Collective Properties of Cohesive Frictionless Granular Aggregates

Collective Properties of Cohesive Frictionless Granular Aggregates

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Abstract

In this thesis, I present my experimental work on the collective properties of frictionless, cohesive particles. Our main question is how lack of friction as well as a well-distributed, well-controlled cohesive interaction among the particles give rise to collective properties that might or might not differ from conventional granular materials with interparticle friction, and cohesion due to capillary bridges. This is a "sandwich" thesis, in which each project is presented as a standalone manuscript in a separate chapter.

In Project 1, inspired by the pendant drop experiment, we extrude dense particle aggregates from an orifice. The aggregate breaks into clusters due to interparticle cohesion, much like a dripping faucet. We analyze the cluster volume while varying the cohesion, orifice size and particle size. Our results show that the volume is proportional to the orifice area multiplied by a characteristic length that balances cohesion and gravity, known as the *granular capillary length* [1]. This finding indicates that the aggregate behaves more like a soft solid than a liquid, as the volume of a classic pendant drop is proportional to the orifice perimeter rather than the orifice area.

In Project 2, we investigate how geometrical constraints influence the spreading of frictionless, cohesive particles. Conducting the spreading experiment in a cylinder, we unexpectedly observe the formation of a conical pile, as the angle of repose in conventional granular materials is attributed to interparticle friction. We vary the cohesive force, particle size, and cylinder size to examine how these factors affect the angle of repose. Our findings indicate that the angle of repose is proportional to the granular capillary length divided by the particle size, and remains independent of the cylinder size within the experimental range. These results underscore the significant role of cohesion and geometrical constraints in aggregate stability.

To those who keep on searching

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Table of Contents

Α	bstra	ict		iii
A	ckno	wledge	ements	vi
1	Intr	roduct	ion	1
	1.1	Introd	luction	1
	1.2	Spread	ding of granular materials	5
		1.2.1	Granular materials	6
		1.2.2	Spreading: The angle of repose	7
	1.3	Disper	rsions	11
		1.3.1	Suspensions	13
		1.3.2	Emulsions	14
		1.3.3	Foams	15
		1.3.4	Colloids	17
	1.4	Partic	culate materials as model systems	18
	1.5	Interp	particle forces	20
		1.5.1	Contact forces	20
		1.5.2	Solid friction	22

		1.5.3	Van der Waals forces	26
		1.5.4	Electrostatic double-layer repulsion	27
		1.5.5	Hydrophobic interaction	31
		1.5.6	Depletion interactions	32
		1.5.7	Steric repulsion	34
	1.6	Capill	arity	35
		1.6.1	Surface tension	36
		1.6.2	Laplace pressure	39
		1.6.3	Capillary bridges	43
		1.6.4	Wetting	45
		1.6.5	The capillary length	49
		1.6.6	Drops on a surface	52
		1.6.7	Measuring surface tension: the pendant drop method $\ . \ . \ .$	54
	1.7	Simila	rities of particulate materials and liquids	57
		1.7.1	Liquid-like instabilities	57
2	Exp	erime	ntal details	60
	2.1	Exper	imental chamber	61
		2.1.1	Micropipettes	63
		2.1.2	Preparing funnels	64
		2.1.3	Other custom parts	66
	2.2	Aggre	gate of droplets	67
		2.2.1	Preparing solutions	68
		2.2.2	Producing droplets	69
	2.3	Imagin	ng and data analysis	71

3	Paper 1: The pendant drop experiment for aggregates of cohesive	
	granular particles	73
	3.1 Paper introduction	73
4	Paper 2: Angle of repose in aggregates of confined frictionless cohe-	
	sive particles	81
	4.1 Paper introduction	81
5	Conclusion	90

List of Figures

1.1	"Dry foam" vs. "wet foam" shown with two styles of latte	4
1.2	Experiments for determining the angle of repose	7
1.3	Friction between sand grains causes a sand pile to grow into a cone .	8
1.4	Microscopic origins of friction and the stick-slip phenomenon	24
1.5	The origins of double-layer repulsion	28
1.6	The depletion interaction	33
1.7	Steric repulsion due to surface-grafted polymer chains	34
1.8	The origins of surface tension	36
1.9	Surface tension as a force	39
1.10	The Laplace pressure for a general surface	40
1.11	A capillary bridge	44
1.12	Types of wetting	46
1.13	The law of Young-Dupré	47
1.14	The meniscus of a liquid near a wall	50
1.15	Edge of a liquid puddle on a solid substrate $\ldots \ldots \ldots \ldots \ldots$	53
1.16	The pendant drop experiment	54
2.1	The experimental chamber	62
2.2	Making dome-shaped funnels out of glass pipettes	65

2.5 JD image of the pipette holder \ldots	2.3	3D image of th	e pipette holder					6
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Chapter 1

Introduction

1.1 Introduction

Aggregates of granular materials are part of our everyday lives. Whether it is a heaping spoonful of coffee grounds to brew and start the day, or a pile of dry breakfast cereal before pouring milk over it, these common examples highlight our frequent handling of granular materials. In nature, some examples of granular materials are sand dunes, river beds and soil in its many forms.

