2.2.1	Wrinkles	54
2.2.2	Fold before self-contact	59
2.2.3	Fold after self-contact	72
2.2.4	Limits of the elastic model and open questions $\ . \ . \ . \ .$	82
2.3 Conclusion		94

This chapter studies the buckling of uniaxially compressed granular rafts. We first show how the buckling of particle laden interfaces has been modelled in the literature and we present the work previously done on our system: the granular raft. Then we present our experimental results; under compression granular rafts wrinkles, then we observe a wrinkle to fold transition and the deformation localises in a unique fold. We develop an effective heavy elastic sheet model similar to the one introduced in chapter 1 and compare it to our data on the fold formation and shape. Finally, we draw the boundaries of this continuum mechanics model by showing the experimental observations that it does not reproduce.

2.1 Introduction

Before we introduce what we call "granular rafts", let us first look at the literature on the buckling of particle laden interfaces mentioned in the Introduction.

2.1.1 Buckling of particle laden interfaces

The buckling of particle covered interfaces has been observed several times in the literature [49, 51, 81, 87–92], however most studies do not focus on the buckling phenomenon itself. Following the approach for Langmuir films, the standard way to determine the mechanical properties of particles at interfaces prior to buckling is to measure the surface pressure-area isotherms. The surface pressure is usually measured with a Wilhelmy plate. The plate measures a surface tension γ_{eff} , the surface pressure is then $\Pi = \gamma - \gamma_{eff}$ where γ is the surface tension of the bare liquid. In a typical experiment one records the surface pressure while the area per particle decreases (the interface is compressed, see Fig 2.1 a)). Fig 2.1 b) shows a typical surface pressure-area isotherm for particle laden interfaces. In general we can distinguish three regions in the isotherms. At low compressions (region A) the particles are far apart and do not really feel each other, the surface pressure rises slowly. As compression increases, it starts to rise more steeply (region B). In this region, the particles become close enough to strongly repel each other. At some point the surface pressure reaches a plateau (usually when particles reach jamming, region C). This indicates that the interface has collapsed, either via particle desorption or buckling of the interface. These isotherms are typically used to compute the surface dilational modulus of the interface or extract the critical collapse pressure $\Pi_{collapse}$. However, after buckling they do not give much informations. Other force sensors exist (e.g. [106]) but the surface pressure measurement is the most common method.

Once the interface has buckled, the relevant mechanical property to describe the interface is the bending rigidity B, which depends on the Young's modulus E and the dimensions of the interface. There are two methods in the literature to measure the "effective" bending rigidity of a close packed particle laden interface.

Vella *et al.* [49] have done a buckling assay to determine the elasticity of the interface. They have compressed a flat interface covered with non-brownian hydrophobic particle (called particle raft) in a Langmuir trough up to the buckling of the interface (Fig 2.2 a)). Particle rafts wrinkle with a characteristic wavelength λ like a floating elastic sheet



Figure 2.1: a) Schematic of the surface pressure measurement. Figure adapted from [93]. b) Surface pressure as a function of the area per particle for $3 \mu m$ polystyrene particles at a water-decane interface obtained with two methods: fitting the shape of a liquid marble (squares) or the Wilhelmy method (diamonds and triangles). The three regions of the isotherms are denoted as A, B, C. Figure adapted from: [105].



Figure 2.2: Source: [49]. a) Schematic of the experiment. b) Wavelength as a function of the particle size. All experimental points are for Pliotite particles at the air-water interface unless otherwise specified by the key. The solid line shows the theoretical prediction (equation (2.1.1)). *Inset* Wrinkling pattern observed with polystyrene particles $(d = 300 \ \mu m)$. Scale bar, $5 \ mm$.

(Inset Fig 2.2 b)). In the case of an elastic sheet $\lambda = 2\pi \left(\frac{B}{\rho g}\right)^{1/4}$ where ρ is the liquid density, $B = \frac{Et^3}{12(1-\nu^2)}$ is the bending rigidity per unit width, t is the sheet thickness, E and ν are the Young's modulus and Poisson ratio. The measurement of λ thus gives the effective bending rigidity of the particle raft. In their paper Vella *et al.* derive a model to predict their measurements. They consider the particles as hard spheres and look at the mean stress and strain in the raft. Since the particles are incompressible, the strain only depends on the liquid surface area. This leads to an effective Young's modulus $E \sim \frac{(1-\nu)\gamma}{(1-\phi)d}$ where ϕ is the two dimensional packing fraction (particle surface fraction). Injecting this Young's modulus in the bending rigidity and considering the thickness of the sheet to be the particle size d yields:

$$\lambda = \pi \left(\frac{4}{3(1-\phi)(1+\nu)}\right)^{1/4} \sqrt{\ell_c d}$$
(2.1.1)

Fig 2.2 b) shows the experimental wavelength λ as a function of the particle size d. They have varied the particle size over three order of magnitude and recovered the $\lambda \sim d^{1/2}$ power law with a prefactor that matches equation (2.1.1). Other studies [92, 107] have found different prefactors but the power law $\lambda \sim d^{1/2}$ is very robust despite all the assumptions of the model. In particular, they have used the relation between B and Efor elastic sheets which is derived by computing the stress and strain in a section of the beam (appendix B). Because we do not know how strains and tresses are distributed inside the particles, it is a big assumption to consider that this relation still holds for particle rafts. The model also neglects the particle wetting properties and particle friction, even though they are the key ingredient that maintain the raft integrity.

Planchette *et al.* [107] have proposed a different method to measure the bending rigidity of particle rafts. Instead of compressing the raft, they oscillate a plate to produce surface waves (see Fig 2.3). The experimental dispersion relation (that relates the wave velocity to the wave number) cannot be described with a pure fluid dispersion relation. But a modified one, that takes into account a bending term and an inertia



Figure 2.3: Source: [107]. a) Schematic of the experiment. b) Surface wave propagation at an air-water interface covered with coated glass particles of diameters $32 \ \mu m$ at a frequency f = 400 Hz. The vertical arrow indicates the oscillating plate and corresponds to $1 \ mm$.

term due to the particles, can fit the velocity-wave number curves. From this fit one can extract the bending rigidity of the sheet B. The bending rigidity that Planchette *et al.* measured recovers the prediction from [49]: $B \sim d^2$. It is worth noting that Planchette et al. have proposed a different model to derive the bending rigidity. Following the work of [108, 109] they calculate the surface energy (per unit area) U_{surf} of a cylinder of radius R covered with particles. Again the calculation is done under many assumptions. Entropy, line tension, gravity or particle interaction (through friction for instance) are neglected. The bending rigidity is then extracted by looking at $\partial_{(1/R^2)}U_{surf}$. This yields a bending rigidity $B = \gamma \phi d^2 f(\theta_u)$ where f is a function that depends on the detailed hypotheses made during the derivation. The idea is that when the interface is bent, the adsorbed particles move upward or downward (depending on the direction of bending and θ_{u}) to fulfil the equilibrium contact angle. This induces a variation of energy when we bend the interface, we thus have a bending rigidity. The model is very different from the one from Vella *et al.* [49] but yields a similar prediction for the bending rigidity. Nonetheless, it varies differently with the particle surface area ϕ and it varies with the contact angle θ_{y} . The interface behaves as a solid when the particles are jammed so we cannot vary ϕ in the experiments to check which model is correct, it is however possible to vary θ_y . Planchette *et al.* [107] varied the contact angle but for only one particle size and the difference in bending rigidity was not significant.

Close packed particle covered interfaces seems to behave like elastic solids under compression. It is clearly possible to extract an effective bending rigidity (or Young's modulus) from buckling experiments even though the underlying physical mechanism is not perfectly understood. Indeed, both models make many assumptions and rely on different mechanisms but yields similar scaling laws for the parameters that we can experimentally vary, it is thus difficult to judge what is the mechanism with experiments. In the meantime, several studies have questioned this idea, exhibiting phenomena that could not be explained with a continuous elastic description. Using the surface pressurearea isotherms Cicuta and Vella [93] have shown that the critical buckling pressure Π_{buck} depends on the width of the raft and the distance to the compressing plates. They have suggested an effect similar to the Jansen effect in granular materials to explain the variation of Π_{buck} . Like in a granular material the stress propagates through force chains and the lateral walls absorb part of the stress such that it decays exponentially. Taccoen *et al.* [98] have compressed particle covered bubbles by changing the pressure of the outside fluid. They have found a critical buckling pressure that does not depend on the particle size and that scales as 1/R with R the radius of the bubble. In the case of a hollow elastic shell, the buckling pressure scales as $1/R^2$ and depends on the shell bending rigidity and thus should depend on the particle size. Other studies have shown a buckling pressure independent of the particle size [97, 105], this suggests a buckling mechanism different from the elastic buckling. Croll *et al.* [95, 96] have studied the buckling of particles adhered to a solid elastic substrate. Upon compression the interface wrinkles with a wavelength independent of both the Young's modulus of the particle and the substrate, but linearly dependent on the particle size. In the case of a beam on an elastic foundation the wavelength is $\lambda \sim t \left(\frac{E}{E_s}\right)^{1/3}$ with t the beam thickness, Ethe beam Young's modulus and E_s the substrate Young's modulus. Even though they recover a linear dependence with the particle size (which is their thickness), varying both particle and substrate moduli has no impact on the wavelength. Their particle covered interface cannot be modelled as a continuous elastic material.

2.1.2 The granular rafts

We have explained in the Introduction that particles denser than water can float if they are small enough such that capillary forces can balance gravity (with the buoyancy taken into account). Moreover, these objects usually attract to minimise the deformations of the interface (Fig 2.4 a)). This attractive force F_{cap} has a range of the order of ℓ_c and its magnitude depends on the properties of the liquid and the particle $(d, \gamma, \rho, \rho_s, \theta_y)$. If we sprinkle many large and dense particles $(d \geq 50 \ \mu m$ for $\rho_s = 2.5 \ g.cm^{-3}$) at a mineral oil-water interface ($\ell_c = 5.4 \ mm$), they spontaneously aggregate via capillary forces in a close packed monolayer that we call a "granular raft". Fig 2.4 b) shows a side picture of a small granular raft. The word granular raft emphasises that the particles are rather large, athermal and heavy, *i.e.* they are a granular material. The main difference with the particle rafts from [49] is that our particles are much denser. The physics of granular rafts is thus dominated by capillarity, gravity and friction while gravity is negligible for particle rafts.

Before this work, several properties of these granular rafts have been studied. For a given set of particles and liquids, if we continuously add particles, rafts that were stable over time (*i.e.* they float) may destabilise or become unstable and sink (see Fig 2.5 a)-b)). In the case of axisymmetric rafts at the oil-water interface, granular rafts destabilise spontaneously when they reach a critical size [68]. At this point the capillary forces cannot sustain the raft's weight and the whole raft or part of it sinks at the bottom of the tank. An interesting feature of the destabilisation process is that it drags down some oil and produces oil in water armoured droplets [110]. The critical size depends on the ratio of the raft's weight to capillary forces through a parameter $\mathcal{D} = \frac{\rho_{eff}}{\Delta \rho} \frac{d}{\ell_c}$, where ρ_{eff} is the effective density of the raft taking into account voids and $\Delta \rho = \rho_{low} - \rho_{up}$ is the difference of density between the two liquids. When \mathcal{D} increases. the maximum stable raft size decreases. Hence, with heavier particles (bigger or denser) the stable rafts we can produce are smaller. This critical size diverges below a certain value of \mathcal{D} , thus with light enough particles we can make stable rafts of any size, they will never spontaneously sink. The destabilisation of the raft can also be triggered by applying forces on it. One can either push on the raft or apply body forces such



Figure 2.4: a) Schematic of two heavy particles at an oil-water interface. The interface is deformed by the weight of the particles. The dashed line shows the undisturbed interface. The blue arrows represent the attractive force between the particles. b) Side picture of a small granular raft at the oil water interface. The deformation of the interface is clearly visible. Mean particle size $d = 900 \ \mu m$.

as centrifugal [110] or magnetic forces [111]. The behaviour of these particle covered interfaces is complex, each particle is attracted differently to its neighbours and cannot move freely due to frictional forces. Abkarian *et al.* [110] have predicted the shape of the armoured droplets with a continuous description of the interface (Fig 2.5 c)). The idea is to include all these effects in an effective internal tension T. At the edges of the raft $T = \gamma_{o/w}$ and as one advances along the raft's interface T varies due to the external body forces. For granular rafts T decreases from the edges to the centre of the raft due to the weight of the raft. This formalism can describe the shape of the interface bent downward by the raft's weight. But also the critical length before destabilisation [68]: when T becomes negative, it leads to the destabilisation of the raft. However, in some cases the granular raft wrinkles just before the destabilisation while the model predicts a flat interface [68]. Fig 2.5 d) shows a picture of a raft during destabilisation, the raft compressed by its own weight folds up during the raft destabilisation.

2.1. INTRODUCTION



Figure 2.5: Figure adapted from [110]. **a**) Stable raft at the oil-water interface seen from the side. **b**) If we increase the number of particles, at some point the raft destabilises. Scale bars, 5mm. **c**) Pictures of an encapsulated oil drop along with numerical calculated shapes (thick grey and blue lines) as the drop volume is increased with a syringe from I to IV. Scale bar, 1 mm. **d** Side picture taken during the raft destabilisation. Source: [68]

2.1.3 Our contribution

Many studies have shown that when the particles reach the jamming concentration, the interface becomes solid-like. We have seen that the interface wrinkles under compression like an elastic sheet and is often described as a continuous elastic material. Yet, other authors have shown that the discrete nature of the particles could not always be neglected. The mechanical behaviour of these object is still not completely understood. In particular, most studies focus on small deformations and we can wonder if the elastic models are still valid for large deformations.

We propose to study the buckling instability under compression of granular rafts both in the linear and non linear regimes. With our knowledge on the buckling instability in floating elastic sheets, we can probe further the continuous elastic description and predict more features of the instability. By doing so, we aim to bring new insights to understand the mechanical properties of particle covered interfaces. Can they really by considered as elastic materials ? What is the influence of the granular nature of the raft ?

2.2 Experiment and general results

To make the granular rafts we fill a custom built glass tank $(12 \times 12 \times 7 \ cm)$ with deionised water. Then we add a thick layer $(> 5 \ mm)$ of light mineral oil ($\rho_o = 0.838 \ g.cm^{-3}$, $\gamma_{o/w} = 46 \ mN/m$, Sigma Aldricht) and we sprinkle the particles above the tank. With their inertia they cross the oil-air interface and slowly sink to the oil-water interface where they remain trapped by capillary forces and attract each other (Fig 2.6). A close packed monolayer that we call granular raft spontaneously forms within a few minutes. We sprinkle the particles far apart from each other to avoid making multilayers. Particles deposited on top of an existing raft are not able to find their way to the interface and are difficult to sweep off. Most of the experiments are conducted with zirconium oxide beads "ZrO" ($\rho_s = 3.8 \ g.cm^{-3}$) or coated glass beads "SiO" ($\rho_s = 2.5 \ g.cm^{-3}$), however we also use occasionally other materials (see appendix D for details). Particle size and oil-water contact angle vary in the range: $20 < d (\mu m) < 900$ and $60 < \theta_u$ (°) < 150.



Figure 2.6: Schematic of the raft formation. Particle are sprinkled from above, pierce the oil-air interface and aggregate at the oil-water interface due to capillary forces.

Once the raft is formed, we proceed to the compression experiment. We incorporate two glass plates in the tank. The first one confines the raft laterally (along z) to control its width (thus its aspect ratio) and the second one is mounted to a step motor of micrometer precision (NRT150/M from Thorlabs) and compresses uniaxially the raft (along x, see Fig 2.7). We do small compression steps (between 150 μm and 500 μm) every 5 s or 10 s to let the raft relax to its equilibrium shape. The width of the compressing plate is slightly smaller than the width set by the other glass plate to let the oil and water level equilibrate. For small particles we add a metal grating behind the compressing plate to allow the liquids to flow while stopping the particles. We either look directly at the raft from the side and the bottom with two cameras (Nikon D800E mounted with macro objectives) or we reconstruct its shape using Fourier transform profilometry or FTP (see appendix C for details). We use ImageJ and/or Matlab for image analysis.

As we have seen earlier, the uncompressed shape of the granular raft is not flat. We have a flat central region below the water surface with curved menisci on the edges (Fig 2.7 a)). The depth of the flat portion of the interface is given by a balance of gravity to buoyancy [68] (see also the model in section 2.2.2). In our experiments we



Figure 2.7: a) Schematic of the compression experiment seen from the side. The dashed line represent the water surface in the absence of the raft. b) Schematic of the compression experiment seen from the top. L_0 and W_0 represent the raft length and width when it touches the compressing plates.

look at the buckling of this flat region below the water surface. We distinguish different phases as we increase the raft confinement. At first the raft changes its aspect ratio to accommodate the compression (Fig 2.8 a)). The particles rearrange allowing the width of the raft to increase. These rearrangements are done along shear bands and highlight the discrete nature of the raft. As compression increases, it becomes more difficult for the particles to move around and fill the available space. The accumulated friction and/or the presence of the walls slows down the rearrangement process and a region of the raft starts to buckle out of plane. We observe localised corrugations on the interface (Fig 2.8 b)). Upon further compression, these corrugations quickly spread on the whole surface of the raft. At some point, we start to see much bigger out of plane displacements, still perpendicular to the direction of compression but with a different shape (Fig 2.8 c)). These patterns grow in amplitude as we increase compression until a sharp transition occurs. One of them starts to grow much faster while the others either decrease or stop to grow: the deformation localises in a fold (Fig 2.8 d)). The fold grows as confinement increases until at some point the raft cannot maintain its integrity and breaks, letting the fold (and some oil) sink at the bottom of the tank.

In the following we will not study the rearrangement process, but only the buckling of the interface. To do so we measure three quantities: the wavelength of the wrinkles λ (Fig 2.9 a)), the amplitude of the wrinkles and the folds A and the distance between the compressing plates L (Fig 2.9 b)). In addition, we extract the shape of the raft with FTP (Fig 2.9 c)).

The compression is monitored by looking at the distance between the compressing plates L. During the compression experiment described above we have several critical distances. In their typical order of appearance: L_0 is the distance between the plates when the raft just start to touch them, L_{sw} is the distance when we start to see the first corrugations that we call "small wrinkles", L_{lw} is the distance when we start to see the larger ones that we call "large wrinkles", L_f is the distance when we start to



Figure 2.8: Bottom pictures of a compressed granular raft at the oil-water interface. Compression increases from **a**) to **d**). Particles: "ZrO" $d = 150 \,\mu m$. **a**) The raft has not buckled yet, the interface is smooth. Scale bar, $1 \,cm$. **b**) We see the first corrugations around the shear bands. **c**) The larger wrinkles appeared. **d**) The deformation is localised in a unique fold in the centre of the raft. The arrow indicates the direction of compression



Figure 2.9: a) Bottom picture of a wrinkled raft at the air-water interface. As a scale bar one can use the particle size $d = 500 \,\mu m$ ("SiO"). b) Side picture of a folded raft. Particles: "ZrO" $d = 150 \,\mu m$. As a scale bar, one can use the fold amplitude $A \approx 2 \,mm$. c) Profile from b) extracted with FTP.

see the fold and L_{sc} is the distance when the fold reaches self-contact. Since our raft changes its shape via particle rearrangement during the experiment, it is not easy to define a one dimensional compression Δ similar to compressed elastic sheets. With that in mind, we first define the excess confinement: $L_0 - L$. For $L_0 - L < 0$ the raft does not touch the compressing plates, the compression is non zero (because the particles have to climb the liquid menisci around the plates and the raft is compressed by its weight) but negligible.

We measure the amplitude A both from side pictures and FTP. From the side pictures we crop the flat region of the raft, then we binarize the picture and extract the contour via edge detection. Then we define A as the vertical distance between the lowest and highest points in the contour. From FTP we get the full three dimensional profile of the fold. To get the amplitude we cut a slice through the profile (Fig 2.9 c)) close to the centre of the fold. Then we can measure A with the same method and compare them to calibrate the profilometry (see appendix C.3). FTP provides us the full raft shape and allows us to monitor adjacent wrinkles amplitude easily. In the side pictures we only get a projection of the contour and it is not unusual for wrinkles to be hidden or out of focus. The downside of FTP is that we cannot extract the profile of large amplitude folds. The fold becomes too steep and discontinuities in the reconstruction give a wrong result.

Fig 2.10 shows the maximum amplitude A as a function of the excess length $L_0 - L$ for a representative raft ("ZrO" at the oil-water interface) with representative side pictures. Fig 2.10 a) highlights all the different phases and the transition between them. During the rearrangement phase $(L > L_{sw})$ the raft is not compressed and the interface is smooth (2.10 b)). The non zero value of the amplitude A is due to the surface roughness and is below one particle diameter. For $L_{lw} < L < L_{sw}$ we start to see the small wrinkles (2.10 c)). Their amplitude is negligible, though and A starts to grow significantly when the large wrinkles appear $(L_f < L < L_{lw}, 2.10 d)$). It slowly grows up to a few particle diameters until the wrinkle to fold transition. After L_f , the fold amplitude grows much faster. A increases linearly with $L_0 - L$ before and after the self-contact (2.10 e)). The maximum amplitude the fold can reach before the granular



Figure 2.10: a) Maximum amplitude A as a function of the excess length $L_0 - L$ for a representative raft ("ZrO" at the oil-water interface, $d = 150 \ \mu m$). The grey horizontal bars indicate the critical compressions, the transition being difficult to determine the width of the bar shows the uncertainty on these critical compressions. b)-e) Side pictures corresponding to the blue symbols in a). Compression increases from b) to e). Scale bar, 1 cm. b) The compression just started, the bottom of the raft is smooth. c) We can see the small wrinkles on the side pictures but measuring their amplitude is challenging. d) The large wrinkles appeared. e) The fold is fully developed and in self-contact.

raft destabilises is several hundred times the particle size.

We immediately see similarities with the experiment presented in chapter 1. In particular, we see a wrinkle to fold transition with a localisation of the deformation. However, we also see many differences. The main ones being the presence of two wavelengths and the difference in buckling shapes. In the following we will study these phases in their order of appearance. We will look at the wrinkles, the wrinkle to fold transition and the fold evolution as compression increases. Finally, we will mention the non elastic behaviours observed.

2.2.1 Wrinkles

2.2.1.1 Wavelength

We first measure the wavelength λ of the two wrinkling patterns that we have observed between L_{sw} and L_f . We measure it directly from the bottom pictures. To be able to see the wrinkles easily we light the raft perpendicularly to them (along x). When a protrusion appears, it blocks the light and cast a shadow behind him allowing us to see it even if its amplitude is very small. Then we measure by hand the projected distance along x between adjacent protrusions (Fig 2.9 a)). We do this measurement for several wrinkles on the same picture and take the mean as the wavelength for this picture. We only select wrinkles close to each other, wrinkles separated by a distance much bigger than the average wavelength are not included. We do not use FTP to measure



Figure 2.11: **a)** Wavelength λ as a function of the excess confinement $L_0 - L$ for a single raft ("ZrO" $d = 150 \ \mu m$). The data points represent the mean, the error bars the standard deviation and the shaded grey area the extreme values, 383 individual measurements have been used. **b)** Histogram of the wavelength measured at two different compressions (coloured points in **a**)). The orange bars represent the histogram before the apparition of large wrinkles $(L_0 - L = 14.4 \ mm)$, the blue bars represent the histogram after the apparition of large wrinkles $(L_0 - L = 17.1 \ mm)$. 74 individual measurements have been used.

the wavelength for two reasons: first we are not able to detect the small wrinkles and thus we cannot access their wavelength; second even though we can measure the large wavelength, since only a portion of the raft is lit the sample size is very small.