Granular materials are immensely important in industrial settings, being the second-most manipulated material after water [2]. As amorphous substances, granular materials can exhibit the properties of solids, liquids, or gases under different circumstances [3, 4]. However, there is currently no unified theory that fully captures the transition points between these phases or the unique characteristics of granular materials, such as intermittent flow [5], jamming [6–8], and avalanches [5, 9]. Given the importance of granular materials in various scientific and industrial fields—such as geology, soil mechanics, civil engineering, and industries dealing with powders

like pharmaceuticals and food—a unified theoretical framework could significantly advance our understanding of granular materials and improve material handling in applied domains.

Early research on granular materials is mainly focused on dry frictional granular materials, ignoring cohesion, with sand being the classic example. However, the presence of cohesive forces from various sources in real systems is more the norm rather than the exception. But shortly before the turn of the millennium, more studies considered the role of cohesion in granular materials [10-14]. In the majority of these studies, liquid is used to induce cohesion among the particles via capillary bridges (see section 1.6.3). However, there are a number of drawbacks in this approach, when the aim is to study solely the effect of cohesion. For example, a non-homogeneous distribution of the capillary bridges between particles, leading to inconsistent cohesive forces. In addition, friction among the grains is still present and affects the collective properties of the aggregate. Therefore, an idealized granular system [15] where friction is eliminated to study the sole effect of cohesion has been experimentally less explored. Given that the macroscopic properties of materials are determined by factors like grain packing, interparticle forces and how energy from various sources (e.g. thermal, kinetic, etc.) compare [4, 16], the granular systems should be explored by varying all the aforementioned factors separately. In the current thesis, we study an idealized system of highly monodisperse, frictionless, cohesive particles; a rather unconventional configuration for classic granular materials.

Another category of material which is ubiquitous, though not quite well-understood is dispersions. Dispersions are a mixture of at least one species dispersed into a continuous material [17], and belong to the category of amorphous materials, similar

to granular materials. Everyday examples of dispersions are hot cocoa, mayonnaise and frothed milk. Dispersions are great examples for showing how the assembly of material components plays a significant role in determining the macroscopic physical behaviour, in addition to the material chemistry. Take milk and frothed milk for example: as one steams milk, small air bubbles are formed and are stabilized by the milk proteins. Even though the chemistry of the milk remains unchanged, we observe that the viscosity of the resultant foam-a macroscopic physical property-increases. Moreover, the viscosity could be controlled by changing the bubble size and the overall wetness of the foam |18|: if the overall liquid content is low and the bubbles are relatively large, like the foam on top of a classic Italian latte, we have "macrofoam" or "dry foam" that retains its shape and resembles solid-like behaviour, as long as the bubbles are stable (Fig. 1.1 (a)). However, if the resulting foam has a high liquid content and the bubbles are small, this foam is called "microfoam" or "wet foam", which can be poured like a viscous liquid in a cup of espresso to make fascinating latte art patterns (Fig. 1.1 (b)). It is both interesting and practical that simply adjusting the particle size or packing fraction in dispersions allows for the creation of materials with a wide range of collective properties for various applications.

Multiple studies on granular materials and different dispersion, such as dense suspensions, foams or emulsions have shown us that these two categories of materials, previously deemed to be different share many similarities [7, 8, 19–21]. In this thesis, I use a densely packed emulsion consisting of oil droplets in an aqueous solution as a model system to study the collective properties of cohesive frictionless granular aggregates, by means of two experiments: 1) the granular pendant drop, presented in paper 1, and 2) the spreading of droplet aggregates in a confined geometry, presented



Figure 1.1: Liquid content and bubble size determine collective properties of foams. (a) A classic Italian latte macchiato with "dry foam" on top. Dry foams have bigger bubbles and a low liquid content, which makes them more solid-like, as seen in the way the foam holds its dome shape and does not readily flow. Big bubbles are visible from the side view and along the top interface. (b) Modern latte with "wet foam". Wet foams have relatively small bubbles and high liquid content. Therefore, wet foams have more liquid-like properties and can be poured over espresso and form various patterns, known as latte art. Note how the surface of the foam in cup (b) is flat. Cocoa powder is used for enhancing contrast. Both cups prepared and photographed by the author.

in paper 2.

This thesis is a "sandwich" thesis and is structured as follows: Chapter 1 provides the necessary background for understanding the research. Chapter 2 discusses the experimental methods used for each project, along with additional details not included in the manuscripts. Chapters 3 and 4 introduce each research project, detail author contributions, and present the manuscripts. Chapter 5 discusses the main results and suggests future research based on similar systems.

In the introduction chapter, I will present all the physical concepts, as well as the mathematical models needed to fully understand the research I conducted during my Ph.D. Section 1.2 will discuss the spreading of dense granular materials. This section is particularly important for understanding the background of the theory suggested for paper 2. Section 1.3, discussing dispersions, provides context for the specific system of droplets that I work with. Application of particulate materials–both granular materials and dispersions–as a model system in various settings is discussed in section 1.4. In section 1.5, I point out the different interparticle forces and their origins for both granular systems and dispersions. Section 1.6 is dedicated to capillarity and includes a discussion of the pendant drop method, the primary experiment in paper 1. Section 1.7 focuses on similarities between liquids and particulate materials. In addition, I will discuss some parallel concepts for granular matter and fluids, like instabilities in this section.

1.2 Spreading of granular materials

As mentioned earlier, granular materials are assemblies of particles that can resemble properties of solids, liquids or gas [3, 4]. This thesis focuses on the condensed phases, where granular materials mimic the behaviors of solids and liquids, on the edge of mechanical stability. In this section, I define the essential characteristics of granular materials and discuss the spreading of granular material against a barrier. I then explain how the angle of repose—a bulk property of a granular pile—relates to interparticle friction, a microscopic property.

1.2.1 Granular materials

Granular materials are assemblies of rigid particles of size 100 μ m or larger [4]. Given the relatively large particle size, granular materials are not subject to Brownian motion and are therefore athermal. The main interactions present in granular materials are frictional and contact forces. Given the aforementioned criteria, many different systems can be classified as granular materials, from sand in the desert to soil and rocks, from cereal grains to assemblies of other particulate products, like m&m's or drug tablets. Even large-scale structures like the Saturn's rings and the asteroid belt in our solar system fall into this category of material. Granular materials come in vastly different shapes and surface roughnesses, yet they all exhibit macroscopic behaviors similar to those of solids, liquids, or gases. Granular materials as an amorphous system can be similar to liquids in the sense that one can pour them from a container, but as they spread against a surface, granular materials do not spread out into a liquid-like puddle, but the particles form conical structures with a characteristic angle, called the angle of repose. However, this pile can flow if subjected to a shear force; otherwise, it retains its shape like a solid.



Figure 1.2: (a) The tilting box method. The box is partially filled with the test material and is tilted slowly (clockwise here). As soon as the material starts to flow due to gravity, g, θ is recorded as the angle of repose. (b) The rotating drum test. A drum is partially filled with a test material and rotated slowly (clockwise here). θ shows the angle of repose, where the material starts a large scale flow *i.e.* an avalanche due to gravity, g.

1.2.2 Spreading: The angle of repose

The angle of repose is the angle formed by a granular pile with the horizontal plane and provides a simple way to measure material flowability [22]. The more flowable the material, the shallower the resulting cone will be [23]. A simple configuration for measuring the angle of repose is to pour the material against a surface and measure the angle of repose as the pile forms. Other methods to determine the angle of repose of a given material are the tilting box method or the rotating drum method [24]. In the tilting box method, a box with clear walls is filled halfway with the test granular materials and then is tilted slowly (Fig. 1.2 (a)). The angle of repose is defined as the minimum angle at which the material starts to flow. In the rotating drum test, a disc or a cylinder is partially filled with test material and is rotated slowly about its central axis (Fig. 1.2 (b)). The angle at which the material starts to flow is recorded as the angle of repose.

The experiment in paper 2 though, is more similar to the first case, where the



Figure 1.3: Picture on the right shows a sand pile with an angle of repose of θ_R . Picture on the left models a sand grain as a simple block of mass m on a ramp at an angle θ . g shows the direction of gravity and f_s indicates the static friction force. N is the normal force.

particles accumulate slowly against a barrier and form a conical pile. In those experiments, we consider the angle of repose as the temporal average of the angle at which the pile is stable.