Fig 2.11 a) shows the measured wavelength (mean, standard deviation and extreme values) as a function of the compression (between L_{sw} and L_f). The data include the wavelengths of all wrinkles, small and large. We observe a significant increase of the mean wavelength (along with the standard deviation and extreme values) at a critical compression. In Fig 2.11 b) we plot the wavelength distribution before and after this critical compression. We see that after the transition to large wrinkles, the distribution becomes much wider toward large wavelength. Both large and small wrinkles coexist after this transition and the mean wavelength is no longer a relevant measurement. However, the shape of small and large wrinkles is quite different such that it is easy to distinguish them (Fig 2.12 a)-b)). We can thus measure their wavelength independently and get a mean value for the small λ_{small} and the large wavelength λ_{large} . We measure both wavelengths for all our particles, at the oil-water and air-water interface. Fig 2.12 c) shows both wavelengths as a function of the particle size in a log-log plot. We immediately see that both wavelengths grow with the particle size d but with different power laws. The large wavelength depends on the particle size with a power law close to 1/2 while the small wavelength varies with a power law closer to 1. Both wavelengths have no obvious dependence with the material properties (density ρ_s and contact angle θ_{y}) or the raft aspect ratio. However, the big wavelength is smaller at the air-water



interface while changing the liquids does not impact the small wavelength.

Figure 2.12: Bottom pictures of small **a**) and large **b**) wrinkles. Particle size $d = 150 \,\mu m$ ("ZrO"). **c**) Wavelength as a function of the particle size. Blue symbols represent the large wavelength, red symbols represent the small wavelength. The symbol indicates the particle type, closed symbols represent oil-water experiments while open symbols represent air-water experiments. The horizontal error bars show the polydispersity given by the manufacturer. The vertical error bars show the standard deviation of the mean wavelength per picture from different rafts (and not the standard deviation for individual measurements). The solid and dashed lines are guide to the eye.

Remark. The wavelength at the air-water interface for small particle $(d < 100 \ \mu m)$ should be interpreted cautiously. These particles are powdery and are hard to sprinkle correctly. It is not easy to produce monolayers, especially at the air water interface where there is no oil layer to help separate the particles. In particular, in Fig 2.12 c) the wavelength for "SiO" beads of size $d = 55 \ \mu m$ and $d = 90 \ \mu m$ is higher than the global trend. We suspect it comes from multilayer formation (like in [92]) during the sprinkling process.

The small wavelength seems to only depend on the particle size with a power law close to 1. In Fig 2.13 a) we plot the small wavelength as a function of the particle size with linear axes. The data lie on a straight line and a linear fit gives $\lambda \sim 6.8d$. The small wrinkles look very different from the wrinkles on floating elastic sheets. Here we have small dimples which extend over a few particle diameters and with a very small amplitude (below one particle diameter) while they extend on the whole width of the sheet for elastic materials and they reach amplitudes several times above the sheet thickness. The fact that it only depends on the particle size and the linear dependence suggests a physical mechanism that originate from the discrete nature of the raft but we do not have a model to explain our data. The small wrinkles always appear at a smaller compression. This is the initial buckling event and we may want to compare it to the one observed by Taccoen *et al.* [98]. We do not have any buckling pressure measurement

2.2. Experiment and general results

so a direct data comparison is not possible, however they have observed a non elastic buckling. To model the buckled interface they consider a sinusoidal displacement of the particles with a wavelength equal to two particle diameter $\lambda = 2d$ and an amplitude of the order of the particle size. We can also compare our wavelength to the one observed by Croll *et al.* [95, 96]. They study a very different system, particles are colloidal and stick to an elastomer through Van der Waals forces. Upon compression the monolayer buckles with a wavelength that only depends on the particle size linearly (they find $\lambda \sim 5.3d$). They present a granular chain on foundation model to analyse their results. We can wonder if the underlying physical process is identical for our small wrinkles.



Figure 2.13: a) Wavelength of the small wrinkles λ_{small} as a function of the particle size d. The solid line is the best linear fit to the data $\lambda_{small} = 0.2 \ (mm) + 6.8d \ \mathbf{b}$) Wavelength of the large wrinkles λ_{large} as a function of $\sqrt{\ell_c d}$. The solid line is the best linear fit (through the origin) to the data $\lambda_{large} = 3.39\sqrt{\ell_c d}$. For both plots the symbol indicates the particle type, closed symbols represent oil-water experiments while open symbols represent air-water experiments.

The large wavelength depends on the particle size with a power law close to 1/2 and also depends on the liquids used. Their shape is very similar to the wrinkles already observed in many studies [49, 51, 81, 87–92] and λ_{large} does not depend on the particle contact angle like in [49, 107]. Fig 2.13 b) shows the large wavelength as a function of $\sqrt{\ell_c d}$. We recover the prediction of [49] (eq (2.1.1)) but with a slightly lower prefactor (3.39 instead of 4.84). Two other studies[92, 107] already confirmed this prediction and also found lower prefactors, however we here vary the liquids and can confirm the dependence on ℓ_c . This confirms that the wavelength of the large wrinkles can be predicted with a floating elastic sheet model. In the case of heavy elastic sheets (section 1.2.2) the wavelength does not depend on the sheet density and this is also true for λ_{large} . However, for heavy enough particles (dense and/or large) we do not observe the large wavelength. As compression increases we go from the small wavelength directly to the fold.

2.2.1.2 Amplitude and wrinkle to fold transition

We have seen that the amplitude starts to be measurable for large wrinkles. Fig 2.14 a) shows the amplitude A as a function of the excess length $L_0 - L$ zoomed around the wrinkle to fold transition for several adjacent wrinkles. The full range of the FTP is displayed, for lower compressions the signal to noise ratio is too low and for higher compressions the fold is too stiff and the signal presents unphysical discontinuities. Within this range, the amplitude measured with FTP matches the one measured from side pictures. We see in Fig 2.14 a) that before the wrinkle to fold transition nearby wrinkles grow at the same rate and have similar amplitudes. After the wrinkle to fold transition, only one of them continues to grow while its neighbours decreases in amplitude. This is the signature of a localisation process.



Figure 2.14: a) Amplitude A as a function of the excess length $L_0 - L$ for a "ZrO" raft at the oil-water interface $(d = 150 \ \mu m)$. Red open squares represent the maximum amplitude measured from side pictures, blue closed circles represent the amplitude of four nearby wrinkles measured with FTP. b) Dimensionless amplitude A/λ as a function of the compression $(L_{lw} - L)/\lambda$ for the same raft. The black solid line represents the prediction for a floating elastic sheet in the linear regime and the black dashed line the prediction in the non linear regime. The dashed line stops when the fold reaches self-contact in the model, the dotted line is a guide to the eye. The grey horizontal bars indicate the transitions between the different phases.

Remark (Error bars). Here and in the following, we do not plot error bars in the curves $A/\lambda = f(\Delta/\lambda)$ for clarity. The uncertainties on A and Δ are negligible, however there is a significant uncertainty on λ that propagates through the rescaling.

We have seen that the wavelength of the large wrinkles could be explained with a floating elastic sheet model and now we have a wrinkle to fold transition that looks similar to the one in floating elastic sheets. Let us try to apply the floating elastic sheet formalism developed in the introduction of chapter 1 to our data. As a reminder, for a

floating elastic sheet (without weight) the maximum amplitude A as a function of the compression Δ is given in the linear regime by $\frac{A}{\lambda} = \frac{\sqrt{2}}{\pi} \sqrt{\frac{\Delta}{L_0}}$ where λ is the wavelength of the wrinkles and L_0 the sheet length [32]. In the non linear regime for a sheet of infinite length $A = \Delta/2$ [3] for symmetric folds. To be able to compare an "effective" sheet model to our granular rafts we must first define the "effective" compression and the "effective" initial length of our granular rafts. It is not straightforward because the raft changes its shape during compression. We decide to use L_{lw} as the initial length because the elastic model starts to work only for large wrinkles and for a sheet, as soon as $L < L_0$ the sheet buckles and A grows. Using $L_{lw} - L$ as an effective compression fulfil these requirements. Besides, the relevant wavelength is λ_{large} since only the large wrinkles are of elastic nature. In the following, to be consistent with the notations for elastic sheets we will use Δ for $L_{lw} - L$ and λ for λ_{large} .

Remark. As previously mentioned, for the heaviest particles (large and/or dense) we do not see the large wrinkles. The raft transition directly from small wrinkles to a fold. In some unusual cases even when we see large wrinkles they appear after the fold $(L_f < L_{lw})$. For all these particular cases we define L_{lw} as the length where A stops being negligible and we use it to define the compression: $\Delta = L_{lw} - L$.

Fig 2.14 b) shows the dimensionless amplitude A/λ as a function of the dimensionless compression Δ/λ zoomed around the wrinkle to fold transition for the raft in a) and the result of the floating elastic sheet model. We see that the linearised elastic sheet model is able to predict the amplitude of the large wrinkles. This is not so surprising as this result is mainly geometric, it can be recovered with two simple ingredients: a sinusoidal deformation and the inextensibility constraint. However, all the other predictions from the model fail. The wrinkle to fold transition occurs at a compression much higher than for floating elastic sheets ($\Delta_c \sim 0.9$ instead of ~ 0.3). The amplitude of the fold is linear with the compression but with a different slope ($A \sim \Delta$ instead of $\Delta/2$). The self contact occurs much later than in the model ($\Delta_{sc} \sim 1.5$ instead of 0.89). We have seen in chapter 1 that after the self-contact the amplitude continues to grow at the same rate for elastic sheets and it is also the case for our rafts but the amplitude never follow the slope 1/2. Finally, the fold shape is completely different and the fold is not perfectly two dimensional (see section 2.2.4). Here we demonstrate it for one raft with one particle size but these are general results.

Fig 2.15 shows the dimensionless amplitude A/λ as a function of the dimensionless compression Δ/λ zoomed around the wrinkle to fold transition for two other granular rafts (different material and/or particle size) and the result of the floating elastic sheet model. We can draw the same conclusions: Δ_c and Δ_{sc} are always bigger in the experiment than in the model, the amplitude of the wrinkles is described correctly by the linear floating elastic sheet model but the amplitude of the fold is not well described by the non linear floating elastic sheet model.

2.2.2 Fold before self-contact

For floating elastic sheets, rescaling all lengths by λ collapses all amplitude vs compression curves onto a master curve. If we try to do so with the data in Fig 2.14 and 2.15 we obtain Fig 2.16 (we plot only the maximum amplitude for clarity). As



Figure 2.15: a) Dimensionless amplitude A/λ as a function of the compression Δ/λ for a "SiO" raft at the oil-water interface ($d = 500 \,\mu m$) measured with FTP. b) Dimensionless amplitude A/λ as a function of the compression Δ/λ for a "ZrO" raft at the oil-water interface ($d = 250 \,\mu m$) measured with FTP. For both plots the black solid line represents the prediction for a floating elastic sheet in the linear regime and the black dashed line the prediction in the non linear regime. The dashed line stops when the fold reaches self-contact in the model, the dotted line is a guide to the eye.

expected, the wrinkling regime is rescaled properly. The critical compression for the wrinkle to fold transition is different in each experiment but always superior to the one for floating elastic sheets. It is actually something that is not very reproducible, two experiments with the same parameters may exhibit different Δ_c . Then the fold amplitude is always linear with similar slopes ~ 1.

By comparing our granular rafts to floating elastic sheets we make several unreasonable hypotheses. An assumption that we have made is neglecting the raft weight. Yet it has been shown that the raft weight is important to predict granular rafts properties [68, 110]. We already added the sheet weight in the floating elastic sheet model in chapter 1 and tested its validity with real heavy elastic sheets. Can this model be adapted to predict the behaviour of granular rafts ?



Figure 2.16: c) Maximum dimensionless amplitude A/λ as a function of the compression Δ/λ for the three experiments shown above measured with side pictures The black dashed line the prediction in the non linear regime. The dashed line stops when the fold reaches self-contact in the model, the dotted line is a guide to the eye. The shaded grey area shows the prediction for a floating elastic sheet in the linear regime for the different sheet lengths corresponding to the rafts.

Model

Following the work of Rivetti and Neukirch [101], we now write the model in terms of internal forces and moments using the Euler-Bernoulli beam theory (appendix **B**). This formulation allows us to change the boundary conditions and test non linear elasticity more easily. Let us consider a beam of length L_0 , width W, thickness t and density ρ_s constrained in the (x, y) plane between two fluids of densities ρ_{up} for the upper fluid and ρ_{low} for the lower one. The kinematic, equilibrium and constitutive equations in the intrinsic coordinate system (s, θ) read:

$$\begin{array}{ll} \partial_s x = \cos\theta & & \partial_s n_x = -p_x \\ \partial_s y = \sin\theta & & \partial_s n_y = -p_y \\ m_z = B\partial_s\theta & & \partial_s m_z = n_x \sin\theta - n_y \cos\theta \end{array}$$

Where [x(s), y(s)] are the coordinates of the centreline of the beam. \overrightarrow{n} are the internal forces (per unit width), \overrightarrow{p} are the external forces (per unit width) and m_z is the internal bending moment (per unit width). In the case of a floating heavy beam the external forces are the beam weight (with buoyancy taken into account) and the fluids hydrostatic forces:

$$p_x = \Delta \rho g y \sin \theta$$
$$p_y = -\Delta \rho g y \cos \theta - (\rho_s - \rho_{low}) g t$$

Where $\Delta \rho = \rho_{low} - \rho_{up}$ is the difference between the liquids densities. This gives us six first order differential equations we thus need six boundary conditions. We assume

that the beam is clamped on both ends and that one end starts at (0,0). For the last boundary condition we could choose to impose the horizontal compressive load: $n_x(L_0) = -n_x(0) = P$ like in chapter 1. But we rather impose the horizontal end displacement Δ like in the experiment:

$$y(0) = 0$$
 $y(L_0) = 0$
 $\theta(0) = 0$ $\theta(L_0) = 0$
 $x(0) = 0$ $x(L_0) = L_0 - \Delta$

To facilitate the calculation, we rescale lengths by $\ell_{eh} = (B/\Delta\rho g)^{1/4}$, forces by ℓ_{eh}^2/B and the moment by ℓ_{eh}/B and only use dimensionless quantities in the following of this section.

$$\begin{aligned}
\partial_s x &= \cos \theta & \partial_s n_x &= -y \sin \theta \\
\partial_s y &= \sin \theta & \partial_s n_y &= y \cos \theta + M \\
m &= \partial_s \theta & \partial_s m &= n_x \sin \theta - n_y \cos \theta
\end{aligned}$$
(2.2.1)

Where $M = \frac{(\rho_s - \rho_{low})t}{\Delta \rho \ell_{eh}}$ is the dimensionless mass parameter already introduced. The rescaled boundary conditions are identical:

$$y(0) = 0 y(L_0) = 0
\theta(0) = 0 \theta(L_0) = 0 (2.2.2)
x(0) = 0 x(L_0) = L_0 - \Delta$$

If we set M = 0 we recover the system of equations derived in [101]. We can also check that our system (2.2.1) is equivalent to the equation derived using the energy (1.2.6). To do so we differentiate with respect to s the momentum equilibrium equation and substitute $\partial_s n_x$ and $\partial_s n_y$:

$$\partial_s^2 m_z = -y - M \cos \theta + \partial_s \theta \left(n_x \cos \theta + n_y \sin \theta \right)$$

We differentiate the result with respect to s and substitute $\partial_s n_x$, $\partial_s n_y$ and m_z again:

$$\partial_s^4 \theta = (2M\partial_s \theta - 1)\sin\theta + \partial_s^2 \theta \left(n_x \cos\theta + n_y \sin\theta - (\partial_s \theta)^2 \right)$$
(2.2.3)

We introduce $\check{\mathcal{H}} = \frac{1}{2}m^2 + n_x \cos \theta + n_y \sin \theta - My$. We can show that $\partial_s \check{\mathcal{H}} = 0$, thus $\check{\mathcal{H}}$ is a conserved quantity along the beam and we can evaluate it in s = 0.

Remark (Boundary conditions). The equation energy (1.2.6) has been derived with the boundary conditions $\partial_s \theta(0) = 0$ and if we want to recover the exact same equation we must assume the same boundary conditions. With different boundary conditions, equation (1.2.6) would be different but we would still recover it with this calculation.

$$\breve{\mathcal{H}}(s) = \breve{\mathcal{H}}(0) = \frac{1}{2}m^2(0) + n_x(0) = \frac{1}{2}(\partial_s\theta(0))^2 - P = -P$$

If we substitute $n_x \cos \theta + n_y \sin \theta$ in (2.2.3) using $\tilde{\mathcal{H}}$ we recover the energy equation (1.2.6).



Figure 2.17: Numerical dimensionless sheet profiles obtained by solving equation (2.2.1) for $\Delta = 3.5$, M = 3 and $L_0 = 16\pi$. a) First branch of solution, obtained by increasing M and then Δ . b) Second branch of solution, obtained by increasing Δ and then M.

We solve numerically the system of equations (2.2.1) for very large sheets using the MATLAB routine bvp5c with a continuation algorithm to follow the solutions as we vary the parameters. With numerical continuation, we are able to vary the parameters L_0 , Δ and M independently to explore all the solutions. Depending on the continuation route we identify two different branches of solution. If we first increase M to the desired value and then increase Δ we observe localised buckling near both menisci (Fig 2.17 a)), however if we first increase Δ and then M we observe one fold in the centre of the sheet (Fig 2.17 b)). The last branch with the fold in the centre is the closest to the experiments and we will therefore focus on this one but we will discuss the other branch in section 2.2.4. In Fig 2.18 we plot the profiles we obtain (second branch) with equation (2.2.1) for different compressions for M = 0 and M = 1.

We immediately see that the sheet is shifted down by a value y = -M, we recover a shape similar to the raft with a flat central region below the water surface and menisci connecting this region to the water surface. At this location below the water surface the sheet weight is balanced by the hydrostatic overpressure, this reads for an element dSof the sheet: $(\rho_s - \rho_{low})dgdS = (\rho_{low} - \rho_{up})ygdS$. The second difference is that adding the mass focuses the deformation faster. The wrinkles are nearly invisible and for very low compressions we get a fold. Finally, the shape of the sheet around the fold is also very different.


Figure 2.18: Numerical dimensionless sheet profiles obtained by solving equation (2.2.1) for M = 0 (blue) and M = 1 (orange). The length of the sheet is $L_0 = 12\pi$. Compression increases from top to bottom: $\Delta = 2.0, 2.5, 3.5, 4.5$.

2.2. Experiment and general results

Comparison with experiments

To avoid confusion with the experimental variables, we come back to dimensional quantities except for M in the following. To be able to compare this model to our granular rafts we must first define the "effective" parameters of our granular rafts. We have already defined its effective initial length L_{lw} and its effective thickness d. We must now define its effective density ρ_{eff} . We assume the particles are monodisperse spheres of diameter d, with a contact angle θ_y and we neglect the gravity such that menisci between particles are flat. Under these assumptions the effective density (taking buoyancy into account) is:

$$\rho_{eff} = \frac{2}{3}\phi \left(\rho_s - \frac{\rho_{low} + \rho_{up}}{2} - \cos\theta_y \frac{\rho_{low} - \rho_{up}}{2}\right)$$

Where ρ_s is the particle density and ϕ is the two dimensional packing fraction. In our case we have $\cos \theta_y \frac{\rho_{low} - \rho_{up}}{2} \ll \frac{\rho_{low} + \rho_{up}}{2} \ll \rho_s$ and we can simplify the effective density to:

$$\rho_{eff} \approx \frac{2}{3}\phi\left(\rho_s - \frac{\rho_{low} + \rho_{up}}{2}\right)$$

Remark (Derivation of the effective density). Let us consider an element of volume of this effective sheet dV = dSd where dS is the in plane surface element (in the (x, z) plane). This volume is filled with N particles and both fluids. It has a mass $dm = dm_s + dm_{low} + dm_{lup}$. The volume occupied by the particles is $dV_s = N\frac{4}{3}\pi \left(\frac{d}{2}\right)^3$ and by definition $\phi = \frac{dS_s}{dS} = \frac{N\pi \left(\frac{d}{2}\right)^2}{dS}$ with dS_s the surface of the particles projected in the (x, z) plane. We inject ϕ in the volume occupied by the particles: $dV_s = \frac{2}{3}d\phi dS = \frac{2}{3}\phi dV$. Outside this volume we have both liquids, if we incorporate the buoyancy all the mass coming from this liquid volume is compensated. To determine the effective density with the buoyancy taken into account we just have to look at the volume of each liquid displaced by the particles. The particles are partially wet by each liquid and the position of the contact line without gravity only depends on θ_y . The height of the portion wet by the bottom liquid is $h_{low} = \frac{d}{2} (1 + \cos \theta_y)$ and the portion wet by the top liquid is $h_{up} = \frac{d}{2} (1 - \cos \theta_y)$. Thus a portion h_{low}/d of the whole volume occupied by particles is in the lower liquid and a portion h_{up}/d is in the upper liquid. Finally we have:

$$\rho_{eff} = \frac{\mathrm{d}V_s}{\mathrm{d}V}\rho_s - \frac{\mathrm{d}V_s}{\mathrm{d}V}\frac{h_{low}}{d}\rho_{low} - \frac{\mathrm{d}V_s}{\mathrm{d}V}\frac{h_{up}}{d}\rho_{up}$$
$$= \frac{2}{3}\phi\left(\rho_s - \frac{1+\cos\theta_y}{2}\rho_{low} - \frac{1-\cos\theta_y}{2}\rho_{up}\right)$$

Now we can use ρ_{eff} to calculate the value of $M = 2\pi \frac{\rho_{eff}d}{\Delta\rho\lambda}$ for a granular raft. Measuring ϕ precisely with our rafts is difficult because the liquid menisci between them are difficult to separate with image analysis once the raft is back lit. However, we can look at the variation of ϕ and it is only a few percent during an experiment. Thus, we consider ϕ constant and since the particles are jammed and polydisperse (no crystalisation), we use the value $\phi = 0.84$ to calculate ρ_{eff} . This is the random close packing for a two dimensional system of bidisperse spheres [112]. For our granular rafts $M \sim 1$, this is one order of magnitude above the maximum value we reached with heavy elastic sheets. With equation (2.2.1) we can easily see that if $M << |(y/\ell_{eh}) \cos \theta|$ the sheet weight is negligible while if $M >> |(y/\ell_{eh}) \cos \theta|$ it will be dominant. For a sheet without weight $y/\ell_{eh} \sim 1$ and $\cos \theta < 1$ thus we expect minor changes with $M \sim 0.1$ like in chapter 1. But for our rafts M is no longer negligible and we can expect visible differences compared to the weightless case.

Before we can make a comparison, we still have to address one difference between the model and the experiment. In the model, for $\Delta = 0$ the sheet is flat at y = 0 and the beginning of the compression ($\Delta \leq 0.4\lambda$) is only putting the sheet to its equilibrium position at $y = -M\ell_{eh}$ without any buckling while with our experimental definition of $\Delta = L_{lw} - L$ as soon as $\Delta > 0$ we see wrinkles. To start the buckling at $\Delta = 0$ in the model we will remove the menisci by setting a new set of boundary conditions:

$$y(0) = -M\ell_{eh} \qquad y(L_0/\ell_{eh}) = -M\ell_{eh} \theta(0) = 0 \qquad \theta(L_0/\ell_{eh}) = 0 x(0) = 0 \qquad x(L_0/\ell_{eh}) = \frac{L_0 - \Delta}{\ell_{eh}}$$
(2.2.4)

We now solve equation (2.2.1) with the boundary conditions (2.2.4), *i.e.* we look at the compression of the flat part of the sheet. Most of the time we recover the same fold shape with both boundary conditions but at different values of Δ (Fig 2.19). However, at low compression, solving with the boundary conditions (2.2.2) bifurcate to the first branch (Fig 2.17 a)) while with the boundary conditions (2.2.4) we get a uniform wrinkled state like in the experiments.



Figure 2.19: Numerical sheet profiles obtained by solving equation (2.2.1) for M = 1 with the two sets of boundary conditions. The orange solid curves correspond to the boundary conditions (2.2.2), the dashed green curves to (2.2.4). We recover the same fold shapes but at a different compression. The length of the sheet is $L_0 = 12\pi \ell_{eh}$.

Remark. The solution we obtain when we solve the energy equation (1.2.6) in chapter 1 is identical to the solution we obtain with the force/moment equations (2.2.1) without

the menisci, *i.e.* with the boundary conditions (2.2.4). This is surprising because we use the boundary conditions $y(\pm L_0/2\ell_{eh}) = 0$ to solve the energy equation. This comes from the particularity of equation (1.2.6) to absorb the changes in boundary conditions by shifting the value of P. Since we impose $\partial_s \theta(\pm L_0/2\ell_{eh}) = 0$, the only possible solution is the one without menisci and it shifts the profile in the vertical direction by adjusting P.

Now we can compare the model to the data. We have four parameters in the model: ℓ_{eh} , M, Δ and L_0 . However, since the deformation is very quickly localised in a narrow region of size $\sim \ell_{eh}$ the sheet length L_0 has no impact in the model as long as it is much larger than ℓ_{eh} . It is the case in our experiment and we thus just set $L_0 >> \ell_{eh}$ in the model and do not bother adjusting it to experimental values. The other parameters being accessible experimentally, we have no free parameters. To compare this heavy floating elastic sheet model to our granular rafts we first look at the dimensionless amplitude as a function of the compression in Fig 2.20. The model is again far from the data but we can notice a few improvements. The slope obtained with the model is much closer to the experimental slope $A \sim \Delta$ and the self-contact occurs at a similar



Figure 2.20: Dimensionless amplitude as a function of compression for a "ZrO" raft at the oil-water interface $(d = 150 \,\mu m)$ measured with FTP. The black solid line represents the prediction from equation (2.2.1) with the boundary conditions (2.2.4), M = 3.25 and $L_0 = 25\pi \ell_{eh}$. It stops when the numerical profile reaches self-contact. The grey horizontal bars indicate the transitions between the different phases.

dimensionless amplitude in the model and the experiment.

We can also use the whole profile measured with FTP to compare the model to the experiment. We have seen in Fig 2.20 that for a given compression Δ/λ , there is a big discrepancy between the experimental and numerical amplitude. It is the same for the profiles, the experimental and numerical profile for a given compression Δ/λ are different. However, if we now compare for a given dimensionless amplitude A/λ . the experimental and numerical profiles are very similar. Fig 2.21 shows a comparison between the numerical profiles obtained from equation (2.2.1) with the boundary conditions (2.2.4) (M = 3.25) and the experimental profiles measured with FTP of a "ZrO" raft at the oil-water interface $(d = 150 \ \mu m)$. The numerical solution matches very well the experimental fold profile for every amplitudes except close to self-contact. At this amplitude, we see in the model the formation of a construction in the fold that we call a neck. This neck eventually self-contact in the model while we do not see it in FTP. However, if a neck forms in the experiment, FTP would not be able to see it. Besides, the model predicts a neck whose width is one or two particle size and since only the sheet centreline is drawn we can question the relevance of both the numerical and experimental profiles around the fold close to self-contact.



Figure 2.21: a) Reproduction of Fig 2.20. We added the green dotted lines to indicates the data used for the profiles. b)-d) Numerical (blue) and experimental (red) fold profiles corresponding to the green lines in a). The black open circles indicate the particle size ($d = 150 \ \mu m$). Compression increases from b) to d). The profiles have been translated such that the centre of the fold is at x = 0 and the flat portion of the raft is at y = 0.

We present results in Fig 2.21 for one raft with one particle size but these are general results. Fig 2.22 shows comparisons between numerical and experimental profiles at the same dimensionless amplitude for other rafts. It is interesting to note that for Fig 2.22 b) we have calculated M and rescaled the profile with $\lambda = 4.7$, a value extrapolated

68



from the fit in Fig 2.13 b) since we have never seen large wrinkles for these particles.

Figure 2.22: Numerical (blue curve) and experimental (red squares) fold profiles for the same dimensionless amplitude. The black open circles indicate the particle size. The profiles have been translated such that the centre of the fold is at x = 0 and the flat portion of the raft is at y = 0. **a**) "ZrO" particles, $d = 250 \,\mu m$, M = 5.01. **b**) "ZrO" particles, $d = 350 \,\mu m$, M = 4.66. **c**) "SiO" particles, $d = 625 \,\mu m$, M = 3.35.

Taking into account the weight of the sheet in the model is still not enough to give a full quantitative description of the buckling of granular rafts. It is better than neglecting it tough, as we have seen some improvements. The experimental fold shape is well reproduced by the model but at a different compression. The discrepancy between the experimental and numerical wrinkle to fold transition critical compression Δ_c is worse though, since adding the weight in the model reduces the theoretical Δ_c . But for $\Delta > \Delta_c$ the amplitude as a function of the compression curves have slopes similar to experimental ones. To sum up, except for the compression Δ the heavy floating elastic sheet model reproduces well the experimental observations.

Influence of the menisci

How can we explain this discrepancy in the compression ? Again we have made many assumptions, and by removing the menisci in the model by changing the boundary condition we implicitly assumed that they were rigid and that they conveyed all the compression to the flat region. If we focus on a meniscus during an experiment we see that this is not true. Fig 2.23 shows a close up view of the left meniscus during the compression experiment presented in Fig 2.10. We can see that as compression increases, its curvature increases, absorbing some of the compression. Until the fold becomes big enough to pull on the meniscus, decreasing its curvature and releasing some of the stored compression. Moreover, the meniscus shape and behaviour depends on other factors such as the particle size or the position of the fold. For instance the left and right menisci in Fig 2.10 e) are different due to the position of the fold.



COMPRESSION

Figure 2.23: Close up on the left meniscus of the raft in Fig 2.10. Compression increases from left to right. Scale bar, 2 mm.

To make any quantitative predictions on the compression Δ , we must remove the effects of the menisci from the experimental compression. Aside from numerical difficulties with the boundary conditions (2.2.2), we choose to remove menisci in both the experiments and the numerics instead of keeping them because they behave differently. Indeed, the experimental meniscus is a combination of the pure fluid meniscus due to the water wetting the compressing sheet and the raft meniscus due to its weight. It therefore distorts more than the numerical one and leans on the compressing sheet. Besides, we do not really know how to describe properly the experimental boundary conditions. We thus simplify the problem by removing the menisci and consider a flat interface.

Removing the menisci in the experiments allows us to extract L^* , the length of the flat region of the raft (Fig 2.24 a)). The compression of the flat region is then $\Delta^* = L_{lw}^* - L^*$. To remove the menisci in the experiments, we first extract the projected contour from the side pictures. Then we detect the position of the flat region below the water surface and define H_{men} the depth of that region (which is also the meniscus height). Then we cut a percentage β of the meniscus, *i.e.* we remove the portion of the contour for which $y > -\beta H_{men}$. The procedure is shown in Fig 2.24 b)-c). We can easily measure L^* from the contour without the menisci. We can see that between Fig 2.24 b) and c) the ratio L/L^* is different, it shows that the meniscus absorb some of the compression. However, the result is highly dependent on the value of β . If $\beta \to 0$ then we keep most of the meniscus and $L \approx L^*$, but if $\beta \to 1$ we remove most of the meniscus and L^* grows while we reduce L (which makes no sense since the amplitude of wrinkles and folds never decreases). Most of the time $\beta \sim 0.8 - 0.85$ is the highest value for which L^* is monotonically decreasing. We choose $\beta = 0.8$ in the following, but we should keep in mind that this is almost a free parameter.

Now that we have extracted the compression of the flat portion of the raft Δ^* , we can compare the experimental and numerical compressions. Fig 2.25 a) shows



Figure 2.24: a) Side picture of a "ZrO" raft at the oil water interface $(d = 150 \ \mu m)$. The length of the full raft L and the length of the flat region L^* are drawn. Scale bar, $5 \ mm$. b) Contour extracted from a) (blue curve), height of the flat region (black dashed line), contour with the meniscus removed (orange curve, $\beta = 0.85$). c) Contour from the same raft at a higher compression. The height of the meniscus H_{men} is drawn.

the dimensionless amplitude A/λ as a function of the dimensionless compression (without menisci) Δ^*/λ for several rafts at the oil-water interface. We can see that the experimental and numerical curves are closer, the wrinkle to fold transition appears much sooner. This means that menisci deform and absorb compression while the wrinkles develop. However, the critical wrinkle to fold compression is still sometimes far of the one in the model. And more than that it is not reproducible, the two curves for $d = 150 \mu m$ share the same parameters but have very different Δ_c^* . Another improvement is the shape of the curves in the fold regime, they are very close to the prediction of the model. To highlight it we shift the curves such that the apparition of the fold is the zero of compression both in the experiment and the model (Fig 2.25 b)). It is interesting to note than changing M within the range explored in the experiment has a low impact on the curves $A/\lambda = f(\Delta^*/\lambda)$ both in the model and the experiments.

Once we have removed the menisci both in the numerics and in the experiments, the model reproduces very well the experimental observations during the fold regime. The variation of the amplitude with the compression, the moment of self-contact, as well as the fold shapes are well predicted. However, the wrinkling regime is sometimes much longer in the experiments. Firstly, since the raft is not a continuous material, stresses and strains do not propagate uniformly in the raft. We have several experimental evidences to back up this claim; rearrangements still occur after the buckling of the interface and wrinkles sometime do not relax into the fold, especially far from it (Fig 2.8)



Figure 2.25: a) Dimensionless amplitude A/λ as a function of the dimensionless compression (without menisci) Δ^*/λ for different rafts at the oil-water interface ($\beta = 0.8$). The black solid curves represent the prediction from equation (2.2.1) with the boundary conditions (2.2.4) with M = 5.01, 3.25, 2.65 (from top to bottom) and $L_0 = 25\pi \ell_{eh}$. They stop when the numerical profiles reach self-contact. b) Same data shifted by $L_{lw}^* - L_f^*$, such that the zero of compression correspond to the apparition of the fold.

d) and Fig 2.10 e)). Secondly, our experimental system is three dimensional, while the model is bidimensional. In particular, the granular rafts are almost incompressible in three dimensions (because the particles are very stiff) but we can question the validity of the incompressible assumption in two dimensions when the raft continuously changes its aspect ratio during the compression (as we shall explain in section 2.2.4).

2.2.3 Fold after self-contact

We have several ways to know when the raft reaches self-contact. We can either view the raft from the bottom (with large particles) or the top of the fold (Fig 2.26). Before self-contact, light can go through the fold while after self-contact it becomes opaque.



Figure 2.26: Comparison of a fold before and after self-contact seen from below and from above. Bottom view "SiO" particles at the oil-water interface ($d = 500 \ \mu m$). Prior to self-contact we can still see through the fold (black spots) but not after. Top view Backlit "SiO" particles at the oil-water interface ($d = 350 \ \mu m$). Prior to self-contact we can see the bottom of the fold and light goes through it, but after self-contact the fold is opaque.



Figure 2.27: Side view of a fold post self-contact in a "ZrO" raft at the oil-water interface $(d = 150 \ \mu m)$. We can distinguish the vertical portion in self-contact and the portion connecting the fold to the flat region of the raft. This picture was created from 29 individual pictures with focus stacking using Enfuse.

2.2. Experiment and general results



Figure 2.28: Schematic representing the raft post self-contact. The raft is divided in three parts shown here: the region in self-contact (black), the meniscus (purple) and the rest of the raft (yellow). In inset is a schematic representation of the fold.

From the side view we can also notice changes at self-contact. A region of the fold becomes straight along the vertical direction (Fig 2.27). This is the portion of the fold in self-contact: there are two layers of particles with oil inside. The fold morphology post self-contact is different from the one in elastic sheets. In heavy elastic sheets there is a loop that encapsulates the upper fluid, a vertical portion in self-contact and the rest of the sheet that goes back to the water surface (see Fig 1.6 e) in chapter 1). In granular rafts, we do not see the loop, only the vertical portion. The model predicts a loop of the order of the particle size (Fig 2.21 d)), which is the average thickness of the raft. Thus, with polydispersity, even if this loop was "formed" it would be difficult to see it. A more realistic possibility is that due to the polydispersity, the self-contact occurs in several isolated places and we obtain a complex porous two dimensional material with oil trapped inside like the schematic of Fig 2.28. Fig 2.29 shows picture of a fold post self-contact as compression increases. The vertical region in self-contact grows as compression increases and pulls down the rest of the raft. This is another difference with elastic sheets where the region that connects to the portion in self-contact does not really evolve as compression increases. We believe this is due to the dimensionless mass being much higher for granular rafts than for our heavy elastic sheets. As the fold grows, its mass increases and pulls on the rest of the raft. For elastic sheets, within our range of parameters the force is pointed upward or negligible.

Once we reach self-contact, both sides of the fold interpenetrates in the floating heavy elastic model. We cannot use it to model the part of the fold in self-contact. However, we can try to use it to describe the portion of the raft not in self-contact (see Fig 2.28). We will try to reproduce the experimental profiles of this portion by mimicking the experimental boundary conditions. First, we need to measure the shape of this portion.

Since the folds are symmetric, we only look at one side of each raft. We extract the contour (without the meniscus) with edge detection and cut the vertical portion with a gradient threshold on a smoothed version of the contour. Fig 2.30 a) shows the raw extracted contours as compression increases (they have been translated for clarity). The profiles from Fig 2.30 a) have very similar shapes, and we can try to rescale them. We introduce the maximum deflection and use it as a typical length scale ℓ_{sim} (which varies with Δ). It is defined as the vertical distance between the flat region of the raft and the end of the region which is not in self-contact. In the translated coordinate system of Fig 2.30 a), $\ell_{sim} = -y(0)$. We will use ℓ_{sim} to rescale our profiles and look



Figure 2.29: Side pictures of a "ZrO" raft at the oil water interface $(d = 150 \ \mu m)$. Compression increases from **a**) to **d**). Scale bar, $5 \ mm$.



Figure 2.30: **a)** Raw contours of the part of the raft not in self contact as compression increases ("ZrO" oil-water interface, $d = 150 \ \mu m$). The compression increases from yellow to red. The contours have been translated for clarity, they end at x = 0 and start at y = 0. **b)** Rescaled contours from **a)**, the rescaling length is $\ell_{sim} (\Delta) = -y(0)$ (in the coordinate system of **a)**). The part of the raft not in self-contact shows a self-similar behaviour.

for self-similarity of the form $y/\ell_{sim} = f(x/\ell_{sim}^{\xi})$. With the data from Fig 2.30 a), any value of ξ between 1/2 and 1 gives a proper rescaling, the optimum value being around $\xi = 3/4$. Fig 2.30 b) shows the data rescaled using $\xi = 1$. We can see that the part of the raft not in self-contact is indeed self-similar.

Model

Let us see if we can recover this self-similar shape we have found experimentally using a continuum elastic model. We cannot model the full raft with its complete fold since the model does not prevent interpenetration of the sheet. Hence, we only try to model the part of the raft which is not in self-contact (without the menisci). We consider again a beam of length L_0 , width W, thickness t and density ρ_s constrained in the (x, y) plane between two fluids of densities ρ_{up} for the upper fluid and ρ_{low} for the lower one. We introduce again the intrinsic coordinates (s, θ) in which s is the arc-length and $\theta(s)$ is the local angle between the tangent and the horizontal axis x; we parametrise the beam centreline in terms of arc-length, [x(s), y(s)]. We use the same rescaling as before, length by ℓ_{eh} , forces by ℓ_{eh}^2/B and the moment by ℓ_{eh}/B and use only dimensionless quantities in that section. The equilibrium equations of this beam and the one of the heavy sheet model are identical (equation (2.2.1)), however we dramatically change the boundary conditions. To mimic the experiment we impose the deflection δ and the angle $\theta(s = 0)$ on one end of the beam, the other end represents the flat portion of the raft and is clamped (Fig 2.31).



Figure 2.31: Schematic of the heavy beam in the model. One end of the beam is pulled down over a distance δ with an angle $\theta = -\pi/2$, the other end is clamped (below the water surface, we remove again the meniscus). The Cartesian coordinates (x, y) and intrinsic coordinates (s, θ) are drawn.

The new dimensionless boundary conditions read under this system of coordinate:

$$y(L_0) = -M y(0) = -(M + \delta) \theta(L_0) = 0 \theta(0) = -\pi/2 (2.2.5) \partial_s \theta(L_0) = 0 x(0) = 0$$

We solve numerically the system of equations (2.2.1) for very large sheets with the boundary conditions (2.2.5) using the MATLAB routine bvp5c with a continuation algorithm to follow the solutions as we vary the parameters. In the experiments δ varies between 2 and 6 however we can explore a wider range of parameters in the numerics. We observe the same self-similarity as in the experiment, *i.e.* $y/\ell_{sim} = f(x/\ell_{sim}^{\xi})$ with the same definition of ℓ_{sim} . However, the numerical profiles are self-similar only for $4 < \delta < \leq 0.4L_0$. Any value of ξ between 0.8 and 1 gives a good rescaling, the optimum being around $\xi = 0.9$. Fig 2.32 shows the raw numerical profiles and the rescaled numerical profiles using $\xi = 1$.



Figure 2.32: **a)** Numerical profiles obtained by solving (2.2.1) with the boundary conditions (2.2.5), M = 3.25, $L_0 = 36\pi$. δ increases from 4 (yellow) to 15 (red). **b)** Rescaled contours from **a**), the rescaling length is $\ell_{sim} = -y(0) - M = \delta$ (in the coordinate system of **a**)). The profiles have been translated vertically to match the experimental coordinate system.

Comparison with experiments

Now that we have our experimental and numerical self-similar profiles, we can directly compare them. However, since in the experiments the portion in self contact is removed with a slope threshold, we never reach an angle of $-\pi/2$. To do an accurate comparison, we match this boundary condition to the experimental one, $\theta(0) \approx -70^{\circ}$ and we use the experimental value of M. We again come back to dimensional quantities except for M in the following and we plot the experimental and numerical self-similar profiles in Fig 2.33. Fig 2.33 shows that the experimental and numerical profiles match perfectly. These are general results, Fig 2.34 shows a comparison between experimental



Figure 2.33: Experimental (coloured, corresponding to Fig 2.30) and numerical (black, M = 3.25, $L_0 = 36\pi \ell_{eh}$, $4\ell_{eh} < \delta < 15\ell_{eh}$, $\theta(0) = -70^\circ$) self-similar profiles ($\xi = 1$).



Figure 2.34: Experimental (coloured) and numerical (black, $L_0 = 36\pi \ell_{eh}$, $4\ell_{eh} < \delta < 15\ell_{eh}$, $\theta(0) = -70^\circ$) self-similar profiles ($\xi = 1$) for different rafts. **a**) "SiO", $d = 500 \ \mu m$, compression increases from cyan to magenta, M = 2.65 (numerical). **b**) "SiO", $d = 350 \ \mu m$, compression increases from green to blue, M = 2.47 (numerical). **c**) "SiO", $d = 200 \ \mu m$, compression increases from yellow to green, M = 2.17 (numerical).

and numerical self-similar profiles for different rafts and they always match. In the experimental raft profiles, the meniscus have been cut and profiles where the raft become so short that we do not have a flat region have been omitted. This leads to values of δ below $6\ell_{eh}$. The range of acceptable ξ and its optimum value vary from an experiment to another but $\xi = 1$ always yield good results. We also find that whatever the raft, once rescaled by ℓ_{sim} the profile of the part of the raft not in self-contact are identical (within the experimental uncertainty). If we look at the numerical profiles, changing M induces very minor changes in the rescaled profiles, even with a wider range of M than in the experiments. In fact, even taking M = 0 reproduces very well the experimental data. Fig 2.35 a) shows all the data from 2.33 and 2.34 plotted on the same graph. The weight of the raft has a minor influence on the rescaled profiles, but we expect it to influence the rescaling length ℓ_{sim} . Indeed, the interpretation is similar to the one of section 1.2.4: the weight of the portion of the fold in self-contact

produces a downward vertical force that pulls on the rest of the raft. Fig 2.35 b) shows the evolution of ℓ_{sim} with the compression post self-contact. It seems that the evolution of ℓ_{sim} with the compression depends on the product $\rho_{eff}d$ but more data would be needed to assert this hypothesis. In Fig 2.35 b) we use the parameter $\mathcal{D} = \frac{\rho_{eff}}{\Delta \rho} \frac{d}{\ell_c}$ presented in the introduction. It is a quantity similar to M but rescaled by ℓ_c instead of ℓ_{eh} , as a result \mathcal{D} does not depend on the raft bending rigidity B.



Figure 2.35: **a)** Experimental (coloured) and numerical (black, $L_0 = 36\pi \ell_{eh}$, $4\ell_{eh} < \delta < 15\ell_{eh}$, $\theta(0) = -70^\circ$) self-similar profiles ($\xi = 1$) for all the data from 2.33 and 2.34. **b**) Evolution of the rescaling length ℓ_{sim} as a function of the compression post self-contact $L_{sc} - L$ for all the data from 2.33 and 2.34.

We have shown that after self-contact, we can describe the part of the raft between the menisci and the portion in self-contact with a floating heavy elastic model (even though we cannot describe the full raft). We observe that this part of the raft is self-similar as compression increases, both experimentally and numerically. Moreover, the self-similar experimental and numerical shapes perfectly match. These self-similar profiles however, very weakly depend on M and using a simplified model with M = 0 also yields very good results. Further work is needed to completely understand the evolution of the rescaling length ℓ_{sim} with compression, but it seems to depend on the raft weight. It would be interesting to add the sheet weight in the numerical simulation of Démery *et al.* [102] and see if we can recover the complete raft profile and the evolution of ℓ_{sim} .

2.2.4 Limits of the elastic model and open questions

Up to this section, we have compared the buckling of our granular rafts with the buckling of a heavy floating elastic sheet. However, we have observed many phenomena in our experiments that differ from the continuous description and for which the granular characteristics of the raft must be taken into account. Even though we have not analysed them in detail, we will show in the following a few of them.

Particle desorption

Depending on the system studied, when a particle laden interface is compressed below jamming we can see two outcomes: buckling (e.g. [49]) or particle desorption (e.g. [94]). Few studies, specifically address the problem of buckling vs desorption. Bordacs et al. [87] have compressed coated glass beads at different liquid-fluid interfaces and measured the surface pressure area isotherms. Rafts made of hydrophilic particles ($\theta_y < 40^\circ$) collapse through irreversible particle expulsion, while rafts made of hydrophobic particles ($\theta_y > 40^\circ$) collapse through buckling. Their work has been extended in [91] and they have found similar qualitative conclusions concerning desorption vs buckling: the collapse mechanism mainly depends on the contact angle. Yet, to our knowledge there is neither a set of strict empirical rules nor a model to predict which collapse mechanism will occur, the problem is still open.

We have also observed particle desorption in our experiments for hydrophilic particles $(\theta_y \leq 70^\circ)$. In this chapter we show no data for "Zirblast", "Microblast" and kaolin beads (see appendix **D**) because compressing granular rafts made of them induces particle expulsion instead of buckling. A second kind of behaviour was observed for moderately hydrophilic particles ($\theta_y \sim 90^\circ$). For some rafts made of 350 μm "ZrO" particles at the oil-water interface we observe both buckling and particle desorption. In general, the raft first wrinkles and if we increase the compression further some particles are expelled. The amount of expelled particles is very low and we can still form a fold, but we choose not to display the data of such experiments. Particle expulsion also explains why there are no amplitude vs compression data for rafts at the air-water interface. Except for the very hydrophobic lycopodium powder, we always see particle expulsion if we compress past the wrinkling instability. From our contact angle measurements (appendix **D**) we can determine the critical wettability between pure buckling and buckling with expulsion around $\theta_y \approx 80^\circ$.