The factors that determine the angle of repose are the particle shape, surface roughness, interparticle friction and cohesion [24]. For example, the angle of repose of dry sand is 34°. If some water is added, such that sand particles become cohesive through capillary bridges (see section 1.6.3), the angle of repose increases to 45° [24]. In the following, we show how the characteristic angle of repose, as a macroscopic property emerges from the interparticle static friction coefficient, which is a microscopic property.

Frictional particles

Let us consider a grain of sand as a block of mass m on a ramp with angle θ , shown in Fig. 1.3. The block and the ramp have a static friction coefficient of μ_s . The forces acting on the mass are the gravitational force mg, the static friction force along the ramp f_s and the normal force N. Our main axes are along the ramp x and normal to the ramp y. At mechanical equilibrium $(\Sigma \vec{F} = \vec{0})$, we decompose the gravitational force along x and y, and write the two force balance equations:

$$f_s = mg\sin\theta \quad \text{and} \tag{1.2.1}$$

$$N = mg\cos\theta , \qquad (1.2.2)$$

along x and y respectively. We can divide the force balance equation along x (1.2.1) by the equation along y (1.2.2) and get a single condition for equilibrium:

$$\frac{f_s}{N} = \tan\theta \ . \tag{1.2.3}$$

The angle of repose θ_R is the maximum angle of stability, after which the block starts sliding. On the edge of stability, at $\theta = \theta_R$, the maximum friction force is the maximum static friction $f_s^{\text{max}} = \mu_s N$, according to the Coulomb law of friction (see section 1.5.2). In order to find the maximum angle of stability or the angle of repose, we substitute θ_R for θ and f_s^{max} for f_s in equation 1.2.3, and simplify to get:

$$\mu_s = \tan \theta_R \,. \tag{1.2.4}$$

This simple model and calculation enables us to show how the angle of repose of a granular pile depends on the interparticle friction. However, many other factors affect the angle of repose. Experimental studies have shown that particle shape [25– 30], surface roughness [31], and cohesive forces due to liquid content [10, 12] can affect the angle of repose.

Frictionless particles

As mentioned, conventional granular materials have interparticle friction. However, aggregates of other particulate systems with no friction, such as emulsions or foams, help us understand an "idealized granular system" [15]. We showed above that conical piles form due to interparticle friction. However, friction with the base is also important. A conical pile from frictional materials cannot form unless there is friction with the base, as mechanical support is needed to sustain the weight of the pile. If the base in frictionless, the particles would just slip at the bottom and spread horizontally [32]. Therefore, in the absence of interparticle friction or lack of friction with the base, one might expect that a conical pile would not form.

However, formation of conical piles in particulate systems in the absence of friction has been observed. The angle of repose in such systems is small but measurable. Shearing simulations of packed frictionless particles show a non-zero effective friction, equivalent to an angle of repose of 3.5° for polydisperse [33] and 5.7° for monodisperse particles [34]. In experiments, different approaches are taken to eliminate friction and the results are comparable to the simulations. Ortiz *et al.* [35] have used slightly repulsive particles and have measured a flow-driven angle of repose of up to 7°. Perrin *et al.* [36] have also employed short-range repulsive forces to get a non-frictional system. In a rotating drum experiment, they have measured a mean avalanche angle of around 6.0° . Shorts and Feitosa [37] have observed that air bubbles, upon accumulation in a ring against a barrier, form a conical pile with an angle of repose of 3.7° . Shorts and Feitosa point out that the angle of repose emerges due to geometrical constraints that support the pile structure. Given that they use air bubbles as their particles, the system is metastable, meaning that the heap flattens as soon as the flow of air bubbles subsides. Therefore, it is not quite clear whether the formation of the heap is flow-driven, like the work by Ortiz *et al.* [35] or due to geometrical constraints. One of the issues we aim to address in paper 2 is to pinpoint whether the geometrical constraints from the container give rise to a non-zero angle of repose in the absence of both friction and cohesion. The advantage of the system we use is that unlike bubbles, our droplets are stable for much longer than the course of the experiment. The emergence of a non-zero angle of repose in our experiments in paper 2 are indeed due to geometrical constraints, as spreading experiments of the same system of cohesive frictionless droplets [1, 32] against an infinite barrier does not yield a conical pile and slip on the surface after the aggregate reaches a certain height, similar to a liquid puddle (see section 1.6.6). In addition, it can be shown theoretically that the contact forces cause the particles to form mechanical entanglements and form a pile with a non-zero angle of repose [4].