Fold destabilisation

At a critical compression and fold amplitude, the fold destabilises. Fig 2.36 shows the destabilisation process: the fold starts to sink toward the bottom of the tank and pulls on the rest of the raft which flows behind like a jet. A Rayleigh-Plateau like instability

finally pinches and breaks this jet and the destabilisation stops. At the end, we obtain a smaller raft, with sometimes a stable conical tip structure of particles where the jet occurred. This destabilisation process is not present in our model. In our experiments



Figure 2.36: Sequence of images showing the destabilisation process in a "ZrO" granular raft at the oil-water interface $(d = 350 \ \mu m)$. Time advances from left to right, the intervals between each pictures are $d\tau = 0.4, 0.25, 0.2, 0.2 \ s$.

the critical destabilisation compression is not very reproducible (because the wrinkles stay longer on some raft). However, the maximum fold amplitude before destabilisation A_{max} is reproducible. Protière *et al.* [68] have studied the spontaneous destabilisation of granular rafts under their own weight. They have shown that the maximum raft size results from a balance of the raft weight (which depends on the raft size) to capillary forces holding the raft together. It is likely to be the same mechanism that governs the fold destabilisation. Here the fold amplitude is analogous to the critical size since the fold is heavy and pulls on the rest of the raft. Fig 2.37 shows the dimensionless maximum fold amplitude before destabilisation A_{max}/ℓ_c as a function of \mathcal{D} . We see that the data from particles with different densities and sizes rescale in a master curve. The trend is the following: the smaller the value of \mathcal{D} is, the bigger the fold can be. An extension of the model from [68] is not straightforward as most of the time the fold is in self-contact when destabilisation occurs but the underlying mechanism should be similar: the raft destabilises when the tangential internal forces become negative.



Figure 2.37: Dimensionless maximum fold amplitude A_{max}/ℓ_c as a function of the dimensionless weight \mathcal{D} . Colours indicate different particle composition, the black dashed line is a guide to the eye. Please note that small vertical error bars indicate a lack of data to calculate the standard deviation rather than a low uncertainty.

Fold position

In the data presented above, the fold always starts to grow far enough from the compressive wall to not interact with them. However, three possible fold position can be observed: a unique fold can be located in the centre (centre fold, Fig 2.38 a)), at one of the extremity on a meniscus (edge fold, Fig 2.38 b)), or in between an extremity and the centre (side fold, Fig 2.38 c)).

If we start with an edge fold, as compression increases, it is not uncommon that its amplitude saturates and that a second fold starts to grow. If the second fold grows in the centre or on the side, it will absorbs the first edge fold and destabilise. If the second fold grows on the other edge (double edge folds), a third fold will most likely nucleate in the centre and absorb both of them (Fig 2.39).

In our experiment we can control the tank width W_{tank} with a plate that confines the raft laterally (Fig 2.7 b)). As a result it also directly impacts the raft dimensions for a given number of particles. We observe in preliminary experiments on 150 μm "ZrO" particles at the oil-water interface, that the fold position varies with the raft dimensions. Since the raft becomes larger as compression increases, the raft dimensions are not well defined quantities. We construct effective dimensions that do not depend on the compression by looking at the raft surface area S. If we assume the raft reaches a rectangular shape of width W_{tank} , the tank width, then its length is S/W_{tank} . This hypothesis is unrealistic (especially for large particles) but it allows us to measure a



Figure 2.38: Side pictures displaying the possible fold positions for "ZrO" rafts at the oil-water interface ($d = 150 \ \mu m$). **a**) Fold in the centre of the raft (center fold). **b**) Fold at the edge of the raft (edge fold). **c**) Fold on one side of the raft but far from the edge (side fold).

quantity independent of compression and raft preparation. Fig 2.40 shows an effective width W_{tank} - length S/W_{tank} phase diagram for the fold position. Firstly, centre folds and edge folds occur more often than side folds. Secondly, short and wide rafts are more likely to produce centre folds while long and narrow raft are more likely to produce edge folds. The position depends on the raft aspect ratio S/W_{tank}^2 and centre folds appear only when this aspect ratio is small. Using the more realistic values L_0 and W_0 , *i.e.* the raft dimensions when it starts to touch the compressing plates, yields similar qualitative results (the data are more scattered, probably because it strongly depends on the preparation). Although no quantitative work has been done for other particles, this general rule always holds. However, it seems that the raft weight (through M) also plays a role in the fold position. Lighter rafts (smaller M) need an even shorter aspect ratio to produce a centre fold. For air-water experiments (small M) we never managed to produce a centre fold.



Figure 2.39: Side pictures of a "ZrO" raft at the oil water interface $(d = 150 \ \mu m)$ showing the double edge folds. Compression increases from top to bottom.



Figure 2.40: Effective width W_{tank} - length S/W_{tank} phase diagram for the fold position for 150 μm "ZrO" particles at the oil-water interface. The dashed line and the colours are guide to the eye to distinguish the centre folds phase (blue) and the edge folds phase (brown).

More work is needed to completely understand where the fold starts grow, but the problem looks similar to the one in [93]. We can wonder if there is a strain propagation length that depends on the width like a Jansen effect, which dictates the fold position. The edge folds also reminds us the first branch in the heavy floating elastic sheet model when we include the menisci (Fig 2.17). Another possible explanation for the fold position could be the competition between the two branches of solutions. Can we recover the tendency to make edge folds for long raft by looking at the energy of the branches ? Fig 2.41 shows the total energy of each branch for a sheet with M = 3 and $L_0 = 24\pi \ell_{eh}$. We see a crossover at Δ_{trans} , at low compression $\Delta < \Delta_{trans}$ the first branch should be stable while at high compression $\Delta > \Delta_{trans}$ the second branch should be stable. The inset of Fig 2.41 shows the evolution of Δ_{trans} with the sheet length L_0 . Within the range of parameters explored we do not see any significant variation of Δ_{trans} . The heavy elastic sheet model with menisci cannot explain the experimental observations for the fold position. Besides, the model is invariant along the width, it thus does not predict the variation of the fold position with the width.



Figure 2.41: Dimensionless energy as a function of the dimensionless compression for the two branches of solution of equation (2.2.1) with the boundary conditions (2.2.2) and M = 3, $L_0 = 24\pi \ell_{eh}$. The range of compression spanned by each branch shows the limits of our naive continuation algorithm. *Inset:* Dimensionless transition compression Δ_{trans}/ℓ_{eh} as a function of the sheet dimensionless length L_0/ℓ_{eh} for M = 3 (red circles) and M = 1 (blue squares).

Three dimensional fold shape and compression

For floating elastic sheets like in chapter 1, the wrinkles and folds are two dimensional: their shape is (almost) invariant along the width. By analogy and because the wrinkles are aligned in one direction we considered the raft invariant along the width. But it is clear from Fig 2.8 that this is not the case: the fold has a three dimensional structure. Fig 2.42 shows pictures of a fold seen in the direction of compression (x). The fold as a crescent like shape in the width direction (z) that evolves as compression increases. Moreover, the fold width W_{fold} (Fig 2.43 a)) is not equal to the raft width W, and it grows as compression increases. Fig 2.43 b) shows W_{fold} as a function of $L_f - L$ for different rafts as we vary all the experimental parameters (d, ρ_s, W_{tank}) . We observe two final outcomes depending on the particle size and density (through \mathcal{D}). Either the fold length grows as the compression increases until it reaches the raft width and saturates $(\mathcal{D} \leq 0.5)$ or it grows until the fold destabilises before reaching the plateau $(\mathcal{D} \gtrsim 0.5)$. It seems the evolution of W_{fold} does not depend on the particles used (apart for the destabilisation) but only on the tank width W_{tank} . Indeed, rescaling W_{fold} by the tank width W_{tank} gives a master curve for all our particles (Fig 2.43 c)). This fold evolution cannot be understood with the elastic model. It is as if the two dimensional compression Δ varies along the width of the raft. Its value peaks around the centre of the fold, where the amplitude is maximal and it decreases as we move away from it.

Another problem with the two dimensional reduction we have done comes from the inextensibility hypothesis. The raft being made of very hard beads, when there is



Figure 2.42: Side pictures in the direction of compression of a fold in a "ZrO" raft at the oil-water interface $(d = 150 \ \mu m)$. Compression increases from top to bottom and is perpendicular to the sheet. As a scale bar the raft width is about $4 \ cm$.

no particle desorption it can be considered incompressible in three dimensions. The particles are in contact at the beginning of the experiment such that the packing fraction does not vary much: the raft surface area S is roughly constant. But since the raft changes its aspect ratio the projected contour length is not constant. With our code that computes L^* (Fig 2.24 b)-c)) it is easy to compute the contour length of the flat portion of the raft. From our definition of the compression, the contour length (without menisci) should be L_{lw}^* and if we assume inextensibility, it should be constant. Fig 2.44 shows the variation of the contour length $L_{lw}^*(\Delta^*) - L_{lw}^*(0)$ (without menisci) as a function of the compression $\Delta^* = L_{lw}^* - L^*$. For $\Delta^* \leq 0$, *i.e.* before the apparition of large wrinkles, the contour length $L_{lw}^*(\Delta^*)$ decreases as we increase the compression with a slope of one: the material is fluid-like. It absorbs almost all the excess length by expanding in the lateral direction through rearrangements. At some point that roughly



Figure 2.43: a) Bottom picture of a "ZrO" raft at the oil water interface $(d = 150 \ \mu m)$. The fold width W_{fold} and the tank width W_{tank} are shown. b) Fold width W_{fold} as a function of the compression (past the wrinkle to fold transition) $L_f - L$ for different rafts. The colours indicate the tank width, the symbols indicate the different particles. The grey bar show the uncertainty on L_f . c) Dimensionless fold width W_{fold}/W_{tank} as a function of $L_f - L$. Same legend as b).



Figure 2.44: Variation of the contour length $L_{lw}^*(\Delta^*) - L_{lw}^*(0)$ (without menisci) as a function of the compression $\Delta^* = L_{lw}^* - L^*$ for different rafts. The black solid line is a guide to the eye, the black dashed line is what happens for an incompressible material. *Inset:* Schematic showing the contour length L_{lw}^* .

coincides with the apparition of large wrinkles ($\Delta^* \sim 0$), the contour length becomes roughly constant: the raft becomes solid-like and the excess length is mainly absorbed through buckling. This shows that the incompressibility hypothesis in two dimensions after the apparition of large wrinkles is not foolish, however the raft is not perfectly incompressible and the discrepancy we have with the model in Fig 2.25 most likely comes from the "effective" compressibility we find in two dimensions. Note that we are not able to image the small wrinkles properly, the contour length in that region is thus biased and we expect a precise measurement to see a change in the contour length variation at the apparition of small wrinkles. Moreover, we shall keep in mind that the wrinkles and folds are projected on the side pictures and they do not perfectly represent a true profile. Future work with Fourier transform profilometry could refine these measurements.

Loading cycles and hysteretic behaviour

For heavy floating elastic sheets, we expect the buckling experiment (shape, amplitude, pressure) to be fully reversible. What about granular rafts ?

We start by loading the raft like in the other experiments but we stop the compression before the fold destabilisation. Then we unload the raft the same way (we displace the compressing plate in small quasi-static steps) until it does not touch the compressing plates any more. Finally, we can repeat these loading-unloading cycles while slowly increasing the final compression until we reach the fold destabilisation. Fig 2.45 shows bottom pictures of a raft during a loading-unloading-loading path, the distance between the compressing plates is identical in each row. First, we see that we can unfold completely the raft, however there are some changes during unloading; we do not go back through a fully wrinkled state (Fig 2.45 2.2), we can see a "scar" at the position of the fold and the raft does not recover its initial aspect ratio (part of the rearrangements are irreversible, Fig 2.45 2.1). From this point, if we load again the raft, it folds back at the same position, but again the wrinkling phase is weakened and we localise very quickly in a fold (Fig 2.45 3.2). If we keep loading and unloading, as long as we do not destabilise the fold we recover the behaviour of the second loading and first unloading. It seems that the raft is irreversibly changed after the first compression.

Since we do not really see large wrinkles after the first loading, we cannot really define L_{lw} for each loading/unloading phase. We measure L_{lw} from the first loading phase and use this value for computing Δ during the rest of the cycles. Another possibility is to take as a reference length the moment where the amplitude starts to be non zero, this yields very similar results. Fig 2.46 a) shows the maximum amplitude measured from the side A as a function of the compression Δ (with menisci) during cycles. We clearly see a hysteresis between loading phases and unloading phases. If we look at the pictures used to measure A (not shown), we see that there is also a hysteresis on the menisci shapes. The hysteresis observed in the amplitude-compression curves of Fig 2.46 a) could be due to the menisci. They absorb compression at the beginning of loading, maybe they release this compression at the beginning of unloading. That would explain the shape of the cycle seen in Fig 2.46 a). Thus, we try to measure Δ^* with the process described in Fig 2.24. Strangely, the value of the cutoff $\beta \approx 0.8$, valid during loading, gives unphysical results during unloading: the compression Δ^* increases



Figure 2.45: Bottom pictures of a "ZrO" raft at the oil-water interface $(d = 150 \ \mu m)$ during loading-unloading cycles. Compression increases from top to bottom: $L = 53.6 \ mm, \ L = 42.2 \ mm, \ L = 44.2 \ mm$. The black arrow indicates the path taken by the raft.



Figure 2.46: Amplitude (from the side) A as a function of compression: **a**) $L_{lw} - L$ (with menisci) **b**) $L_{lw}^* - L^*$ (without menisci, $\beta = 0.65$), for a "ZrO" raft ($d = 150 \ \mu m$) at the oil-water interface during loading-unloading cycles. Closed circles indicate loading phases, open circles indicate unloading phases, colours indicate the cycle number. Arrows are guides to the eye to follow the path taken by the raft.

while we are unloading the raft. We have to lower it to $\beta < 0.7$ to have a monotonically increasing L^* during unloading. Fig 2.46 b) shows the maximum amplitude measured from the side A as a function of the compression Δ^* (without menisci) during cycles. To be consistent we have used the value $\beta = 0.65$ both for loading and unloading. The hysteresis is greatly reduced once we have removed the menisci. Nonetheless, even if we do not look at the first loading, where we see large wrinkles and where the localisation occurs latter, there are still discrepancies at low Δ^* between loading and unloading. We do not understand yet what is happening in that region, but we believe this comes from the menisci. At first sight, apart from the hysteresis, the menisci have similar shapes during loading and unloading. Yet, the fact that we have to change the value of the cutoff β to keep realistic values of Δ^* in that region indicates that the menisci behave differently during loading and unloading phases.

The behaviour of the raft during compression/expansion cycles have only been observed for $d = 150 \ \mu m$ and $d = 250 \ \mu m$ "ZrO" particles at the oil-water interface. For these two particle sizes we see similar results: irreversible changes in aspect ratio, weakening of the large wrinkles' region, "scar" at the fold position and hysteresis in amplitude during loading/unloading mainly due to menisci. The irreversible changes after the first compression clearly show the limits of the elastic description of the raft and should be investigated in future work. When we stir the raft to induce a lot of "random" particle rearrangements, we recover the behaviour of the first loading. This indicates that the particle arrangement plays a role in the wrinkle to fold transition.

2.3 Conclusion

We have studied the buckling of uniaxially compressed granular rafts and compared it to the heavy floating elastic sheet model developed in chapter 1. Under compression the raft first changes its aspect ratio through particle rearrangements. At some point it starts to buckle and small wrinkles appear on the surface of the raft. Upon further compression, larger wrinkles appear and finally the deformation localises into a fold that grows until it destabilises. With Fourier transform profilometry and direct visualisation we have characterised: two wrinkles wavelengths, the large wrinkles amplitude as well as the fold amplitude and shape. The large wavelength is the one already described in the literature and follow the theoretical prediction of the elastic model proposed by Vella et al. [49]. However, we have been able to vary other parameters: particle density, contact angle, aspect ratio, but more importantly the liquids densities. The fact that the large wavelength varies with the liquid densities accordingly to the prediction for buckling on a liquid foundation confirms that this description is correct. The small wavelength however, does not follow the elastic prediction: it does not depend on the liquid properties and varies linearly with the particle size. This demonstrates that the physics behind this wavelength is different, probably of granular nature and not well understood yet. The small wrinkles share the same properties with the wrinkles observed by Croll et al. [95, 96] on a very different system. We can wonder if the physical mechanism is identical in these two experiments. We observe and measure for the first time the wrinkle to fold transition in these systems. The wrinkle amplitude obey the (geometric) prediction from buckling on foundation given in Introduction: $A \sim \lambda \left(\frac{\Delta}{L_0}\right)^{1/2}$. However, the critical compression at which the wrinkle to fold transition occurs is not well reproducible and always much higher than the prediction from the heavy elastic sheet theory. The fold shape and amplitude are also different from the floating elastic sheet model. However, when we include the raft's weight in the model and remove the menisci (whose complex behaviour is not understood yet), we recover almost quantitatively the experimental fold behaviour; amplitude as a function of compression, shape and amplitude of self-contact. At high compression the fold contacts itself and our model is not able to reproduce the complete raft shape because it allows both sides of the fold to overlap. Nevertheless, the model is able to predict the shape of the portion of the raft which is not in self-contact. This shape is self-similar with a similarity length that grows linearly with compression. Despite the evident discrete nature of our granular rafts we have shown that a continuous elastic model gives very good results on the buckling of granular rafts. In the last section, we highlight many of the unelastic phenomena that we have observed while compressing granular rafts. It clearly sets the boundaries of the elastic description of these materials and provide guidance for future work.

Chapter 3 Drops floating on granular rafts

Contents

3.1 Coalescence vs flotation	
3.1.1	Inhibiting coalescence $\dots \dots \dots$
3.1.2	Experiment and results
3.2 Floating drop shape and raft deformation $\ldots \ldots \ldots \ldots \ldots 102$	
3.2.1	Droplet shapes on various substrates 102
3.2.2	Experiment $\dots \dots \dots$
3.2.3	Results
3.3 Potential applications	
3.4 Conclusion	

This chapter deals with the interaction of a water droplet with a granular raft. Under certain conditions, the raft can prevent the coalescence of a water droplet deposited on top of it. We investigate the mechanism that allows floating and unveil the necessary conditions for a drop to float on a granular raft. These floating drops deform the raft and large ones take unusual shapes that we examine. To provide a sound basis for our analysis, we start each section by a literature overview; on how to prevent coalescence and on the shape a drop takes depending on its substrate. Finally, we present some potential applications for these floating drop.

3.1 Coalescence vs flotation

Before we present our experiment and results, let us first look at the usual mechanisms to prevent coalescence.

3.1.1 Inhibiting coalescence

When a droplet is gently deposited on a bath of the same liquid, the drop will merge with the bath to minimize the overall surface energy. This seemingly inexorable process is called coalescence. This is a very old problem, already studied in the 19^{th} century [113] that is relevant for many applications such as: the formation of rain drops in clouds, ink jet-printing, coating or sintering. In recent years, with the development of experimental, numerical and theoretical tools many advances have been done to understand this mechanism (*e.g.* [114–117]). However, in many cases such as in emulsions or foams, one wants to prevent coalescence. Indeed, when you make your mayonnaise or whip your egg white until stiff you invest a lot of mechanical energy (such that your arms usually hurt) and you do not want coalescence to undo your work.

There are several ways to prevent coalescence, the most common being to use surfactants to lower the interfacial energy. The driving mechanism behind coalescence is to minimise the liquid-fluid surface to minimise the energy, so if one lowers the energy per unit area of each interface this driving force will be weaker. Surfactants are well known to stabilise emulsions and foams, for instance one can add mustard (which contains surfactants) to a vinaigrette to prevent coalescence and enhance its stability. Another approach is to prevent the two interfaces (the droplet and the bath or two droplets) to come in contact. At the microscopic scale one can try to make two droplets in an emulsion repel each other by adding salts and/or use ionic surfactants. The electric double layer that forms around the droplets does not want to overlap with another one because it would reduce its entropy. This produces a net repelling force between two droplets at intermediate distances (DLVO theory) that prevent their contact and thus coalescence. At the macroscopic scale one can generate an air flow that prevent a droplet to contact the bath. For instance, this can be done by vibrating the liquid bath (*e.g.* [118]).



Figure 3.1: Schematic showing how the particles separate the liquid interfaces and prevent coalescence.

We have seen in the Introduction that just like surfactants, particles at interfaces can also hinder droplet/bubble coalescence in emulsions/foams. This is also true at the individual drop level. A water drop can be rolled over a hydrophobic powder to completely coat its surface with particles and make a "liquid marble". These particle covered drops have also demonstrated the ability to prevent droplet coalescence: when two liquid marbles are colliding they do not coalesce [77] and some liquid marbles can float on water (e.g. [119, 120]). The mechanism by which coalescence is prevented



Figure 3.2: Source: [122]. Left: Pictures of the different coalescence behaviour for oil-inwater droplets covered with silica particles ($d = 1.5 \ \mu m$, $\theta_y \sim 70^\circ$). Scale bars 50 μm . Right: ϕ_1 - ϕ_2 coalescence phase diagram for the same system. The dotted line indicate the maximum surface coverage (particles are jammed), and the dashed line si the curve $\phi_1 + \phi_2 = 1.43$.

is purely steric. The particles at the interface prevent the liquid-liquid interfaces to come close enough to trigger coalescence (Fig 3.1). To achieve a result like in Fig 3.1, one must either coat completely both interfaces [77] or use particles that can form multilayers [121]. Fig 3.2 shows what happens when two particle covered drops, of particle surface coverage ϕ_i , are put in contact. If the interfaces are not completely coated ($\phi_i < 0.9$), arrested coalescence or regular coalescence is observed [122, 123]. The key thing to prevent coalescence is to coat completely the interfaces such that no patches without particles can form.

The mechanism described in Fig 3.1 is the most common to explain the stability against coalescence of particle covered droplets. However, another mechanism called "particle bridging" has been reported in the literature [124–127]. In that case, coalescence is prevented by a monolayer of hydrophobic particles partially wet by both droplets (Fig 3.3). Since the particles prefer to be wet by the outer fluid (air or oil), a thin layer of this fluid is trapped between the two droplet and prevents the two interfaces to come in contact. Between the classic steric repulsion and particle bridging there is one important difference: particle bridging involves adhesion between the two drops while this is not the case with steric repulsion. Indeed, we have seen in the Introduction that wetting a particle decreases the surface energy. When particles bridge two droplets. there is a net energy gain and separating the droplets becomes difficult. Although not very common in Pickering emulsions, particle bridging occurs when the particles are hydrophobic and do not cover completely the drops ($\phi << 0.9$) [128]. Nevertheless, particle bridging can have a strong influence on the emulsion properties [129, 130]. It is more commonly observed in particle stabilised foams where the film between two bubbles slowly drains until bridging occurs and it plays an important role in the foam stability [131].



Figure 3.3: Schematic showing the bridging mechanism: a thin layer of the outside fluid is trapped between the two droplets. The particle diameter d and contact angle θ_y are drawn.

3.1.2 Experiment and results

The experiment starts identically as in chapter 2. We make the granular rafts in a custom built glass tank $(12 \times 12 \times 7 cm)$ by sprinkling particles at the interface between light mineral oil and deionised water (see section 2.2 for details on the procedure and appendix D for details on the particles). Then we gently deposit small water drops $(< 30 \ \mu L)$ on rafts made with different particles (different size d, density ρ_s and contact angle θ_y) and look at the outcome.

When we do the experiment at the air-water interface, we always observe coalescence, whatever the particle used. Fig 3.4 shows a sequence of images displaying the coalescence process at the air-water interface. As soon as the drop touches the raft, it merges entirely with the water bath and produces surface waves, after a short time ($\sim 10 \text{ ms}$) the raft recovers its initial shape. Although the presence of the raft probably modifies the coalescence dynamics [132], the overall picture is similar to bare liquid interfaces.



Figure 3.4: Sequence of images showing a $5 \,\mu L$ water droplet deposited on a "ZrO" raft at the air-water interface. Time advances from **a**) to **f**), the intervals between each pictures are $d\tau = 7.5, 1.5, 1.6, 4.3, 5.7 \,ms$. As a scale bar, one can use the particle size $d = 250 \,\mu m$.



Figure 3.5: Side picture of a 100 μL water drop (dyed in red) floating on a "ZrO" raft at the oil-water interface ($d = 250 \ \mu m$).

At the oil-water interface, depending on the particles used to make the raft we can observe three different behaviours. The drop can float on the raft indefinitely (we waited up to 5 days). Fig 3.5 shows a small water drop (dyed in red) floating on a raft. It can float on the raft for some time and then coalesces. This survival time is not reproducible and ranges between 30 s to 30 min. Finally, the drop can coalesce immediately. Fig 3.6 shows a sequence of images displaying the coalescence process at the oil-water interface. At the oil-water interface, the presence of the raft changes the coalescence process compared to a bare liquid interface. First of all, the oil film drainage is much faster than on a bare interface. The oil being viscous, a $30 \,\mu L$ drop can take up to $2 \min$ to coalesce with a bare water bath. The same droplet deposited on a raft (where coalescence occurs) coalesces almost instantly. As soon as the drop touches the particles, the gain in surface energy by wetting them drives the coalescence. Another difference is the hole left in the middle of the raft after coalescence (Fig 3.6h)). This hole formed in a few milliseconds can persist several minutes before being sealed by the raft. Its opening is interesting as we can sometimes see cracks similar to the one observed when one introduces surfactants in a particle raft [85, 86] and the expulsion of particles from the interface for very hydrophilic particles ($\theta_y < 70^\circ$).

Although the coalescence dynamics on granular rafts is new and worth studying, we will focus here on the transition between floating and coalescence. We classify the outcomes in three categories: floating, immediate coalescence and delayed coalescence and plot them in Fig 3.7 on a particle diameter-contact angle phase diagram. We see that $\theta_y \approx 90^\circ$ separates immediate coalescence from floating. The data point for $350 \ \mu m$ "ZrO" rafts is both categorised as immediate coalescence and floating because we could observe both behaviours, depending on the drop location on a raft. Again this batch behaves differently from the others, in the compression experiment we could also observe particle expulsion on a few rafts with this batch (section 2.2.4). The plain glass data points are also above $\theta_y = 90^\circ$, however we measured the contact angle with another particle size. We have not measured the contact angle of kaolin beads (see appendix D) but we know they are hydrophilic because in the compression experiment particles were expelled from the interface and we did not observe buckling. A drop deposited on a kaolin raft also coalesces immediately.

Let us try to understand this boundary. First we notice that floating drops are anchored to the raft. When we try to move the drop on the raft by pushing on it with a spatula, the force is transmitted to the raft that moves along with the drop as a single entity. If the raft is constrained, the particles around the drop can eventually rearrange such that the drop moves on the raft but the particles below the drop are


Figure 3.6: Sequence of images showing a $30 \,\mu L$ water droplet deposited on a Microblast raft at the oil-water interface $(d = 94 \,\mu m)$. Time advances from **a**) to **h**), the intervals between each pictures are $d\tau = 3.0, 4.0, 7.6, 6.8, 9.2, 16, 21.6 \,ms$. The individual particles seen inside the hole have been expelled from the interface and slowly sink at the bottom of the tank. As a scale bar, the drop diameter is $\approx 4.5 \,mm$.

attached to it. This observation and the fact that we have a monolayer confirms that the particles are bridging the two water surfaces (see Fig 3.3). In that case, if we neglect the menisci due to gravity, using elementary geometry we get that the oil layer thickness is $h_o = -d \cos \theta_y$. If $\theta_y < 90^\circ$ then $h_o < 0$ and bridging is impossible. In reality, we have menisci between the particles and the interface may fluctuate at the microscopic scale. The true limit is probably very slightly above 90° depending on the particle size. This also explains why we never see a drop float at the air-water interface, the measured contact angle of our particles is always $\leq 90^\circ$.

The delayed coalescence-floating boundary on the other hand, depends mainly on the particle size. Even for high contact angle values, particles smaller than $d = 200 \ \mu m$ are not able to make the drop float. It is rather surprising because bridging has been observed in the literature for much smaller particles (*e.g.* [125]) and before the coalescence our drop are also attached to the raft and are thus bridged. Our first hypothesis was that as the drop sinks toward the raft, it (and the associated oil flow) pushes the particles and creates a hole below it that allows the two interfaces to touch and triggers coalescence. Small particles having less inertia, they would be displaced more easily. This idea comes from the work of Planchette *et al.* [133] where they impact water drops on particle laden air-water interfaces. They have observed coalescence only at high impact speed and argued that the kinetic energy of the drop was converted in surface energy: the drop deforms the interface and creates a bare interface (or hole) that allows coalescence. In our experiment we do see a hole which is of the order of 3 to 5 particle diameters. However, many facts discard this hypothesis: in some cases the drop could sit long enough such that the hole could close itself before coalescence. Repeating



Figure 3.7: Particle diameter-contact angle $(d-\theta_y)$ coalescence phase diagram at the oil-water interface. Closed circles is for floating drops, open squares for immediate coalescence and open triangles for delayed coalescence. The symbol colour indicate the particle material. The solid line is the lowest possible contact angle where bridging can occur. The dashed line and background colours are guide to the eye. Please note that we do not have measured the contact angle for every particle batch. For unmeasured batch we used the closest measured value (same material, closest particle size) and drawn the vertical error bar in brown.

the experiment on a compressed raft (which has already wrinkled) inhibits the hole formation but leads to the same outcome. Finally, doing the experiment by placing the needle very close to the raft with a very slow injection speed in order to minimise the oil flow also inhibit the hole formation but yield to delayed coalescence. The fact that the coalescence is time dependent and that this time is not reproducible rather indicates that the interface slowly becomes polluted. Indeed, even in clean conditions it has been shown that the lifetime of a drop deposited on an interface covered with hydrophilic particles decreases with time due to the pollution of the interface [134]. Because we do not conduct our experiments in a clean environment, some dust adds up in our system. Since the delayed coalescence time is not reproducible, the most likely mechanism is that dust particles of the order of the oil layer thickness (which depends on d) get deposited on the interface and trigger the coalescence. Typical house dust is very polydisperse and its median size is of the order of $\sim 10 - 100 \,\mu m$ [135]. For rafts made of particles smaller than $200 \,\mu m$, the theoretical oil layer thickness is of the order of the dust size ($h_o = 75 \ \mu m$ for $d = 150 \ \mu m$ and $\theta_y = 120^\circ$). Moreover, preliminary experiments where we seal the tank surface with plastic wrap seems to increase the drop lifetime.

Now that we have explained the drop flotation mechanism, we can focus on floating drops and study their interaction with the raft. The first thing we observe is that large drops deform the raft which in turn modify the drop shape. This interaction produces unusual shapes that we study in the next section.

3.2 Floating drop shape and raft deformation

3.2.1 Droplet shapes on various substrates

We first look at the different shapes a drop can have depending on its substrate and we start with the simplest substrate, an undeformable solid substrate. To simplify further we consider that the drop do not wet the substrate, *i.e.* its contact angle is $\theta_y = 180^\circ$. The shape of this droplet would result from a balance of gravity to surface tension which gives the Young-Laplace equation:

$$\gamma \mathscr{C} = \rho g h$$

With γ the liquid surface tension, $\mathscr{C} = \overrightarrow{\nabla} \cdot \overrightarrow{N}$ the curvature of the interface whose normal vector is \overrightarrow{N} ($\overrightarrow{\nabla}$ is the nabla operator), ρ the liquid density and h the interface height. To evaluate which contribution dominates we use the capillary length $\ell_c = \sqrt{\frac{\gamma}{\rho g}}$ or the (dimensionless) Bond number $Bo = \frac{\rho g R^2}{\gamma}$ where R is the typical length scale of the problem (the radius of the drop in our case). When the droplet is small enough $(Bo << 1 \text{ or } R << \ell_c)$, gravity is negligible and capillary forces are dominant: the drop is spherical. On the other hand, when the drop is big enough $(Bo >> 1 \text{ or } R >> \ell_c)$, gravity is dominant and the drop flattens: we have a puddle. The transition between these two asymptotic regimes is shown in Fig 3.8 where we plot the shape of a droplet with $\theta_y = 180^\circ$ as its volume increases (shapes computed by solving numerically the axisymmetric Young-Laplace equation with MATLAB solver ode45). The perfect non wetting scenario may seems unrealistic but there are several experimental realisations;



Figure 3.8: Numerical profiles of a non-wetting drop on a solid substrate for $V = 10 \,\mu L$, 50 μL , 200 μL , 1 mL, 3 mL, 10 mL and $\ell_c = 5.4 \,mm$.

for a rough and hydrophobic (or superhydrophobic) substrate, we reach the Cassie-Baxter state: a layer of air remains in the roughness of the substrate and the drop almost does not touch the solid substrate. Lotus leaves are natural superhydrophobic substrates and we can see drop shapes similar to Fig 3.8 on them. Another possibility is Leidenfrost drops: the drop is on a very hot substrate and floats on its own vapour layer. Such drops are visible when we spill water on a hot electric hob. Finally, we have liquid marbles where the particles prevent the liquid to touch the substrate.

This simple scenario allows us to understand the effect of capillarity and gravity on the shape of a sessile drop, but for our large floating drops the raft is deformed and we must take into account the substrate's response. How can we treat such problems, when the drop can deform the substrate which in turn can deform the drop.

Recently, droplet on very soft elastic material have seen a surge of interest. It has been shown that the capillary forces at the edges of the drop could deform the solid substrate (e.q. [136]). But soft elastic substrates are not the only ones likely to be deformed by a droplet, slender materials are easily bent and can also be deformed by drops (e.g. [137]). There is an abundant literature on both of these topics and we do not aim at discussing them in details. However, we would like to point out that in both cases small drops are used and the drop exert capillary forces on the substrate, gravity is negligible. A last case to mention, which might be closer to our drops floating on raft. is the case of droplet deposited on floating elastic sheets [34]. In that case, the sheet is bend by surface tension but also adhere on the liquid bath. We see a small bulge below the drop and radial wrinkles around it. The problem starts to be quite complicated as the sheet and both liquids have to be taken into account to predict the bulge and the wrinkles [35] but again everything is done with small drops, in the capillary regime. What about larger drops where gravity also plays a role? Studies with large droplets on compliant substrates mostly use liquid baths as substrates. Ooi et al. [120, 139] study the shape of water liquid marbles floating on a water bath. They found out that small marbles keep a spherical shape, and the interface deformation is identical to that of a solid sphere floating on water. However, when the marble size increases, its shape becomes oblate and dissymmetric and the interface deformation becomes more complicated (Fig 3.9 a)). Yet, they do not explore the case of very large marbles and



Figure 3.9: a) Side picture of a floating liquid marble. Source [120]. b) Side and top pictures of a large silicon oil drop on a vibrated silicon oil bath. Source [118]. c) Numerically determined shapes of an ethanol Leidenfrost drops on a liquid pool of silicone oil V20 for the radii $R/\ell_c = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4$. Source: [138].

remain in the regime Bo < 1. By vibrating a liquid bath Couder *et al.* [118] are able to make a droplet bounce on a thin air layer that is renewed at every oscillation of the bath and prevents the droplet coalescence. Small drops as expected remain spherical, but a surprising hemispherical shape arises when the drop volume increases (Fig 3.9 b)). This paper do not focus on the drop shape but an interesting transition should occur between these two regimes. Very recently Maquet *et al.* [138] managed to make rather large Leidenfrost drops (ethanol, low boiling point) on liquid pools (silicon oil, large boiling point). The drop is able to float on its own vapour layer and does not spread on the surface of the liquid pool. They measure the pool deformations as a function of the drop radius and predict the complete drop shape numerically (Fig 3.9 c)). They observe an oblate shape that is not up-down symmetric.

3.2.2 Experiment

We make the rafts like in the previous section 3.1.2 but we only use particles that allow drops to float. Once the raft is formed, we create a drop by injecting dyed deionised



Figure 3.10: Schematic of the experimental apparatus. With a syringe pump we produce a water drop on top of a granular raft. We then control the droplet size by injecting or withdrawing water.

water on top of the raft with a custom needle. The needle is placed above the centre of the raft to keep the experiment axisymmetric. It is linked to a syringe controlled by a syringe pump (Fig 3.10) in order to control the drop volume. The dye is regular food colouring (Vahiné): a mixture of water, acidifying agents and dye molecules (red: Azorubin, blue: Brilliant Blue FCF, yellow: Tartrazine). We have checked that the dye does not significantly alter the surface tension of our dyed water solutions, even at high concentration. We have found a maximum difference of $-1 \ mN.m^{-1}$ which is the resolution of the tensiometer (Du Noüy ring Kruss). We use a custom needle to be able to leave it inside the drop, besides it blocks only a small portion of the field of view. It is made with a flexible fused silica capillary tubing from Cluzeau Info Labo (CIL) (outside diameter: $375 \ \mu m$, inside diameter $150 \ \mu m$) cut at the desired length and connected to standard tubing (Tygon E-3603 St Gobain) with NanoTight fittings (IDEX). The other side of the tubing is connected to a standard syringe (Terumo) with a Luer lock. The syringe pump (PHD Ultra from Harvard Apparatus) allows us to inject or pump a desired volume of liquid with a desired flow rate. The needle being very thin and long, it induces a high pressure drop. As a result, the small amount of air present in the syringe or the tubing gets compressed when the syringe piston moves. To achieve the desired volume we have to wait at least 1 min after the piston movement for the gas to return to equilibrium. We thus program the syringe pump to do small inject/withdraw quasi-static steps. The desired volume (between $30 \,\mu L$ and $300 \,\mu L$) is injected/withdrawn and then we wait $1 \min 30$ or $2 \min$ before the next step. After each step we take a picture from the side and a picture from the top (with two cameras Nikon D800E mounted with macro objectives). The raft being concave due to its weight, we slightly tilt the side camera ($\approx 8^{\circ}$) to see the deformation below the raft and the drop on top of it. To be able to see the surface of the raft and the drop through it we use two lights, a strong focused light is pointed toward the drop from the top and a regular light from the side illuminates the raft surface. We analyse the pictures with ImageJ and/or Matlab.

In the following, we look at the shape of the drop and the shape of the raft as the drop volume is increased or decreased.

3.2.3 Results

3.2.3.1 Shape evolution when the drop volume increases

We first look at the shape of the drop and the raft deformation when the drop volume only increases. Fig 3.11 and Fig 3.12 shows side and top pictures obtained with this set-up as the drop volume increases ("SiO" particles, $d = 350 \ \mu m$). From top pictures we immediately see that the drop shape and the raft deformation remain axisymmetric during the whole injection. We will thus project the drop shape and the raft deformation in two dimensions. For small volumes, the shape of the drop is spherical and the raft is not deformed (a)). In this regime the drop looks like a non-wetting sessile drop (see Fig 3.8). As volume increases, the shape of the drop evolves toward an oblate spheroid shape (b), c)) and starts to deform the raft. The drop shape becomes qualitatively different from a non-wetting sessile drop and looks more like large floating Leidenfrost drop (see Fig 3.9 c)). At high volumes, the drop is no longer up-down symmetric (d), e), f)), it heavily deforms the raft and adopts a bizarre hemispherical shape similar to [118] (see Fig 3.9 b)). At a critical volume V_{max} the raft destabilises (see section 3.2.3.2).

If we want to characterise both the drop shape and the raft deformations we must measure several parameters which are defined on Fig 3.13, yet we will introduce them gradually. We first look at the drop radius R measured automatically from top pictures with Hough Transform¹ or manually from the side and the radius of the portion of the drop in contact with the raft R_{cont} measured manually from the side. Fig 3.14 a) shows the evolution of R and R_{cont} as the drop volume is increased on a "ZrO" raft $(d = 250 \ \mu m)$. Both radii follow a similar curve: they grow as the volume increases but their rate of growth decreases monotonically until both radii saturate. The last point corresponds to the maximum volume the raft can bear before it destabilises. During the whole experiment $R_{cont} \approx R$. This is especially true at high volumes (V > 2.5 mL). It shows that the drop contacts the raft over its entire radius. Then we look at the drop total height H, the height of the portion of the drop in contact with the raft H_{cont} and the amplitude of deformation of the raft A all of which are measured manually on side pictures. Fig 3.14 b) shows the evolution of H, H_{cont} and A as the drop volume is increased on the same raft as a). The drop height H increases with the drop volume and reaches a linear dependence with the volume for V > 1 mL. Similarly, H_{cont} and A also grow linearly with the drop volume with the same slope for H_{cont} and a slightly higher one for A.

In order to compare the drop shape to a spherical shape we introduce $R_0 = \left(\frac{3V}{4\pi}\right)^{1/3}$ which is the radius the drop would have if it was a sphere and make our data dimensionless by rescaling lengths with ℓ_c . A characteristic length (R_0 in our case) divided by ℓ_c is the square root of a Bond number, we thus expect that for $R_0/\ell_c << 1$ capillarity is dominant and that for $R_0/\ell_c >> 1$ gravity is dominant. Fig 3.15 shows the same data as Fig 3.14 but expressed as a function of R_0 instead of V. We indeed see a transition close to $R_0 \approx \ell_c$, the drop evolves from a roughly spherical shape toward a more oblate shape. For $R_0 > 1.5\ell_c$ it becomes more complicated shape: the drop clearly

¹We use the "Hough transform for circles" code from David Young https://www.mathworks.com/matlabcentral/fileexchange/26978-hough-transform-for-circles



Figure 3.11: Side pictures of a water drop (dyed in red) floating on a "SiO" raft $(d = 350 \ \mu m)$. The drop volume increases from **a**) to **f**) : $V = 50 \ \mu L$, $0.7 \ mL$, $1.45 \ mL$, $3.4 \ mL$, $5.8 \ mL$, $9.75 \ mL$. As a scale bar, the drop diameter in **f**) is $\approx 3 \ cm$.



Figure 3.12: Top pictures corresponding to the side pictures of Fig 3.11.



Figure 3.13: Schematic of a water drop floating on a granular raft. The measured shape parameters are drawn. The dashed line represents the undisturbed raft level.



Figure 3.14: Evolution of the shape parameters as the drop volume V is increased until destabilisation ("ZrO" raft $d = 250 \ \mu m$). **a**) shows the radii R (red) and R_{cont} (green). **b**) shows the heights H (red), H_{cont} (green) and A (purple).

Remark. We lack some data at low volume due to the curvature of the raft. Tilting the camera allows us to measure H, otherwise the top of the drop is below the top of the raft during most of the experiment, but it prevents us to measure H_{cont} and R_{cont} for low volumes. To measure everything accurately two side views are needed, one horizontal and one tilted.



Figure 3.15: Evolution of the dimensionless shape parameters as the dimensionless drop equivalent radius R_0 is increased until destabilisation ("ZrO" raft $d = 250 \ \mu m$). The dashed lines represent a perfect sphere. The dotted vertical line indicates the volume for which Bo = 1. Insets Same data plotted in logarithmic scale. **a**) shows the radii R(red) and R_{cont} (green). **b**) shows the heights H (red), H_{cont} (green) and A (purple).

has two interfaces (the bare one and the bridged one) that behave differently.

Since the drop adopts this peculiar shape because it interacts with the granular raft, we expect that different rafts will produce different shapes. We first look at the effect of the raft size on the drop shape. Fig 3.16 shows the dimensionless drop aspect ratio: H/ℓ_c as a function of R/ℓ_c , for rafts of different size made with the same particles. We



Figure 3.16: Dimensionless drop aspect ratio for "ZrO" $(d = 250 \ \mu m)$ rafts of different sizes: r_{drop} is the minimum projected distance between the centre of the drop and the edge of the raft. It roughly coincides with the raft radius. The black lines are guide to the eye.

quantify the raft size with r_{drop} , the minimum projected distance between the centre of the drop and the edge of the raft (seen from the top). Since the rafts are axisymmetric and the drop deposited in the centre, r_{drop} is roughly the raft projected radius seen from the top. Qualitatively the drop shapes are similar, we recover the three regimes mentioned above. For $R < 0.5\ell_c$, $H \approx 2R$: the drop is spherical. Then it evolves toward an oblate spheroid for $0.5 < R/\ell_c < 1.5$ as $H \approx 1.15R$. Finally, H starts to evolve non linearly with R and the shape become more complex for $R > 1.5/\ell_c$. However, we find small differences for $R > \ell_c$: for a given drop radius, its height is larger for small rafts. This size dependence vanishes when the raft becomes much larger than the deformation due to the drop. If the raft is too small, the deformation due to the drop interacts with the raft edges and modifies the drop shape. In the following we use rafts much larger than the floating drops and do not look at the raft size.

Then we look at the effect of the particle size d and density ρ_s on the drop shape. Fig 3.17 a) shows the dimensionless drop radius R as a function of R_0 for a representative



Figure 3.17: **a)** Dimensionless drop radius R as a function of R_0 . **b)** Dimensionless drop height H as a function of R_0 . **c)** Dimensionless drop height H as a function of R. Closed circles represent "ZrO" rafts ($\rho_s = 3800 \ kg.m^{-3}$), open circles represent "SiO" rafts ($\rho_s = 2500 \ kg.m^{-3}$). The parameter \mathcal{D} is colour coded, from light blue (lowest \mathcal{D}) to orange (highest \mathcal{D}).

raft of each particle type. The evolution of R is identical for different particle sizes and densities except just before the destabilisation. The maximum value of R_0 (or maximum drop volume before destabilisation) however, depends on the particles used and will be discussed in the next section. The fact that the evolution of R does not depend on the raft properties suggests that the drop radius is mainly governed by the upper bare interface of the drop. On the other hand, the drop height H evolution depends on the raft weight. Fig 3.17 b) shows the dimensionless drop height H as a function of R_0 . For a given particle density, the larger the particles the higher H is for a given volume. Like in chapter 2 we introduce the dimensionless parameter \mathcal{D} which balances the raft weight to capillary forces. We use the same definition: $\mathcal{D} = \frac{\rho_{eff}d}{\Delta\rho\ell_c}$, except this time the expression of ρ_{eff} is slightly different since the particles are wet twice more by water. Using the same assumptions as in chapter 2 we get $\rho_{eff} = \frac{2}{3}\phi \left(\rho_s - \rho_w\right)$ (In our case ρ_w is close to ρ_o so the change is not significant). We see on Fig 3.17 b) that the evolution of H with R_0 solely depends on this parameter \mathcal{D} : the two curves for $\mathcal{D} = 0.45$ and $\mathcal{D} = 0.48$ are similar despite having different particle sizes and densities. Since $R = f(R_0)$ is independent of the particles used, the drop aspect ratio H = f(R) also depends on \mathcal{D} . Fig 3.17 c) shows H as a function of R for the same data as a) and b). Aside from the impact on the maximum drop volume (discussed next section), changing the particles mainly modify the critical volume for which we observe the transition toward the complex shape where H = f(R) is no longer linear. This transition occurs later for lower values of \mathcal{D} . A proper modelling of both interfaces still needs to be done, we believe an approach similar to [138] where the bare interface and the bridged part are solved and reconnected should yield a good description of the drop and raft shape. We could start with an effective tension model like in [110] for the raft part as bending does not seem to play a role here.



3.2.3.2 Destabilisation of the raft due to the drop weight

Figure 3.18: Sequence of images showing the destabilisation of a "SiO" raft $(d = 625 \mu m)$ by a 1.8 mL water drop. Time advances from left to right, the intervals between each pictures are $d\tau \approx 1, 0.2, 0.06, 0.06, 0.3 s$. Inset Picture taken during the destabilisation of another raft (same particles) focused in the centre of the jet to see its composition. The arrow shows the water inside the jet.

When the drop becomes too heavy for the raft, it cannot sustain the drop weight any more and destabilises. Let us look at this destabilisation process. It is very similar to the natural destabilisation of heavy granular rafts [68] and the fold destabilisation under compression (section 2.2.4). Fig 3.18 shows a sequence of image of the destabilisation process shot with a high speed camera. The drop starts to sink toward the bottom of the tank and elongates itself in the vertical direction at the same time. The raft is pulled by the drop and flows around it. A multiphase jet is formed with a core made of the water from the drop and an annulus made of oil with its outer surface covered with particles (Inset Fig 3.18). A Rayleigh-Plateau like instability finally pinches and breaks this jet and the destabilisation stops.