1.3 Dispersions

A dispersion is a heterogeneous system composed of at least two immiscible materials, where one or more materials are dispersed into another [17]. Therefore, we have a continuous phase and at least one dispersed phase in a dispersion. The state of matter of the dispersed and the continuous phases could be similar or different. Dispersions are common in daily life, industrial, as well as scientific setting with a variety of properties. Some examples are milk, blood, whipped cream, emulsified sauces like mayonnaise, ink, paint and drug delivery agents [38].

Dispersions are categorized in two ways: first, based on the size of the dispersed particles, and second, based on the states of the dispersed and the continuous phases.

Systems with particle sizes between 1 nm and 1 μ m are called colloidal dispersions or simply colloids, which we will briefly discuss in section 1.3.4. However, dispersions may also contain particles larger than 1 μ m. In this thesis, we focus on dispersions where the continuous phase is a liquid–namely suspensions, emulsions and foams–with dispersed phases being solid, liquid, and gas, respectively.

A characteristic property of dispersions is the large interfacial area between their multiple phases, which makes dispersions valuable for applications such as drug delivery [38]. However, this large surface area also makes dispersions highly susceptible to phase separation. To prevent spontaneous phase separation, it is crucial to stabilize dispersions using appropriate techniques.

Phase separation can have undesirable consequences, as the physical properties of a dispersion can differ significantly from those of its components. For instance, mayonnaise is an emulsion (see 1.3.2) composed of vinegar and oil, which are both liquids. However, when emulsified, mayonnaise is a paste-like substance and can be spread on a piece of bread with a knife. However, if a novice college student accidentally warms their mayonnaise-containing sandwich, the emulsion may phase separate into its components, leaving an unpleasant coagulated liquid mixture will remain, which does not share physical properties with the original emulsion. While this is a rather benign example of the stability problem of dispersions, the consequences can be far more severe in industrial or medical applications. For example, dispersions play a critical role in drug [39] and vaccine delivery [40], and therefore, it is crucial that the dispersions are well controlled, to prevent phase separation. Some ways in which dispersions become unstable are aggregation, due to domination of cohesive forces between the dispersed particles, sedimentation or creaming, in case the density of the dispersed phase is larger or smaller than the continuous phase.

The type of interparticle forces in a dispersion, their strength and range, will give a dispersion its properties. We will discuss some important interparticle forces that can exist among particles in a dispersion in section 1.5. If the interparticle forces are mainly attractive, then the dispersion should be stabilized by introducing repulsive forces, such as steric repulsion (see section 1.5.7), or double-layer repulsion (see section 1.5.4).

1.3.1 Suspensions

Suspensions consist of solid particles dispersed in a liquid [17]. Some examples are gravel in water, corn starch in water and milk of magnesium. As the particles in suspensions are relatively large (1 μ m or larger) and non-Brownian, they might sediment, based on the density difference with the liquid they are suspended in. Suspensions can be made of hard or soft solids. It is shown that adding particles to a liquid to make a suspension increases the viscosity of the suspension [41]. Therefore some collective properties of the resultant suspension can be compared to a molecular liquid of matching viscosity, given the volume fraction of the suspended particles is low. There are two considerations regarding this statement. First, high volume fraction of particles can result in non-Newtonian behaviours [41]. Another consideration is when the size of the suspension sample is comparable to its particle size. For example, if one considers suspension drops instead of a large amount of suspension, the similarity with a molecular liquid of matched viscosity breaks [42, 43] and local particle dynamics gain importance. Drops of suspensions are relevant in printing industries, for both ink-jet printing [44, 45] and bioprinting [46]. Another area where the properties of suspension drops are important is spray-painting.

1.3.2 Emulsions

Emulsions are made of droplets of liquid A dispersed in liquid B [17]. Some examples of emulsions are milk and salad dressing. Many cosmetic products are also emulsions. The emulsions are categorized based on the types of the dispersed and the continuous phases. For example, milk is made up of fat droplets dispersed in water. Therefore milk is an oil-in-water emulsion. On the other hand, moisturizers are usually a waterin-oil emulsion, where water is the dispersed phase and oil is the continuous phase.

Similar to other dispersions, emulsions have a high unfavorable interfacial area. When oil and water get mixed due to mechanical agitation, they spontaneously separate into two distinct phases, in order to minimize their interfaces, as there is a certain energy cost associated with interfaces, determined by the interfacial energy. More on interfacial energy is discussed in section 1.6. In order to stabilize emulsions against separation, a substance called emulsifier is needed. The molecules of emulsifiers, also called stabilizers, surface active agents or surfactants are added to the water-oil mixture to reduce the interfacial energy and make stable emulsion that do not readily separate.

Surfactants

The surfactant molecules are special in the sense that they have both a polar head that is soluble in water and a non-polar tail that is soluble in oil. Due to the hydrophobic interaction (see section 1.5.5), the surfactant molecules move to the interfaces and reduce the interfacial energy. Therefore, if surfactants are added to a water-oil mixture, the energy cost of interfaces reduces and droplets of the dispersed phase would not readily coalesce or merge together to minimize their surface area. Therefore, a stable emulsion can be produced. In milk, the main emulsifier are the milk proteins, casein and whey [47]. In mayonnaise, vinegar or lemon juice are mixed with oil and egg yolk or whole eggs, with several components in eggs contribute to the emulsifying properties [48].

In my experiments, I have an oil-in-water emulsion. The surfactant that keeps the oil droplets from coalescing is sodium dodecyl sulfate (SDS), which has a polar head group that is soluble in water and a non-polar hydrocarbon tail, soluble in oil. More details on preparing this systems is discussed in section 2.2.

1.3.3 Foams

Foam is a system of gas bubbles dispersed in a liquid [18]. Similar to emulsions, foams should be stabilized with a surfactant. Making stable foams or sometimes breaking them is important for different industries: having stable foams are important for pharmaceutical, food and cosmetic products, like drug delivery agents [39], whipped cream and shaving foam. However, oil industries or chemical processing industries need to destroy the unwanted foams in pipes, which can block flow.

Foams that are not well stabilized will first coarsen and then slowly collapse over time [18]. Foam degradation involves a few mechanisms. The first mechanism is the coarsening due to Ostwald ripening [49], where smaller bubbles with higher Laplace pressure (Laplace pressure discussed in 1.6.2) vanish in favor of bigger bubbles by emptying their gas content into the bigger bubbles. Bigger bubbles then become unstable by a gradual drainage of liquid content of their surrounding film. The liquid film becomes progressively thinner until a hole nucleates in it and the bubble bursts [18].

Controlling physical properties of foams are important. The physical properties of foams, such as their viscosity depend on the liquid content, as well as the bubble size [18]. This knowledge is utilized, for instance, in food industry for determining the texture of foams, which impacts important properties of the final product, such as mouthfeel [50]. To understand how liquid content and bubble size determine the viscosity of a foam, let us take meringue as an example, which is a mixture of air bubbles and egg whites. The proteins of egg white become denatured during the whipping process and act as stabilizers [51]. During the process of making a meringue, one can span a viscosity range from a runny liquid to the "stiff peaks" state, in which the resultant matter can keep its shape firmly. This material is neither a solid, nor a liquid. This type of matter is called a yield stress material: solid-like if left undisturbed, but deformable when subject to a shear force higher than a certain yield threshold. Stress yield materials are actually common in soft condensed matters, such as colloids foams and emulsions [52].

If the liquid content is low in foams, the gas bubbles get compressed together and make polyhedral, or cellular structures, and are divided by thin liquid films. These cellular foams can serve as a simple model to study the mechanical properties of biological tissues [53]. In an interesting study by Hayashi and Carthew [54], the researchers found a striking similarity between pattern formation of *in vivo* cornea cells and soap bubbles. The cornea cells are cohesive and move toward configurations, which maximize the bonds between cells. This spontaneous process is similar to systems driven by surface tension and therefore results is a similar packing pattern as soap bubbles.

1.3.4 Colloids

As mentioned, any dispersion with particles that have at least one dimension between 1 nanometer and 1 micrometer [17] is categorized as a colloidal dispersion (also called a colloid) [17]. Examples of colloids in everyday life can be a long list: milk, blood, ink, paint, in addition to many cosmetics and food products. In addition to the particle size, one of the main differences between a general dispersion and a colloidal dispersion is that colloidal particles are subject to Brownian motion, as the particles are small. In fact, one of the important factors in determining whether a colloid will remain stable, such that the particles remain suspended, is if the energy from the attractive forces, such as the van der Waals interactions (see section 1.5.3) is smaller than $k_{\rm B}T$, the thermal energy, with $k_{\rm B}$ being the Boltzmann factor and T, the absolute temperature of the colloid. Some ways to stabilize colloids are electrostatic stabilization (see 1.5.4) and steric stabilization (see 1.5.7).