In Fig 3.19 we plot the maximum dimensionless drop volume (we use R_0) a raft can carry as a function of \mathcal{D} . We obtain a master curve that rescales the data for different particle sizes and densities. Like the maximum raft size or the maximum fold amplitude, the maximum drop volumes comes from a balance of gravity to surface tension through \mathcal{D} . Surface tension holds the particles together and allows dense rafts to float while the drop pushes on the raft and increases the system's weight eventually leading to destabilisation. The shape of the curve in Fig 3.19 is similar to the destabilisation of rafts under compression (Fig 2.37). The maximum drop volume increases monotonically when \mathcal{D} decreases, *i.e.* lighter rafts can carry bigger drops.

During the destabilisation we encapsulate a water drop covered with a thin layer of oil and particles. Fig 3.20 shows a picture and a schematic of this encapsulated drop. This unusual object, similar to antibubbles, is stable in time but fragile: we can move it around carefully with a spatula but any abrupt movement or sharp object will break the shell and release the inside drop content in the water bath. To form these encapsulated drops a few conditions must be satisfied. The height of the water bath must be sufficient, otherwise the jet does not destabilise and we obtain a column like drop (Fig 3.21). Another condition is that we must coat completely the drop. When the raft is too small and there is not enough particles (like in Fig 3.11), the inside drop coalesces with the bath during the destabilisation.



Figure 3.19: Dimensionless maximum drop size R_0 before destabilisation as a function of \mathcal{D} . Colours represent different materials, with different densities. The dashed line is a guide to the eye.



Figure 3.20: **a)** Picture of an encapsulated drop after destabilisation ($V \sim 1 mL$, particles: "SiO" $d = 500 \ \mu m$). We have a multiphase object: a dyed water drop in the centre, a thin layer of oil around it and particles bridging the two water phases. **b)** Schematic representing the sectional view of the encapsulated drop in **a**).



Figure 3.21: Pictures of the spontaneous destabilisation of a drop on a "ZrO" raft $(d = 250 \,\mu m)$ when the bath height is small. The raft wrinkles during the destabilisation. Scale bar 1 cm.

3.2.3.3 Shape evolution when the drop volume decreases

Up to now we have increased the drop volume, what happens when we decrease it ? The experiment starts with the injection process described above, then at some point we stop the injection at $V_{inj} < V_{max}$ and start to pump out the water. The experiments presented here have only been carried with the 250 μm "ZrO" particles and the 500 μm "SiO" particles. They have yet to be generalised to other particles. Depending on the drop shape before we start to pump out the water we can observe two very different behaviours. The first one is presented in Fig 3.22. It shows sides pictures of a drop on a "ZrO" ($d = 250 \ \mu m$) raft as its volume decreases. At first, the contact line is pinned by the particles and the upper part of the drop (not in contact with the raft) is the first to recede (Fig 3.22 b)). Then the contact line finally depins and also recedes in stick-slip motion while sometimes tearing off particles from the raft (Fig 3.22 c) and d)). This pinning and stick-slip motion is a consequence of the net energy gain obtained when the drop wets the particles. It is energetically favourable to distort the bare interface and produce shapes that are even more oblate, but eventually the particle dewet and we can remove the whole drop from the raft.

The second one is presented in Fig 3.23. The contact line is also pinned by the particles and the upper part of the drop is also the first to recede (Fig 3.23 b)). However, when the edge of the region of the drop in contact with the raft becomes almost vertical, the contact line does not recede any more. The drop shape becomes hemiellipsoidal because the bare portion is the only one receding. At the same time, as the drop volume continues to decrease, the portion of the raft in contact with the drop is compressed and buckles to accommodate the excess of surface (Fig 3.23 c) and d)). We see wrinkles in the azimuthal direction that break the axisymmetry. At some point the compressed



Figure 3.22: Side pictures of a 3 mL dyed water drop on a "ZrO" raft $(d = 250 \ \mu m)$ being pumped out. The drop volume decreases from **a**) to **d**): $V \approx 3.0, 1.6, 1.0, 0.4 mL$.



Figure 3.23: Side pictures of a 3.2 mL dyed water drop on a "ZrO" raft ($d = 250 \ \mu m$) being pumped out. The drop volume decreases from **a**) to **d**): $V \approx 3.2$, 1.8, 1.2, 0.8 mL.

raft destabilises and we can never completely remove the drop.

The transition between these two behaviours is continuous and we can also see intermediate behaviours such as the one presented in Fig 3.24. In that case the contact line is also pinned and the drop reaches the hemispherical shape with azimuthal wrinkles (Fig 3.24 middle pictures) but the raft never destabilizes. Instead, we can pump almost all the liquid and obtain a shapeless pocket of water trapped in the raft (Fig 3.24 right pictures).

To quantify these observations we measure the drop aspect ratio H = f(R) during successive injections and withdrawals for the two particle types investigated in Fig 3.25. The first two withdrawals from Fig 3.25 a) and the first one from Fig 3.25 b) corresponds to the first situation seen in Fig 3.22. After a first period where the drop height decreases while the radius is roughly constant (aspiration of the upper part), the withdrawal curves recovers a slope similar to the injection curves. But for a given drop radius R its height H remains smaller during withdrawal than during injection. This indicates that the drop shape is even more oblate. After these withdrawals we remove completely the drop and when we inject again we recover exactly the same injection curves. The second withdrawal of Fig 3.25 b) corresponds to the intermediate behaviour of Fig 3.24. Even though the situation is different from the previous withdrawal, the H = f(R) curve is very similar, this is because we are not able to measure H for small volumes. At small volumes H plateau while R continues to decrease (see Fig 3.24). The last withdrawal corresponds to the second behaviour (Fig 3.23) in both cases. The aspect ratio curves are different: at first both H and R decrease as we pump out water. Then H plateau while R continues to decrease and the raft quickly destabilises.



Figure 3.24: Top and side pictures of a 2.2 mL dyed water drop on a "SiO" raft $(d = 500 \,\mu m)$ being pumped out. The drop volume decreases from left to right: $V \approx 2.2$, 0.7, 0.2 mL.



Figure 3.25: **a)** Dimensionless drop aspect ratio during successive injections-withdrawals on a "ZrO" raft ($d = 250 \ \mu m$). Closed symbols are for injection, open symbols for withdrawal. Red and blue withdrawals correspond to the first behaviour (Fig 3.22), the green one corresponds to the second behaviour (Fig 3.23). **b)** Same plot on a "SiO" raft ($d = 500 \ \mu m$). The blue withdrawal corresponds to the first behaviour (Fig 3.22), the red one to the intermediate behaviour (Fig 3.24) and the green one to the second behaviour (Fig 3.23).

Remark. The last injection in **a**) is not perfectly superimposed to the first two because the experiment was done on a different raft.

3.3. POTENTIAL APPLICATIONS

What controls the transition between the two behaviours is not very well understood yet but we believe that it depends on the shape of the drop at the end of the injection. The second behaviour only occurs when the drops are large enough to reach a very asymmetric shape (when the H = f(R) curve is almost vertical). Our hypothesis is geometric, the energy necessary to dewet particles over a small radial distance drdepends on the local slope at the edge of the raft. It is much higher for large slopes, when the drop is large and heavily deforms the raft. As a result, the raft prefers to deform itself rather than letting the contact line move.

Pumping out the drop could be an interesting way of probing the raft mechanical properties, in particular controlling the pressure instead of the volume could give us informations on the critical buckling pressure that we do not have with the compression set up.

3.3 Potential applications

One way to use these floating drops is to polymerise them. As a proof of concept, instead of using pure water or dyed water to make our floating drops, we have used a hot water-gelatine mixture. When the mixture is hot, it is liquid like pure water (though much more viscous) and we can make a regular floating drop on a granular raft. Then, we wait for the drop to cool down and gel. Once the drop is solid, we remove it from the raft and gently rub it to get rid of the particles attached to it. The result is presented in Fig 3.26: we obtain an aspherical object like in [140] but it is textured on one side by the particles. The texture is concave (like a golf ball) and can be controlled by changing the particle size and wetting properties. For spherical particles, the size of the removed spherical caps depends on both d and θ_y , their arrangement is hexagonal for monodisperse particles and disordered for polydisperse particles. Different particle shapes (cuboids or cylinders for instance) could also produce different textures. In



Figure 3.26: Pictures of a water-gelatine encapsulated drop after polymerisation and removal of the particles ("SiO" $d = 500 \,\mu m$). Inset: Zoom on the texture, the irregularity of the holes comes from the irregularity of the particles.



Figure 3.27: Figure adapted from [144]. **a**) Schematic of the fabrication process. The PDMS is melt down with a femtosecond laser pulse. **b**) Picture of a macroscopic microlens array. **c**) - **e**) Scanning electron microscopy images of the concave microlenses under different magnifications.

the optics community, great efforts are made to produce array of microlenses (e.g.[24, 141, 142]). Convex microlenses (like fly eyes) are the most sought after but concave ones are also produced (e.q. [143, 144]). It usually involves complex photolithography or engraving techniques and is restricted to flat geometries. As an illustration, Fig 3.27 a) shows how they produce a concave microlens array in [144]. A femtosecond laser etches periodically a PDMS sample by scanning its surface. The sample is then cleaned in an ultrasound bath and they obtain the microlens array in Fig 3.27 b). The microlens are shown in Fig 3.27 c) - e), their size can be controlled by changing the laser power or exposure time but they become irregular at large powers. The raw polymerised drop is an aspherical concave microlenses and could be used as it is, as a diffuser for instance. It could also be used as a mould to produce a convex texture. The polymerised floating drop can be a mould to make a convex texture on a concave object while the flat portion of an encapsulated drop (in contact with the bottom of the tank) can make a flat array of convex microlenses. Using the floating drops has several advantages: it is cheap and does not require complex equipments such as femtosecond lasers, the texture is predictable and can be easily modified by changing the particles, finally curved geometries (spherical or aspherical) are easily accessible.

The fact that drops are anchored to the raft also allows producing stable drops of different shapes by forcing the coalescence of adjacent drops. Fig 3.28 shows an elongated drop formed by forcing two adjacent drops to coalesce and a pseudo tetrahedral one with three adjacent drops. The result and the mechanism are similar to arrested coalescence presented in Fig 3.2 but there are a few differences. To achieve a spherical shape after coalescence, it is necessary to either dewett some particles which is not energetically favourable or rearrange the particles which is prevented by bridging and friction. For

colloidal drops, the particles can move around, as a result arrested coalescence is observed for a narrow range of surface coverage. In our case any raft can produce these droplets. Since those drops are stable, they could also be polymerised to extract their shape.



Figure 3.28: Top view of stable water drops floating on a "SiO" raft $(d = 500 \,\mu m)$. Left: One small drop, axisymmetric and almost spherical. Centre: Two adjacent drops have coalesced, since they were both anchored to the raft this results in an elongated almond shape. Right: A third drop has coalesced and leads to a pseudo tetrahedral shape.

We have seen that these drops coalesce when the interface is polluted by dust. They could be used as a cheap detector to check if the interface is clean. Here we are using macro scale particles so we are sensitive to macro scale dust (~ 100 μ m). The thickness of the oil film between the bath and the drop (see Fig 3.3) gives the lower bound for the detectable dust particle size. If we go down in scale, for instance with 10 μ m particles the oil film becomes much thinner ($h_o < 10 \ \mu$ m) and this method becomes sensitive to smaller dust particles ($\gtrsim 10 \ \mu$ m).

Liquid marbles have already been used with success as chemical or bio-chemical micro reactors (e.q. [145, 146]). Drops floating on granular rafts share many properties with liquid marbles and we believe they could make very good micro reactors. Even though they are less easy to handle they have some unique properties that marbles do not have. Several drops can float on a raft at the same time to carry multiple reactions in parallel. Our floating drops are anchored to the raft and are not mobile, but the raft itself can move easily. Placing a hydrophilic needle in the drop and moving it carries away the raft. We can also simply push the drop with a spatula and the whole raft will move. Anything that produces a flow should also be able to propel the raft and applications targeted for floating marbles (e.g. [147]) should also work here. The top of the drop is bare so we can monitor the reaction inside it without fluorescence, we can also inject reactants or withdraw products easily. Fig 3.29 demonstrates that: we inject a yellow dye in the drop via the bare interface and follow the change in colour. Since the drops are in oil, there is almost no evaporation and long reactions can occur. But the most interesting feature of these floating drops is the possibility to encapsulate an aqueous drop in water. Indeed, we have seen in section 3.2.3.2 that when the drop becomes too big, the raft spontaneously destabilises and encapsulates a portion of the floating drop (see Fig 3.20). But we can also force the raft destabilisation. Fig 3.30shows a sequence of images where we push sharply on the drop with a Teflon stick. By doing so we give the drop an acceleration sufficient to destabilise the raft. The drop



Figure 3.29: Side view of a water droplet (dyed in blue) floating on a "SiO" raft $(d = 500 \ \mu m)$. The top of the droplet is accessible we can easily inject reactants (water dyed in yellow here) and monitor the reaction visually. The arrow indicates the capillary used for injection.



Figure 3.30: Side view of a water droplet (dyed in green) floating on a "SiO" raft $(d = 500 \ \mu m)$ being pushed down with a Teflon stick. Time advances from left to right, the interval between each pictures is $d\tau \approx 0.25 \ s$. The red arrow indicates the motion of the stick. We obtain an encapsulated drop below the destabilisation volume.

sinks toward the bottom of the tank and gets encapsulated. Remote destabilisation methods such as centrifugation or magnetic pulling have been used to sink bare granular rafts [110, 111]. They should also work to remotely encapsulate the content of the floating drop. The volume of this encapsulated aqueous drop can be controlled by changing the volume of the floating drop and it can be manipulated with a spatula. We believe the use of magnetic particles would allow them to be moved remotely like liquid marbles [148]. This allows to have water soluble compounds isolated from the water bath delivered wherever they are needed. Fig 3.31 shows how we can trigger the delivery. We pierce the bridged interface of a floating drop and the upper interface of an encapsulated drop with a hydrophilic needle. It induces coalescence and the content of the drop is immediately released in the water bath. Other methods used with liquid marbles should also work: under a strong electric field, liquid tips forms between the particles, they come in contact and induce coalescence [149, 150]. But an even simpler method would be to make pH responsive particles like in [151, 152]; since bridging only occurs when $\theta_y > 90^\circ$ if a change in pH can lower the contact angle it can remove bridging and induce coalescence. Another advantage of our floating drops is that unlike floating liquid marbles, once they are pierced the interface is not "altered", the hole in the raft closes itself in a few seconds (for large particles) and the same raft can be used to create other floating or encapsulated drops.



Figure 3.31: Top: Water droplet (dyed in blue) floating on a "SiO" raft ($d = 500 \ \mu m$) pierced with the needle used for injection. Time advances from left to right, the intervals between each pictures are $d\tau \approx 0.2$, 0.1, 15 s. Bottom: Water encapsulated droplet (dyed in green, same particles) pierced with a needle. Time advances from left to right, the intervals between each pictures are $d\tau \approx 0.5$, 0.06, 2 s. The red arrows indicate the first holes where coalescence starts.

We are just scratching the surface here and we already found many ideas for these floating drops. We believe that like liquid marbles, floating water drops are interesting from a fundamental point of view and could lead to promising applications in the future.

3.4 Conclusion

We have shown that water drops can float on a granular raft at the oil-water interface only if the particles are hydrophobic ($\theta_y > 90^\circ$) and large enough ($d \gtrsim 200 \ \mu m$). The particles below the water drop bridge both interfaces and a thin oil layer prevents the drop coalescence. Since it is energetically favourable for the particles to be wet by both the bath and the drop, it is very hard to dewet them. The resulting floating drop is thus attached to the raft.

Granular rafts can carry drops of very large volumes ($V_{max} = 12 \, mL$ for our lightest rafts). Large floating drops push on the raft with their weight and deform it. It produces unusual shapes with two distinct interfaces: the upper one is bare and seems to follow the classical Young-Laplace equation while the bottom one, anchored to the raft, is ellipsoidal and its shape depends on the raft deformation. We show that the drop (and raft) shape at a given volume depends on the parameter \mathcal{D} which balances the raft weight to capillary forces. We still have to model these two interfaces to explain the drop shape in detail. It seems there is no bending rigidity involved and a purely tensional description of the interface should be enough to predict the drop shape and the interface deformation. Finally, similarly to compressed granular rafts, at a critical volume V_{max} the weight of the drop is too high for the raft which cannot withstand it and destabilises. The drop starts to sink toward the bottom of the tank and brings with it a portion of the raft. The interface pinches off and we obtain an encapsulated water drop in water. This maximum volume V_{max} also depends on the parameter \mathcal{D} .

If we make a floating droplet of volume $V \leq V_{max}$ and pump it out, we can observe two different behaviours depending on the droplet initial shape. When $V \ll V_{max}$, the droplet can be pumped completely with a stick-slip motion of the contact line which gives them a very oblate shape. When $V \sim V_{max}$, the contact line eventually stops receding and the raft starts to buckle to accommodate the reduction of volume. Under this configuration we cannot pump out completely the drop because the raft will destabilise. We do not understand yet the transition between these regimes and a generalisation of our experiments with more particles size would help us to make a theoretical model.

Finally, we discussed the potential applications for these floating drops. Like liquid marbles they look promising as chemical micro-reactors. One of their most interesting feature is that we can encapsulate easily the content of the drop by forcing the raft destabilisation. We thus have an aqueous capsule isolated from the surrounding water by an oil layer. This capsule can be transported and its content can be released at will. We can also take advantage of the possibility to make complex shapes. For example, since the drops are stable and robust, they can be polymerised to produce non spherical textured objects. This texture could be used to produce arrays of microlenses on curved surfaces at low cost.

Conclusion

Summary of the results

Folds are present in all sort of compressed floating materials, ranging from biological membranes to giant ice sheets. Yet, a complete description of the fold only exists for the simplest material: a weightless elastic sheet. In this thesis, we extend these results up to very large deformations, with more complex materials: heavy elastic sheets and granular rafts.

In the first chapter, we study the effect of the sheet density on the buckling of floating elastic sheets. To do so we synthesised sheets of varying weight, placed them at a liquid-fluid interface and performed uniaxial compression experiments. We show that the sheet density does not impact the wrinkle wavelength or amplitude: it does not play any role in the wrinkling regime. The wrinkle wavelength is however not constant, it decreases as compression increases. We propose a weakly non linear analysis to explain this phenomenon. During the wrinkle to fold transition, the deformation localises in a unique fold. We observe that the sheet can go from an antisymmetric configuration to a symmetric one via a series of non symmetric configurations. However, unlike theoretical predictions on weightless sheets, we always end up with a downward symmetric fold. For a given set of fluids, as the sheet density increases the fold amplitude increases for a given compression. To understand these results, we include the sheet gravitational energy in the theory of Diamant and Witten [3]. This introduces a new non dimensionless number M that accounts for the sheet weight. Adding this term in the model reduces the energy of the downward symmetric fold compared to the other configurations and explains why we only see this one in our experiments. Minimising the total energy yields a set of non linear differential equations that we solve numerically. The results of our model recovers the shift in amplitude due to the sheet self weight that we have observed. Then, we explore the regime of very large deformations, when the two sides of the fold come in contact. A column of the upper fluid gets encapsulated into a loop formed by the sheet. Depending on the sheet and fluid densities, the fold in self-contact can sink deeper or bend back toward the interface. We use a heavy Elastica model to qualitatively explain this phenomenon. Finally, we discuss the effect of surface tension acting at the sheet edges and the reversibility of the experiment.

In the second chapter, we focus on the buckling instability of compressed granular rafts. We perform uniaxial compression experiments and use a custom Fourier Transform profilometry set up to capture the morphology of the rafts. When the compression starts the raft initially behaves like a fluid, the particles rearrange and the raft spreads in the lateral direction to accommodate the compression. At some point when the accumulated friction or the walls of the tank block the lateral expansion, the raft becomes solid-like and buckles out of plane. We first observe small wrinkles, localised, with a wavelength that only depends on the particle size. As compression increases, we see a transition toward larger wrinkles. Their wavelength and lateral extension is larger. The large wavelength depends on both the particle size and the fluid densities. Finally, upon further compression the deformation localises in a unique fold, which grows until it destabilises the raft. The buckling observed in granular raft is very close to the one in elastic sheets studied in chapter 1. We thus try to use a continuum elastic description to predict the buckling of granular rafts. Using the floating beam model we can predict the wavelength and amplitude of the wrinkles but this model fails to describe the fold. If we now add the weight of the raft in this model like in chapter 1 and neglect the menisci at the edges of the raft, we are able to recover the fold shape and the evolution of its amplitude as the compression increases up to self-contact. The agreement is not perfect as we still have discrepancies in the compression value in the model compared to the experiment, in particular in the wrinkling region. Yet, it validates the raft elastic behaviour despite its evident granular nature. At higher compressions, we do not know how to model the portion of the fold in self-contact but we can describe the portion of the raft which is pulled down with it. We find that the shape of this portion is self-similar and well described by this heavy floating plate model. Finally, we discuss the origin of the discrepancies between the elastic model and our experiments and show the phenomena that are not explained by the elastic model.

In the last chapter, we tackle the interaction of a water drop with a granular raft. We show that if we deposit a water drop on a raft made of hydrophilic particles, it will immediately coalesce with the water bath below. On the other hand if the particles are hydrophobic they will bridge the drop and form a thin oil layer that protects the drop from coalescence. However, for small particles, this layer becomes too thin and contaminants larger than the oil film such as dust can induce coalescence. In the case where coalescence is prevented, we can vary the drop size by injecting or withdrawing water. When we increase the drop volume, its shape evolves from an oblate spheroid to a more complex shape. The bare interface and the part in contact with the raft behave differently, breaking the up-down symmetry of the drop. This shape is reminiscent of the one taken by a large water drop floating on a water bath and isolated from it by a thin vapour layer. If we now decrease the drop volume, depending on the drop initial size we can observe buckling of the raft in the azimuthal direction. Since the particles bridge the interface, dewetting them come with a high energetic cost. The contact line can become pinned and the raft prefers to deform rather than letting the drop dewet the particles. Finally, we provide proofs of concept to illustrate possible applications for these floating drops.

Future work

There are still many open problems on both the buckling of floating elastic sheets and granular rafts. We hope the work done in this thesis will contribute to the general understanding of the mechanical properties of these objects. Nonetheless, our work also highlights several aspects that we do not fully understand yet and need further study.

In floating elastic sheets, the effect of surface tension (acting at the edges of the sheet) on the fold formation or the influence of adhesion when the sheet touches itself are poorly understood. They are neglected in theoretical analysis for simplicity, and yet they could be essential for technical applications or modelling complex objects such as biological membranes. An experimental and theoretical investigation of these effects is to be done. Going to non-planar geometries and study the effect of curvature on the formation of folds is the next step to go toward the description of capsules. The strip is also an interesting geometry where we could observe a competition between in plane buckling and out of plane buckling.

In our experiments with granular rafts, we are not able to explain the small wavelength and we have a discrepancy between the compression in the experiment and the model even after removing the menisci. Measuring the side force we impose and how it propagates inside the raft, would help us to improve the model as we believe that one of the main difference with elastic materials lies here. Understanding how stresses propagate is also fundamental to grasp the influence of the aspect ratio and the three dimensional effects. Another interesting direction is to look at the plastic rearrangements that occurs during the first loading. The problem of particle desorption instead of buckling is also important, both from a fundamental point of view and to design emulsions and foams. The experiments show that the contact angle dictates if the particles are expelled or if the interface buckles but a detailed study and a theoretical description is lacking. Before we can apply our findings to Pickering emulsions and particle stabilised foams, we again have to study non-planar geometries and the influence of curvature on buckling. The experiment presented in chapter 3 where we pump out a floating drop could be one way to do this but a more simple experiment could be done with a large oil in water (or water in oil) pendant drop. Finally, we could also look at the pinch off of the jet during the raft destabilisation. The particles in that region modify the weight and thus the inertia but probably also the rheology of the interface.

Concerning floating drops, we need to make a model to derive the drop shape as its volume increases. The experiments where we decrease the drop volume need to be carried on with more particles to understand the non-planar wrinkling instability we have observed. Another direction could be to study the coalescence dynamics with hydrophilic particles. When coalescence occurs at the oil-water interface, the particles are pushed back, a hole opens in the raft and capillary waves are generated. Understanding these phenomena should also give us insights on the raft mechanical properties. Finally, we could develop our ideas of applications. For instance, it would be interesting to show how to remotely control and pierce an encapsulated drop or how to modify the texture properties with different particles after polymerisation.