Colloids are used in cutting edge technologies, such as vaccine delivery [40], targeted drug delivery [55] and targeted cancer treatment [56]. In addition to their practical applications, colloids are used as a model system to study fundamental phenomena in condensed matter, as colloidal particles can usually be seen using optical microscopy. In high concentrations, colloids can model condensed phases in molecular systems. Studies have shown that dense colloids with particles of the same size, *i.e.* monodisperse colloids, form crystalline systems [57]. However, when a dense colloid is composed of particles of different sizes, *i.e.* a polydisperse colloid, it will no longer form a crystalline structure, but a glass instead [58, 59]. Therefore, polydisperse colloids can be used to model a super-cooled liquid, or even a glass. Dense colloids are good model systems for glasses due to emergence of jamming and lack of long-range order. Such colloidal glasses have been studied to understand the glass transition [60, 61], which has been one of the unsolved fundamental questions and a subject of ongoing research [62, 63]. Colloids are not only important for practical applications but also play a crucial role in addressing fundamental scientific questions.

1.4 Particulate materials as model systems

An important aspect of particulate systems (both dispersions and granular materials) is that they can be used as models to study other systems that are not easy to directly investigate in laboratory. An example in modeling atoms and molecules. The advantage of dispersions and granular systems is that their particles are larger and can be seen individually, using optical microscopy [61]. Therefore, studying the structure and dynamics of the system can be conducted at the particle level. In addition to optical microscopy, which reveals local structure and rearrangements, one can use light scattering to study colloids and dispersions. This technique is useful, when the particle size is on the range of the visible light wavelength. Light scattering can be used to reveal the average structural and dynamical properties of the whole sample [60].

A classic example of using dispersions as models for atomic structures is the use of bubble rafts to study the crystal structure of metals by Bragg and Nye in 1947 [64]. They prepared different crystals with faults, such as dislocations, defects, and poly-crystals with grain boundaries, and studied the resultant mechanical properties. Another significant example is the use of colloidal glasses for studying the microscopic origins of glass transition [60].

In biology, soft tissues (embryonic or cancer cells) can be modeled by soft materials. These models are used to study the response of soft tissues to mechanical stresses, or to predict how soft tissues spread [65]. Of course, biological cells are alive and respond to stimuli, and are therefore more complex than inert soft materials. However, using passive soft systems are useful for studying the mechanical properties of living cells, as these models reduce the complexity of the problem, while still being mechanically relevant. Some of the soft matter systems used to model mechanical properties and spreading of biological tissues are viscoelastic paste [66], emulsions [67], foams [54] and colloidal gels [68].

Dispersions can also be used to model complex phenomena in geology. The Earth's surface can be thought of as a combination of granular materials and fluids. Therefore, immersed granular materials *i.e.* suspensions and colloids are a great model system to study geomorphology and interaction of different media. For example, Houssais and colleagues [69] investigated the local rheology of sediment transport, using colloidal suspensions. In another study [70], researchers studied how a jet of liquid erodes a bed of cohesive granular material. A recent example is a study by Saddier and colleagues [71], who expose particle rafts to gravitational waves to model the interaction of sea ice and waves. Even though the mechanical parameters of this model do not match specifically for the sea ice, this study is relevant for analyzing general features of ice sheet fragmentation.

1.5 Interparticle forces

In particulate materials, the interparticle forces can play an important role in determining the macroscopic material properties [3, 4], similar to how the inter-molecular or inter-atomic bonds determine the macroscopic properties of molecular or atomic materials [16]. In this section, I will briefly discuss the common interparticle forces that can be present in granular materials, as well as dispersions. Note that by definition, granular materials can have solid or elastic contact forces as well as friction between the particles. If an interstitial fluid is added, capillary bridges can form which introduce cohesion among the particles (more on capillary bridges in section 1.6.3). The other forces discussed in this section are the van der Waals forces, and the forces in solutions, namely electrostatic double-layer repulsion, hydrophobic interaction, depletion interaction and steric repulsion.

1.5.1 Contact forces

Solid contact forces: hard spheres

Solid sphere interaction is the simplest interaction between two particles, where the particles have a high Young's modulus and the compressive force is not strong enough to deform the particles. In this case, the interaction between the particles can be modeled as follows. Let us consider two spheres i and j with radii R_i and R_j . The hard sphere interaction is modeled by a potential $V(r_{ij})$ that is zero when the particles are apart, namely have a distance r_{ij} (measured from their centers) that is larger that the sum of their radii $(R_i + R_j)$. As soon as the particles make contact, the potential increases to infinity, which basically prevents the particles from overlapping:

,

$$V(r_{ij}) = \begin{cases} \infty, & \text{if } r_{ij} \le (R_i + R_j) \\ 0, & \text{otherwise.} \end{cases}$$

Even though the hard sphere model seems too idealistic to be practical, it has been shown that this model provides a good approximation for sterically stabilized (see section 1.7) colloidal particles [60]. In addition, the hard sphere model has proven to effectively represent the key characteristics of bulk metallic glasses [72, 73]. In my experiments, the forces are not strong enough to significantly deform the droplets, as there is a high Laplace pressure associated with the droplets, due to their small radius. Therefore, we can treat the droplets as hard spheres. More details are given in section 1.5.1 under "Droplets as hard spheres".