From a broader perspective, several other discrete systems bear a resemblance with those studied in this thesis and might be tackled with a similar continuum mechanics approach. For instance liquid interfaces covered with globular proteins such as β -lactoglobulin or lysozyme are often treated as particle laden interfaces. The proteins are considered as "soft" particles and such interfaces wrinkle and fold under compression.

Can we apply the buckling formalism for interfaces covered with solid particles to these "soft" particle ? We could also think about active materials. To cite a few examples: epithelial cell monolayers have the possibility to jam and become solid-like, fire ants can link themselves to make solid rafts that float on water [153]. How these materials buckle once compressed and how the buckling pattern is influenced by their activity ? Many complex materials whose mechanical properties are not well understood fold under compression like elastic sheets and the approach of this study (and many others) that consist in studying the buckling instability could be an efficient way to characterise them.

126

Appendix A Sheet production and analysis

Contents

A.1	Shee	t production
A.2	Shee	t properties
	A.2.1	Sheet thickness
	A.2.2	Tensile test
	A.2.3	Beam deflection
	A.2.4	Swelling and boundary condition $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 131$

A.1 Sheet production

We produce the sheets by spin coating vinyl polysiloxane VPS (elite double 32, Zhermack) mixed with iron powder (97%, -325 mesh, Sigma Aldricht) on a Polos 300 HD spin coater. The VPS comes in two bottles a base and a catalyst. To make the cross linked elastomer one has to mix the base and the catalyst (with a ratio of 1:1), stir for about 1 min and then wait about 10 min for the polymer to solidify. The base density of bulk cross linked VPS is $\rho_{vps} = 1.20 \ g.cm^{-3}$, and the iron density is $\rho_{fe} = 7.87 \ g.cm^{-3}$. The protocol is the following. We mix a mass m_{vps} of polymer with a mass m_{fe} of iron powder. We stir for about 1 min and use half of the mixture to spin coat a first sheet using one of the recipe in table A.1. Once the spin coating is

recipe n ^o	acceleration 1 $(rpm.s^{-1})$	speed 1 (rpm)	time 1 (s)	acceleration 2 $(rpm.s^{-1})$	speed 2 (rpm)	time 2 (s)
1	100	500	15	100	800	45
2	100	500	15	100	1000	45
3	100	500	15	100	1300	50
4	100	500	15	100	1500	50
5	100	800	15	100	2000	50

Table A.1: Spin coater recipes.

over we use the second half of the mixture to spin coat a second sheet (with another recipe). Then we wait for the curing of both sheets. The final sheet thickness depends on the spin coating recipe (acceleration, speed, time) but also on the liquid viscosity. After mixing the base and the catalyst the polymer mixture viscosity increases with time, thus with the same recipe we do not get the same sheet thickness for the first and second sheet. Besides, adding the iron powder also increases the mixture viscosity. We adapt the recipe for each sheet in order to narrow the range of sheet thickness A.2.

If we assume the iron powder is distributed homogeneously in the mixture then the density is:

$$\rho_s = \rho_{fe} \rho_{vps} \frac{m_{vps} + m_{fe}}{m_{vps} \rho_{fe} + m_{fe} \rho_{vps}}$$

We checked with two bulk samples the predicted density ($\rho_s = 2.0 \ g.cm^{-3}$ and $\rho_s = 3.0 \ g.cm^{-3}$). Within the experimental uncertainties the values were correct.

With this protocol we are able to make sheets of density up to $\rho_s = 2.6 \ g.cm^{-3}$. We cannot go higher, the mixture is too viscous and an instability develops during spin coating. It makes heavier sheets non uniform.

A.2 Sheet properties

The VPS we use has already been characterised in the literature (e.g. [154–157]). We find the following properties: 0.78 < E < 1.36 MPa, $\nu \approx 0.5$ et $1.0 < \rho_s < 1.2 g.cm^{-3}$. The small variations between sources probably come from a different fabrication protocol.

A.2.1 Sheet thickness

To measure the thickness of our spin coated sheets, Fourier transform profilometry is not a good candidate. The sheets are black and do not reflect properly the projected fringes. Besides, their thickness is too small to have a precise measurement. We use two other methods to measure the thickness. We weigh the sheets on a milligram scale, knowing the density, length and width we get an average thickness. The other method consists in illuminating the sheets with a laser line tilted with an angle β (Fig A.1) a)). Seen from above the laser line is deflected by the sheet, and the line shift dx is proportional to the sheet thickness $t = dx \tan \beta$. If the angle β is small then the shift is detectable even if the thickness is very small, but as β gets smaller the line gets thicker and the uncertainty on the shift measurement increases. With our set-up we have to stay above 15° . To measure the shift dx, we fit the intensity peak due to the laser line with a Gaussian (whose centre gives us the shift). The angle being difficult to determine it is more precise to do a calibration. We put an object of known thickness under the laser line, the measurement of the deflection gives an accurate measurement of the angle. We can then recover the height profile (Fig A.1 b)). One can see that the sheets are uniform except on its sides where a small edge bead is present. The flat part mean value gives us the thickness and its standard deviation gives us an estimation of the uncertainty. Table A.2 shows the thickness we obtained with both methods.



Figure A.1: a) Schematic of the sheet thickness measurement. We place the sheet on a flat surface and illuminate it with a laser line. The line deviation seen from above is proportional to the thickness of the object. b) Typical height profile once the line deviation is extracted from the picture.

$\stackrel{\rho_s}{(\rm gcm^{-3})}$	W (mm)	L (mm)	$t_{weight} \ (\mu { m m})$	$t_{laser} \ (\mu { m m})$	$M_{air/water}$	$M_{oil/water}$
1.20	50	75	74 ± 6	54 ± 4	0.007 ± 0.001	0.030 ± 0.004
1.20	60	90	93 ± 6	65 ± 5	0.008 ± 0.001	0.029 ± 0.004
1.40	50	75	81 ± 5	90 ± 11	0.023 ± 0.004	0.100 ± 0.019
1.40	60	90	89 ± 4	89 ± 14	0.023 ± 0.005	0.091 ± 0.020
1.54	50	75	73 ± 4	79 ± 11	0.026 ± 0.005	0.104 ± 0.021
1.54	60	90	89 ± 4	109 ± 12	0.031 ± 0.005	0.131 ± 0.022
1.78	50	75	79 ± 4	78 ± 6	0.039 ± 0.005	0.144 ± 0.020
1.78	60	90	90 ± 4	98 ± 9	0.045 ± 0.007	0.178 ± 0.026
2.00	50	75	85 ± 4	92 ± 10	0.051 ± 0.008	
2.00	60	90	91 ± 3	104 ± 7	0.054 ± 0.007	
2.12	50	75	83 ± 3	99 ± 12	0.058 ± 0.01	
2.12	60	90	94 ± 3	117 ± 28	0.061 ± 0.018	
2.36	50	75	64 ± 3	80 ± 8	0.059 ± 0.009	
2.36	60	90	63 ± 2	70 ± 6	0.060 ± 0.009	
2.55	50	75	49 ± 2	64 ± 7	0.078 ± 0.013	
2.55	60	90	55 ± 2	69 ± 5	0.077 ± 0.010	

Table A.2: Sheet properties. The values of M displayed are calculated using $M = 2\pi(\rho_s - \rho_w)t_{laser}/(\Delta\rho\lambda)$.

A.2.2 Tensile test

To measure our sheets Young's modulus we first do a tensile test. We mould two tensile specimens in a flat and uniaxial dogbone laser cut mould. One is made of pure VPS $\rho_s = 1.20 \ g.cm^{-3}$, the other is made of VPS mixed with iron powder $\rho_s = 2.53 \ g.cm^{-3}$. We make the uniaxial tensile test with a Shimadzu device:

- We draw four markers on the gauge section. Two on the vertical edges to measure the gage length and two horizontal ones close to the centre to measure the gage width. We measure the undeformed dimensions of the specimen with a calliper (L_0, W_0, t_0) .
- We do the tensile test: we impose a vertical displacement at the upper end of the specimen and measure the force F needed. Then we take a picture to measure the gage dimensions (L and W). We do it again for several displacements (staying below the elastic limit of the material).
- We determine the strains $\varepsilon_L = \frac{L-L_0}{L_0}$ and $\varepsilon_W = \frac{W_0 W}{W_0}$ for a given force. The Poisson ratio $\nu = \frac{\varepsilon_W}{\varepsilon_L}$ is given by the slope of the curve $\varepsilon_W = f(\varepsilon_L)$.
- Let S be the cross section of the tensile specimen, for an isotropic material $S = S_0(1 + \varepsilon_L)(1 \nu \varepsilon_L)^2$ where $S_0 = W_0 t_0$. We determine the stress $\sigma = \frac{F}{S}$ and then the Young's modulus E is given by the slope of the curve $\sigma = f(\varepsilon_L)$.



Figure A.2: Stress as a function of the strain curves for the two tensile specimens. The green data are for the pure VPS specimen $\rho_s = 1.20 \ g.cm^{-3}$, the black data are for the VPS mixed with iron specimen $\rho_s = 2.53 \ g.cm^{-3}$, the corresponding lines are fits (forced through the origin).

We get for the pure VPS specimen $\nu = 0.46$, E = 1.03 MPa and for the VPS with iron powder specimen $\nu = 0.49$, E = 2.88 MPa (Fig A.2). The difference in Poisson ratio is not significant, we will take the value $\nu = 0.5$ for all our sheets. But the Young's modulus increases significantly when we add iron powder.

130

A.2.3 Beam deflection

In general the mechanical properties of a material are supposed independent of the sample dimensions. But it has been shown that the Young's modulus depends on the thickness for polydimethylsiloxane (PDMS) [158]. In their study, for thicknesses below 1 mm the Young's modulus becomes significantly larger. Like VPS, PDMS is a silicon based elastomer. To check our measurement on the tensile machine we also measure the Young's modulus of our sheets. To do so we make a beam deflection test. We take two sheets, one is made of pure VPS $\rho_s = 1.20 \ g.cm^{-3}$, the other one is made of VPS mixed with iron powder $\rho_s = 2.39 \ g.cm^{-3}$. We clamp horizontally the sheet and let a part of its length L free under its own weight. In that configuration the deflection at the end of the sheet y_{end} is given by:

$$y_{end} = \frac{\rho_s t L^4 g}{8B} = \frac{3(1-\nu^2)\rho_s g}{2Et^2} L^4$$

For each sheet we measure y_{end} for at least 3 values of L, we then extract the Young's modulus from the slope of the curve $y_{end} = f(L^4)$ (knowing ν , ρ_s and t). We get for the pure VPS sheet $E = 1.46 \pm 0.24 MPa$ and for the VPS with iron powder sheet $E = 2.56 \pm 0.47 MPa$. The uncertainties are much bigger than in the tensile test but the values are in agreement, we are sure our material properties do not depend on the sample dimensions and we will therefore use the precise values from the tensile test. To calculate our sheet bending modulus we make the assumption that E varies linearly with the material density within our data range: $E = 1.39\rho_s - 0.64$.

A.2.4 Swelling and boundary condition

During preliminary experiments, we put the sheets between two PMMA plates screwed together. The part of the sheet pressed by the plates was stretched, resulting in wrinkles around the clamp in the width direction (z). Beside, when we tried oil-water experiments, the sheet swelled. The clamped part could not swell while the free part could, worsening the problem by extending the edge wrinkles. We wanted to conduct the experiments with stress free initial conditions so we modified the clamping system: a macroscopic block of VPS was moulded on both ends of the sheet. We could then grab the blocks without inducing pre stretch. But the swelling problem remained, the sheet was swelling much faster than the blocks, inducing again edge wrinkles in the (z)direction. Finally, we came up with the experimental realisation described in 1.2.1. It allows the sheet to swell uniformly without inducing edge wrinkles but it is still bound to the protruding edges.

Silicon based elastomer (VPS or PDMS) are known to swell in silicon oil [159, 160]. Although VPS has already been used with mineral oil without any mention of swelling [161] we have seen it swell in our experiments. To characterise the swelling of VPS we mould two blocks of VPS and let them swell in a bath of mineral oil for 18 h. We take pictures every 5 min to measure their width and length over time. After 18 h we see a ~ 3-4 % increase in length and width (Fig A.3), and a ~ 7-8 % increase in mass (we weigh the samples after wiping their surface). This mass increase corresponds to a volume increase of ~ 10-12 %, which confirms that the swelling is isotropic ($\varepsilon_V \approx 3\varepsilon_L$). With our clamping system the swelling in length and width is not a big concern but the thickness swelling modify the bending modulus. With the thin sheets we observe a $\sim 4-5 \%$ increase in length in a few minutes, after that no notable swelling occurs. The process is much faster, when we start the experiment the swelling is already done and if we assume it is isotropic the thickness increase is about $\sim 4-5 \%$, *i.e.* lower than our thickness measurement uncertainty.



Figure A.3: Longitudinal strain as a function of time during a swelling experiment with pure VPS samples in light mineral oil.

Appendix B Heavy Elastica model

Contents

B.1	The Euler-Bernoulli	beam theory $\dots \dots \dots$	
B.2	The heavy Elastica		

B.1 The Euler-Bernoulli beam theory

We first briefly present the Euler-Bernoulli beam theory that we are using to derive the heavy Elastica model. Let us consider a beam of length L_0 , width W and thickness t constrained in the (x, y) plane under external forces \overrightarrow{p} . The external forces create internal stresses and strains. We make the Euler-Bernoulli assumption, *i.e.* the beam is inextensible and unshearable so that deformations of the neutral axis do not modify the cross section. Under this assumption the configuration is fully described by the position and orientation of the neutral axis. The internal stresses are averaged on a cross section to produce internal forces \overrightarrow{n} and internal bending moments \overrightarrow{m} . Let us derive the equations describing the equilibrium configuration of the beam under the external forces \overrightarrow{p} . We introduce the intrinsic coordinate system (s, θ) where s is the arc-length and $\theta(s)$ is local angle between the neutral axis tangent and the horizontal axis x; we parametrise the beam neutral axis in terms of arc-length, [x(s), y(s)].

In this coordinate system the kinematic equations are:

$$egin{aligned} &\partial_s y = \sin heta \ &\partial_s x = \cos heta \ &\partial_s x = \cos heta \ &\partial_x^2 y \ &(1+\partial_x y^2)^{3/2} = \partial_s heta \end{aligned}$$

Where \mathscr{C} is the curvature of the neutral axis.

We then consider an infinitesimal portion of the beam (between the point A at s and B at s + ds, see Fig B.1). The forces acting on this portion of beam are: the internal forces on the left $\overrightarrow{n(s)}$ (respectively on the right $\overrightarrow{n(s+ds)}$), the internal bending moment on the left $\overrightarrow{m(s)}$ (respectively on the right $\overrightarrow{m(s+ds)}$) and the external forces

distributed along the portion $\overline{p(s)}ds$. Let us write the equilibrium equations in the Cartesian coordinate system $(\overrightarrow{e_x}, \overrightarrow{e_y}, \overrightarrow{e_z})$.

$$n_x(s + ds) - n_x(s) + p_x(s)ds = 0$$

$$n_y(s + ds) - n_y(s) + p_y(s)ds = 0$$

$$m_z(s + ds) - m_z(s) + \overrightarrow{OA} \wedge \overrightarrow{n(s)} + \overrightarrow{OB} \wedge \overrightarrow{n(s + ds)} = 0$$

Taking $ds \to 0$ gives the equilibrium equations:

$$\partial_s n_x = -p_x$$
$$\partial_s n_y = -p_y$$
$$\partial_s m_z = n_x \sin \theta - n_y \cos \theta$$

We now need one more equation to close our system: the constitutive equation. We will show in our very simple case of planar deformations how to derive it. We look at a section of a 3d beam bend in the (x, y) plane (Inset B.1). The internal stress tensor is σ . The only non zero component of the bending moment is m_z . It reads under our planar deformation:

$$m_z = -\iint y\sigma_{xx} \mathrm{d}y \mathrm{d}z$$

We assume our beam is linear elastic such that $\sigma_{xx} = E\varepsilon_{xx}$ with E the Young modulus. ε_{xx} reads: $\varepsilon_{xx} = \frac{dx(y+dy)-dx(y)}{dx(y)}$. We make the assumption that the beam is slender $(L_0 >> W \sim t)$ such that $\varepsilon_{xx} = \frac{\mathcal{R}-y}{\mathcal{R}} - 1$ where $\mathcal{R} = \frac{1}{\mathscr{C}}$ is the radius of curvature. Under this assumption the bending moment reads:

$$m_z = E\mathscr{C} \iint y^2 \mathrm{d}y \mathrm{d}z = EI\mathscr{C} = BW \partial_s \theta$$

With I the second moment of area. This last equation is the constitutive equation.



Figure B.1: Schematic of an infinitesimal portion of the beam. The forces and moments acting on the beam are drawn. *Inset* Schematic of the strains in the beam under bending. The part above the neutral axis is in extension and the part below is in compression.

B.2 The heavy Elastica

Let us consider a vertical sheet of length L^* , thickness t, width W and density ρ_s immersed in water ρ_w . The sheet is clamped at the top and a vertical force per unit

width F is pushing at the bottom along the full width. We use the Euler-Bernoulli beam theory described above. The problem is invariant along the width of the sheet so we can eliminate W and consider the problem in two dimensions (Fig 1.16 a)) In our case the only external force is gravity (with buoyancy taken into account), thus $p_y = 0$ and $p_x = (\rho_s - \rho_w)gt$ (the vertical direction is x, such that $\vec{g} = g\vec{e_x}$). We integrate between 0 and s the first two equilibrium equations:

$$n_x(s) - n_x(0) = -(\rho_s - \rho_w)gts$$
$$n_y(s) - n_y(0) = 0$$

At s = 0 there is an upward vertical force F (per unit width) so that $n_y(0) = 0$ and $n_x(0) = F$. So finally:

$$n_x(s) = F - (\rho_s - \rho_w)gts$$
$$n_y(s) = 0$$

We insert these results into the internal moment equation and use the constitutive relation to obtain the equation describing the shape of the beam:

$$\partial_s m = B \partial_s^2 \theta = -(F - (\rho_s - \rho_w)gts)\sin\theta$$

The boundary conditions are free-clamped: $\partial_s \theta(s=0) = 0$, $\theta(s=L^*) = 0$. The system is made dimensionless by dividing s by L^* :

$$\partial_s^2 \theta + \left[\tilde{F} - \left(\frac{L^*}{\ell_g} \right)^3 s \right] \sin \theta = 0$$

$$\partial_s \theta(s=0) = 0, \quad \theta(s=1) = 0$$
(B.2.1)

 $\tilde{F} = \frac{FL^{*2}}{B}$ is the dimensionless force and $\ell_g = \left(\frac{B}{(\rho_s - \rho_w)gt}\right)^{1/3}$ is the elasto-gravitational length representing the relative importance of bending to the self weight of the column.

To find the onset of buckling we consider short deformations and linearise equation (B.2.1) *i.e.* $\sin \theta \approx \theta$. This leads to:

$$\partial_s^2 \theta + \left[\tilde{F} - \left(\frac{L^*}{\ell_g} \right)^3 s \right] \theta = 0$$

We introduce the new variable $r = \frac{L^*}{\ell_g} \left(s - \tilde{F} \left(\frac{\ell_g}{L^*} \right)^3 \right)$, so that the equation becomes:

$$\partial_r^2 \theta - r\theta = 0 \tag{B.2.2}$$

The general solution of equation (B.2.2) and the transformed boundary conditions may be expressed in terms of Airy functions as:

$$\theta(r) = C_1 \operatorname{Ai}(r) + C_2 \operatorname{Bi}(r)$$
$$\partial_r \theta \left(r = -\widetilde{F} \left(\frac{\ell_g}{L^*} \right)^{2/3} \right) = 0, \quad \theta \left(r = \frac{L^*}{\ell_g} \left(1 - \widetilde{F} \left(\frac{\ell_g}{L^*} \right)^3 \right) \right) = 0$$
With Ai and Bi the Airy functions of the first and second kind. For non trivial solutions to exist ($\theta(s) \neq 0$, *i.e.* buckling of the column) we need:

$$\begin{vmatrix} \operatorname{Ai} \left[\frac{L^*}{\ell_g} \left(1 - \widetilde{F} \left(\frac{\ell_g}{L^*} \right)^3 \right) \right] & \operatorname{Bi} \left[\frac{L^*}{\ell_g} \left(1 - \widetilde{F} \left(\frac{\ell_g}{L^*} \right)^3 \right) \right] \\ \operatorname{Ai'} \left[-\widetilde{F} \left(\frac{\ell_g}{L^*} \right)^2 \right] & \operatorname{Bi'} \left[-\widetilde{F} \left(\frac{\ell_g}{L^*} \right)^2 \right] \end{vmatrix} = 0$$

We solve this determinant problem with Mathematica, the first root gives us the critical non dimensional force \tilde{F}_c to buckle (in mode 1) as a function of the dimensionless beam length $(\frac{L^*}{\ell_g})^3$.

Appendix C Fourier transform profilometry

Contents

C.1 Principle
C.2 Limitations and adjustments for granular rafts
C.2.1 Limitations $\dots \dots \dots$
C.2.2 Adjustments for granular rafts $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 140$
C.3 Practical application142

C.1 Principle

Fourier transform profilometry (FTP) is a pattern projection method to reconstruct the three dimensional shape of an object from a two dimensional picture. Like all pattern projection methods the principle is to relate the deformations of the pattern due to the object to the local height of the object. Since its introduction by Takeda and Mutoh in 1983 [162], Fourier transform profilometry has been improved (old review [163]) and adapted to many applications [164–166]. The principle is the following: A video projector projects a fringe pattern through a lens on a reference plane parametrized by the Cartesian coordinates (x, y). A camera located at a distance D from the lens and a distance ℓ_0 from the reference plane records the pattern: signal $I_0(x, y)$. We then place the object on the reference plane and we record the deformed pattern: signal I(x, y) (Fig C.1 a)). In the original study, Takeda and Mutoh use a Ronchi pattern *i.e.* a succession of bright and dark stripes in one direction. In our case the projected pattern is a grey level sinusoid of spacial frequency $f_0: g(x, y) = 0.5 (1 + \sin(2\pi f_0 x))$ (see C.2.2.1). In these conditions the general form of the recorded intensity is:

$$I_0(x,y) = 0.5r_0(x,y)(1 + \sin(2\pi f_0 x + \phi_0(x,y))) + \mathcal{N}_0(x,y)$$

$$I(x,y) = 0.5r(x,y)(1 + \sin(2\pi f_0 x + \phi(x,y))) + \mathcal{N}(x,y)$$

 $\phi_0(x, y)$ (respectively $\phi(x, y)$) is the phase induced by the reference plane (respectively the object). The phase difference $\Delta\phi(x, y) = \phi(x, y) - \phi_0(x, y)$ contains all the informations required to compute the object's height h(x, y). Two sources of noise modify the projected signal: a multiplicative noise $r_0(x, y)$ (respectively r(x, y)) and an additive



Figure C.1: a) Schematic of the configuration we use: "crossed optical axes geometry". ℓ_0 is the distance between the camera objective and the reference plane, D is the distance between the camera objective and the achromatic lens and h(x, y) is the object height. b) Typical image recorded by the camera, here a computer mouse lit by sinusoidal fringes.

noise $\mathcal{N}_0(x, y)$ (respectively $\mathcal{N}(x, y)$). $r_0(x, y)$ and r(x, y) are intensity modulations that depend on the local surface reflectivity while $\mathcal{N}_0(x, y)$ and $\mathcal{N}(x, y)$ come from illumination inhomogeneities or background variations. Once these two signals have been recorded the goal is to extract the phase difference $\Delta \phi(x, y)$ from the unwanted amplitude variations. Many methods have been developed in order to do so: 1d Fourier transform [162], 2d Fourier transform [167], wavelet transform [168], empirical mode decomposition [169] ... We present here the original method from Takeda and Mutoh, 1d Fourier transform separation. We compute the Fourier transform of I(x, y) along the direction perpendicular to the fringes (x): $\hat{I}(f_x, y)$.

$$\widehat{I}(f_x, y) = \int_{-\infty}^{\infty} I(x, y) \exp(-2i\pi f_x x) dx$$
$$= \sum_{n=-1}^{1} \widehat{Q_n}(f_x - nf_0, y)$$

Where the \widehat{Q}_n are the different components of the spectra (see Fig C.3 b)). We filter the spectra around the fundamental frequency $\widehat{Q}_1(f_x - f_0, y)$ then we take its inverse Fourier transform (Fig C.3 b), c)) :

$$Q_1(x,y) = \int_{-\infty}^{\infty} \widehat{Q}_1(f_x,y) \exp(2i\pi f_x x) df_x$$
$$= \frac{r(x,y)}{4i} \exp(i\phi(x,y)) \exp(2i\pi f_0 x)$$

C.2. LIMITATIONS AND ADJUSTMENTS FOR GRANULAR RAFTS

We do the same with $I_0(x, y)$ to get $Q_{01}(x, y)$ then we extract the phase:

$$\ln(Q_1(x,y)Q_{01}^*(x,y)) = \ln\left(\frac{r(x,y)r_0(x,y)}{16}\right) + i\Delta\phi$$
(C.1.1)

Where $Q_{01}(x, y)$ is the complex conjugate of $Q_{01}(x, y)$. The imaginary part of equation (C.1.1) gives us the phase difference.

We now have to convert the phase difference to the physical height of our object. There are several "phase to height" derivations that account for all the possible misalignments [170]. In the simple case where the camera and projector optical axis are parallel and the light is collimated, the relationship is given by elementary geometry [162]:

$$h(x,y) = \frac{\ell_0 \Delta \phi(x,y)}{\Delta \phi(x,y) - 2\pi f_0 D}$$
(C.1.2)

C.2 Limitations and adjustments for granular rafts

C.2.1 Limitations

C.2.1.1 Separation of the different spectra Q_n , high slope limitations

When r(x, y) varies much slower than f_0 Takeda and Mutoh define the local frequency of the n^{th} spectrum \widehat{Q}_n [162]:

$$f_n = nf_0 + \frac{n}{2\pi}\partial_x\phi(x,y)$$

The spectra are well separated if the maximum of f_1 is smaller than the minimum of all f_n for n > 1 and if f_1 does not intercept the zero spectrum \widehat{Q}_0 . The width of the f_n is a function of $\partial_x \phi(x, y)$ which is itself a function of $\partial_x h(x, y)$. If $\ell_0 >> h(x, y)$ and $2\pi f_0 D >> \phi(x, y) >> \phi_0(x, y)$ then it follows from equation (C.1.2):

$$\partial_x \phi(x,y) \approx \frac{2\pi f_0 D}{\ell_0} \partial_x h(x,y)$$

Hence, an object of very rapid height variation $\partial_x h(x, y)$ produces very large spectra. They intersect and filtering \widehat{Q}_1 becomes impossible. However, maximising $\frac{\ell_0}{Df_0}$ for a given height profile h(x, y) extends the measurement range by minimising $\partial_x \phi(x, y)$ and thus the width of the f_n .

C.2.1.2 Phase unwrapping

The procedure to separate the phase described above gives a wrapped phase, *i.e.* modulo 2π : $-\pi < \Delta \phi(x, y) < \pi$. The true physical phase can go from $-\infty$ to ∞ . In order to get the object's height h(x, y) we must remove these discontinuities. To do so we scan the wrapped phase: when the difference between two adjacent values is higher than π we add $\pm \pi$ to the remaining wrapped phase. This procedure, called phase unwrapping, is trivial for a one dimensional ideal signal. However, for a two dimensional noisy signal, the phase cannot always be unambiguously unwrapped. There exist several algorithms (often complex) whose purpose are to unwrap the phase in the best possible way (see for instance [171–173]). Some of them have been tested on Fourier transform profilometry in ref [174].

C.2.1.3 Uncertainties in the final profile

If $2\pi f_0 D >> \Delta \phi$ the height relative uncertainty is:

$$\frac{\delta h}{h} = \frac{\delta(\Delta\phi)}{\Delta\phi} + \frac{\delta\ell_0}{\ell_0} + \frac{\delta D}{D} + \frac{\delta f_0}{f_0}$$

The measurement uncertainty is thus linked to the reconstructed phase's uncertainty $\delta(\Delta\phi)$, but also on the geometrical parameters' uncertainty $(\delta\ell_0, \delta D, \delta f_0)$. In addition to the limitations discussed above, the phase uncertainty mainly comes from signal processing (filtering, FFT) and electronic noise. It produces a contribution of almost zero mean but with a non zero variance. On the other hand the contribution from the geometrical parameters produces a systematic error that can be minimised with a calibration scheme.

C.2.2 Adjustments for granular rafts

We had two objectives in mind when we built the FTP set-up. We wanted three dimensional profiles of the deformed raft but we also wanted the wrinkles' amplitude whose measurement is difficult with side pictures. Modern FTP experiments reach high levels of accuracy (below 100 μm [166]) which is enough for our experiments. However, to obtain such performances one must filter \widehat{Q}_1 accurately from the rest of the spectra to get a phase with very low noise. When the object has a uniform reflectivity and slow height variations the spectra are thin and well separated, it is easy to filter \widehat{Q}_1 . But with granular rafts we have a random pattern of white patches and dark holes. The reflectivity is not uniform and varies more rapidly than f_0 , adding a huge uncertainty to the phase and thus on the reconstructed height.

C.2.2.1 Sinusoidal pattern

Using a sinusoidal pattern instead of a Ronchi pattern lifts one of the limitations from the original method. With a Ronchi pattern the signal's Fourier transform has many spectra \widehat{Q}_n centred on the harmonics of f_0 . But for a sinusoidal pattern the only remaining terms are n = -1, 0, 1. It lifts the limitation coming from \widehat{Q}_1 overlapping with \widehat{Q}_n for |n| > 1. With a modern video projector it is very easy to make a perfectly sinusoidal pattern but the idea is older [175, 176]. With this modification the last problem is the overlapping of \widehat{Q}_1 with \widehat{Q}_0 and \widehat{Q}_{-1} .

C.2.2.2 π phase shift

The π phase shift is one of the techniques to remove the zero spectrum \widehat{Q}_0 . The idea is to project a fringe pattern, then the same pattern with a π phase shift. We record I(x, y) but also $I^{\pi}(x, y)$:

$$I^{\pi}(x,y) = 0.5r(x,y)(1 + \sin(2\pi f_0 x + \pi + \phi(x,y))) + \mathcal{N}(x,y)$$

= 0.5r(x,y)(1 - sin(2\pi f_0 x + \phi(x,y))) + \mathcal{N}(x,y)

We then subtract $I^{\pi}(x, y)$ to I(x, y) and obtain a signal without the DC component :

$$I(x,y) - I^{\pi}(x,y) = r(x,y)\sin(2\pi f_0 x + \phi(x,y))$$

This method is simple and effective but can only be used with static objects. For dynamic measurements more complex methods are required to remove the zero spectrum [169, 177]. In our case the compression is quasi static, a 10 s pause between each compression step allows us to record the two images. During this break the raft is not perfectly motionless, slow grain rearrangements and small raft translations can occur. Besides the video projector's illumination is slightly different between the two images. As a result $r(x, y) \neq r^{\pi}(x, y)$ and $\mathcal{N}(x, y) \neq \mathcal{N}^{\pi}(x, y)$, the shifted signal subtraction greatly reduces the DC component but does not cancel it completely.

C.2.2.3 Higher fundamental frequency

There are two benefits in using a fundamental frequency f_0 as high as possible. We approach the limit where r(x, y) variations are much slower than f_0 and the centre of the spectra \widehat{Q}_n are further apart. The drawback is that for a given object and set-up the phase slope $\partial_x \Delta \phi(x, y)$ (thus the width of the peaks) will be higher. We make various modifications to go to higher fundamental frequencies whilst limiting the drawbacks.

- To make our fringe pattern we generate a greyscale sinusoidal image (at the video projector's resolution) with an adjustable wavelength in number of pixels using Matlab. Minimising the wavelength of the source image increases the fundamental frequency on the object f_0 , however if the wavelength is too small we may subsample the sinus (the sampling period being one pixel). The Shannon-Nyquist criterion tells us that we must use a wavelength higher than 2 pixels. In practice we obtain the best results with a wavelength of 8 pixels.
- Our video projector can adjust the magnification. By reducing the magnification we reduce the physical pixel size and thus increase the observed frequency. However, the optical system of the projector accentuates optical aberrations (distortion, blur) and reduces the contrast when we reduce the magnification. An average magnification gives the best results.
- We added a converging lens to the set-up to increase the frequency (by a factor of 2). It greatly reduces the illuminated region but allows a better control of the geometrical parameter (increases the ratio ℓ_0/D , easier alignment). We use an achromatic lens to minimise aberrations (monochromatic light reduces the video projector's contrast).

C.2.2.4 Low pass filter: defocusing

To get a high signal to noise ratio we must separate \widehat{Q}_1 from the zero spectrum. The π phase shift technique is efficient to remove the zero spectrum but it is not perfect in our set-up due to the movements of the raft. Removing the high frequencies from the images makes the zero spectrum thinner and makes the π phase shift technique more efficient. To do so, we intentionally slightly defocus the camera. It creates a low pass filter that has a low impact on the fringe pattern.

C.3 Practical application

We use a full HD (1920×1080) LCD projector EPSON EH-TW3200 and an achromatic lens Thorlabs AC508-300-A-ML to project the fringe pattern. We take the pictures with two Nikon D800E cameras mounted with different macro objectives. The set-up is regularly dismantled and reassembled, in consequence the geometrical values ℓ_0 , D et f_0 are not fixed and the optical alignment is redone every time. An order of magnitude for those parameters is $\ell_0 \sim 0.3 m$, $D \sim 0.1 m$ et $f_0 \sim 1.5 mm^{-1}$. We validate the set-up with a custom built reference object. We engraved with a laser cutter a periodic pattern on a white PMMA plate and measured its dimensions with a calliper (Fig C.2 a)). The experimental procedure for rafts is:

- We fill the tank with purified water until we reach the desired level. We place on the water surface a thin white plastic sheet that will serve as a reference plane. We project the fringes on it and adjust the optical set-up. We then record the pattern and its π shifted version.
- We remove the sheet, add the mineral oil and sprinkle the particles to make the granular raft. In the meantime we set up the step motor: we adjust the speed and acceleration to achieve the desired displacement in 2 s, then the motor stops for 8 s and start again. The projector displays the fringe pattern for 5 s, then the π shifted version for 5 s (sideshow made with XnView). The bottom camera takes a picture every 5 s while the side camera takes a picture every 10 s.
- We crop the images and convert them to 8-bit greyscale with ImageJ. Then we process them with Matlab to extract the height profile. For each line, the algorithm computes the 1d fast Fourier transforms of $I - I^{\pi}$ and $I_0 - I_0^{\pi}$ (Fig C.3) a), b), c)). A peak detection with a threshold locates the centre of the spectrum Q_1 and the fundamental frequency f_0 . To estimate the width of the fundamental spectrum we fit the five data points before f_0 with a line. When this line cuts the horizontal axis it gives us an estimate of the half width of the spectrum HW. We then filter Q_1 by multiplying the signal with a Gaussian function centred in f_0 of height 1 (Fig C.3 c)). The variance σ^2 must be chosen accordingly. Too small we filter out part of the signal and too high we add noise (Fig C.2 b)). To reconstruct properly all the details of our reference object we need a standard deviation higher or equal to the half width HW estimated above, we therefore use this value. Then, we do the inverse fast Fourier transforms to obtain Q_1 and Q_{01} and take the imaginary part of $\ln(Q_1 Q_{01}^*)$ to get the wrapped phase $\Delta \phi$. We unwrap the phase line by line with a simple 1d algorithm. We check that the phase unwrapping result is correct before we do any measurement. Finally, we use equation (C.1.2) to reconstruct the height with the measured values of ℓ_0 , D and f_0 (Fig C.3 d)).

- Once we have the height profiles, we measure the amplitudes of wrinkles and folds automatically with a custom algorithm. We take a 2d slice of the profile perpendicular to the fold in the desired area. We perform a moving average, then we interpolate a subsample of the result with splines to smooth the signal. We do a peak detection on the smoothed signal to find the local extrema. If the difference between a maximum and its neighbouring minima is lower than the noise level we delete them. We then look for the extrema in the real signal around their location in the smoothed signal. Their height gives us the amplitude (Fig C.3 e)).
- We compare the amplitude we obtain with this algorithm to the one directly measured from the side. Usually there is a small discrepancy because the measurement of the geometrical parameters is not very accurate (especially ℓ_0). We calibrate ℓ_0 and D so that the amplitudes match.



Figure C.2: a) Picture of the reference object in the final set-up (with defocusing). The engraved periodic pattern consists in half circles and triangles. The pattern starts every 6 mm in the y direction and the periodicity in the x direction is 4 mm. The depth is 0.55 ± 0.05 mm (measured with a calliper). As a scale bar the total width of the engraved pattern is 2.4 cm. b) Reconstructed profiles of the reference object (central portion of a)) for different Gaussian filters standard deviation $\sigma = HW/3$, HW, 2HW. Top row: full 3d profile, the colour bar indicate the height in mm. Bottom row: 2d slice at $0.75x_{max}$. Wider filters give more details in the (x, y) plane, but also increase the noise in the height profile.



Figure C.3: a) $I - I^{\pi}$ for a compressed granular raft. b) 1d Fourier transform of I along x for a given y. The three peeks are the spectra: $\widehat{Q_{-1}}, \widehat{Q_0}$ and $\widehat{Q_1}$. c) Normalised 1d Fourier transform of $I - I^{\pi}$ along x for a given y. The π phase shift almost removes the zero spectrum $\widehat{Q_0}$. In orange we plot the Gaussian filter used to recover the phase. d) Reconstructed height profile. e) Slice of the height profile in $x_{max}/2$: the raw signal is blue, the smoothed one is red. Black circles show the local maxima kept by the algorithm.

Appendix D Particle characterisation

Our particles come from different suppliers depending on their composition. Almost all of them are polydisperse and not perfectly spherical (their primary use is grinding/blasting or decoration). Here are the different materials we have: glass, coated glass, kaolin, 4 variety of zirconium oxide and lycopodium powder. Glass beads and two variety of zirconium oxide come from Glen Mills (regular zirconium oxide: 69% ZrO₂ 31% SiO₂ called "ZrO", very high density zirconium oxide: 95% ZrO₂ 5% Y₂O₃ called "VHD"). The two other variety of zirconium oxide particles come from St Gobain (Zirblast and Microblast: 60 to 70% ZrO₂ 28 to 33% SiO₂ <10% Al₂O₃). The kaolin beads come from Kingsbeads and the coated glass beads called "SiO" from Sigmund Lindner (sol-gel coating of thickness 1-3 microns). Finally, the lycopodium powder comes from Sigma Aldrich (courtesy of the PMMH laboratory). For all of them (except the lycopodium powder) the supplier gives a size range and a density. For every supplier we observe one batch (at least) under the optical microscope (Leica VZ85RC with DFC-295 camera) to check the size range and the shape. We also measure the oil-water contact angle with direct visualization.

D.1 Shape

Most of our particles are ellipsoids, we use their projected area A to compute their diameter: $d = 2\sqrt{\frac{A}{\pi}}$. To estimate the deviation from the spherical shape we use two quantities: the circularity $Circ = \frac{4\pi A}{P^2}$ (P is the projected perimeter) and the roundness $Roun = \frac{4A}{\pi L_{max}^2}$ (L_{max} is the major axis of the object's bounding rectangle). Both quantities are equal to one for perfect spheres and go toward zero as we deviate from the spherical shape. The circularity is more sensitive to the object's roughness compared to the roundness. All these quantities are automatically measured for a high number of particle (> 30) using ImageJ. The stack is binarized, then we use the plugin "Analyse particles". The outcome of such treatment is overlaid on the original image on Fig D.1 b). The data (mean and standard deviation) are in Table D.1. The size range given by the supplier is almost always correct and is used for all batch to determine the particle size. Almost all particles have a high roundness (overall spheroids) but some of them have a rather low circularity (rough surface).



Figure D.1: a) Microscope picture of Glen Mills zirconium oxide beads (reflected light). b) Microscope picture of St Gobain Microblast beads (back light). The result of the ImageJ algorithm are overlaid in red. c) Histogram of the diameter for a batch of St Gobain Microblast beads. The shaded grey area is the size range given by the supplier, the red line is the mean value of our data set.

D.2 Contact angle

When we make our rafts, we sprinkle the particles above both liquids. They first cross the air-oil interface and are completely wet by the oil. Then they sink to the oil-water interface and the lower part of the particle is wet by water until an equilibrium is reached. The contact angle we obtain is the advancing oil toward water contact angle and it is the one we measure. We measure the contact angle through direct visualisation from the side with a Nikon D800E camera mounted with a special Navitar objective (Zoom 12X with a 2X front lens, a 2X F-mount adapter and an extension tube: maximum resolution $\approx 0.25 \,\mu m.pix^{-1}$). For every tested batch we measure the contact angle of at least 3 particles. We average the values measured on the left and on the right (Fig D.2, the typical uncertainty on a single measurement is $\pm 5^{\circ}$). Table D.1 presents the results (mean and standard deviation). The contact angle we measure is the apparent one, the microscopic interface close to the particle cannot be resolved. For non tested batches we assume that the same material from the same supplier have the same contact angle. To have an idea of the contact angle hysteresis we push down (in water) particles with a spatula for a few seconds (particles stick to the spatula because some oil remain on its surface), then pull them back to the interface and measure again the contact angle. Significant reductions of the contact angle could be observed (as high as 40° for "ZrO" particles).



Figure D.2: Side picture of a ZrO particle from the batch $400-600\,\mu m$ at the oil-water interface. The left and right angle (~ 95°) are drawn in red

supplier	material	density	supplier size	measured size	circularity	roundness	oil-water contact angle	air-water contact angle
		$(g.cm^{-3})$	(μm)	(μm)			$(^{\circ})$	(°)
Glen Mills	ZrO	3.8	100-200	153 ± 29	$0.88{\pm}0.03$	$0.95{\pm}0.04$	112 ± 6	
Glen Mills	ZrO	3.8	200-300				144 ± 5	92 ± 2
Glen Mills	ZrO	3.8	300-400	353 ± 24			90 ± 6	
Glen Mills	ZrO	3.8	400-600				85 ± 10	72 ± 7
Glen Mills	ZrO	3.8	800-1000				107 ± 8	
Glen Mills	VHD	6.0	200				126 ± 3	
Glen Mills	VHD	6.0	400	417 ± 10	$0.89{\pm}0.01$	$0.98{\pm}0.01$	117 ± 2	81 ± 3
Glen Mills	glass	2.5	450-600	635 ± 88	$0.87 {\pm} 0.04$	$0.87{\pm}0.11$	95	71 ± 3
Glen Mills	glass	2.5	2000				$104{\pm}13$	
St Gobain	Microblast	3.8	63 - 125	103 ± 16	$0.76 {\pm} 0.11$	$0.79 {\pm} 0.19$		
St Gobain	Zirblast	3.85	425-600	531 ± 58	$0.77 {\pm} 0.11$	$0.88{\pm}0.14$	64	
St Gobain	Zirblast	3.85	600-850				$59{\pm}10$	
Kingsbeads	kaolin	2.6 - 2.7	600-800	831 ± 49	$0.86{\pm}0.03$	$0.95{\pm}0.05$		
Kingsbeads	kaolin	2.6 - 2.7	800-1200	987 ± 87	$0.84{\pm}0.06$	$0.93{\pm}0.07$		
Kingsbeads	kaolin	2.6 - 2.7	1200 - 1500	1313 ± 88	$0.69{\pm}0.12$	$0.93{\pm}0.09$		
Sigmund Lindner	coated glass	2.5	100-200				116 ± 5	
Sigmund Lindner	coated glass	2.5	150-250	210 ± 24	$0.87{\pm}0.06$	$0.94{\pm}0.10$	121 ± 5	83
Sigmund Lindner	coated glass	2.5	300-400				125 ± 3	77 ± 9
Sigmund Lindner	coated glass	2.5	500-750	674 ± 60	$0.89{\pm}0.02$	$0.96{\pm}0.05$	122 ± 3	$80{\pm}2$
Sigma Aldrich	lycopodium			$24.8 {\pm} 2.7$	$0.79{\pm}0.07$	$0.87{\pm}0.06$		

Table D.1: Measured particle properties. Cell are left blank if the measurement is not performed or the information is not supplied. If there is no uncertainty, the measurement has not been repeated.

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Sujet : Membranes plissées à la surface de l'eau: des films élastiques aux radeaux granulaires

Résumé

Cette thèse porte sur le flambement d'une interface chargée en particules: une monocouche de grains denses et athermaux à une interface liquide-fluide plane que l'on appelle radeau granulaire. Ces radeaux se rident et se plient lorsqu'ils sont compressés comme des films élastiques. Nous étudions cette instabilité de flambement expérimentalement et théoriquement dans ces deux systèmes dans le cadre de la mécanique des milieux continus.

Nous commençons par examiner les plis dans des films élastiques denses. Nous soulignons l'influence du poids du film dans la formation du pli. Puis nous explorons le régime des très grandes déformations, après que le film soit entré en contact avec lui-même. Suivant la densité du film, le pli se replie vers l'interface ou s'enfonce vers le fond de la cuve.

Ensuite nous étudions les rides et les plis dans les radeaux granulaires compressés uniaxialement. A mesure que la compression augmente, nous observons deux motifs de ride distincts, puis la déformation se localise en un unique pli. Nous prédisons la forme et la taille des plis avec un modèle élastique résolu numériquement. Nous insistons sur les limitations de ce modèle et montrons que le caractère granulaire de ces radeaux n'est pas toujours négligeable.

Enfin, nous déposons des gouttes d'eau à la surface des radeaux. Lorsque les particules sont hydrophobes et suffisamment grandes, elles capturent un film d'huile qui sépare la goutte du bain et empêche la coalescence. Puis nous modifions la taille de ces gouttes qui prennent des formes inhabituelles. Ces gouttes peuvent ensuite être encapsulées dans une fine couche de particules et d'huile conduisant à des gouttes d'eau dans l'eau.

Mots clés : flambement, rides, plis, particules aux interfaces, elastique, granulaire, goutte

Subject : Folds in floating membranes: from elastic sheets to granular rafts

Abstract

This thesis is concerned with the buckling of a model particle laden interface: a monolayer of dense, athermal particles at a planar liquid-fluid interface that we call a granular raft. Under compression granular rafts wrinkle and fold like elastic sheets. We investigate this buckling instability experimentally and theoretically for these two systems under the continuum mechanics framework.

We first look at folds in custom made dense floating elastic sheets. We highlight the influence of the sheet's own weight in the fold formation and shape. Then we explore the regime of very large deformations, after the sheet contacts itself. Depending on the sheet density, the fold in self-contact either bends back toward the interface or sinks down toward the bottom of the tank.

We then look at wrinkles and folds in granular rafts. Our experimental apparatus allows us to compress the rafts uniaxially and extract their morphology. As compression increases, we observe two distinct wrinkling patterns, then the deformations localise in a unique fold. We develop an elastic model that we solve numerically to predict the fold shape and size. We then highlight the limitations of the model and show that the granular nature of these rafts cannot always be neglected.

Finally, we deposit water droplets on top of granular rafts. If the particles are hydrophobic and large enough, the raft can inhibit coalescence indefinitely via particle bridging. When we vary the size of these floating drops, they take unusual shapes which depend on the raft properties. These drops can then be encapsulated in a thin composite oil-particle layer leading to water droplets in water.

Keywords : buckling, wrinkles, folds, particle laden interfaces, elastic, granular, drop