Elastic contact forces: soft spheres

When the particles are soft and the forces are strong enough to deform the particles, their interaction is modeled by a potential that allows the particles to virtually overlap [74]. There is an energy cost associated with the particles compressing together that is quantified by the overlap parameter [74] δ_{ij} :

$$\delta_{ij} = 1 - \frac{r_{ij}}{R_i + R_j} \,. \tag{1.5.1}$$

If the particles are apart from each other or just in contact $(r_{ij} \ge R_i + R_j)$, then $\delta_{ij} \le 0$. In this case, the potential will be zero. If the particles are compressed together and their center-to-center distance r_{ij} is smaller than the sum of the particle's radii, then $\delta_{ij} > 0$. In this case, there will be a positive potential associated with

this deformation, resulting in an energy cost, which depends on how the materials respond to deformation. Hence, the potential can be written as:

$$V(r_{ij}) = \begin{cases} \epsilon_{ij} \delta^{\alpha}_{ij}, & \text{if } \delta_{ij} > 0 , \\ 0, & \text{if } \delta_{ij} \le 0. \end{cases}$$

The exponent α and the constant ϵ_{ij} can be set, depending on the nature of the material response. For the Hookean response, $\alpha = 2$ and ϵ_{ij} is half the spring constant associated with the material K/2. Hertzian response is the case where the material gets stiffer as it is compressed, and $\alpha = 5/2$. Another type of response is called Hernian, and is the case when the material gets progressively weaker upon compression, and $\alpha = 3/2$ [74].

1.5.2 Solid friction

One of the most important forces that we experience in the macroscopic world is friction. Although the foundational experiments to determine the laws of friction were conducted centuries ago-written by Amontons in 1699 and further developed by Coulomb in 1785 [4]-friction remains an active area of research [75–77]. The Coulomb laws of friction, taught in basic mechanics courses are as follows [4]:

• There exists a threshold force f_s for the minimum tangential force required to set an object into motion F_T , and its magnitude is equal to $f_s = \mu_s N$, where N is the normal reaction force applied on the object from the surface and μ_s is the static friction coefficient. If the object does not move relative to the plane, there is no formula to find the value of the friction force. However, the inequality $F_T < f_s$ holds true and the magnitude of the friction force can be deduced from force balance equations.

- After the object is set into motion, the friction force will be equal to $f_k = \mu_k N$, where μ_k is the dynamical friction coefficient. The direction of the friction force will be opposite to the object's direction of motion.
- The friction coefficients μ_s and μ_k are constant and depend on the material properties of the two surfaces in contact. This inequality usually holds true:
 0.1 < μ_k < μ_s < 1.

The microscopic origins of friction laws were first suggested by Bowden and Tabor in their book published in 1950 [78]. The key point in the microscopic origins of friction is the roughness of the surfaces in contact. Due to the microscopic roughness of most solids, the objects are in contact only at the highest asperities (Fig. 1.4 (a)). Therefore, the real surface area in contact S_R is much smaller than the apparent surface area in contact S_A . Experimentally, it has been shown that typically: $S_R =$ $10^{-2}S_A$ [79]. This small contact area accounts for high stresses on the asperities in contact, which can cause these asperities to deform plastically. Therefore, Bowden and Tabor assume that the normal stress at contact is constant and equal to the material hardness H, where $H = F_N/(\pi r^2)$ is the contact pressure in the fully plastic regime. Therefore [78]:

$$S_R = \frac{N}{H} , \qquad (1.5.2)$$

where N is the normal force. This equation means that the actual contact area is linearly proportional to the normal force.

Bowden and Tabor then propose that the deformed asperities fuse together and


Figure 1.4: (a) A microscopic view of a block on a surface. Both surfaces are solid and rough. P_i (with i = 1, 2, 3) shows the point of contact with surface area of S_i . S_A shows the apparent area of contact and $S_R = \sum_i S_i$ the area of real contact. (b) A simple model for stick-slip motion: a block on a rough surface, connected to a spring and pulled with constant velocity v to the right. l_0 is the initial length of the spring and ϵ shows the spring elongation. (c) The spring elongation ϵ plotted versus time. ϵ_s is the elongation caused by the maximum static friction, therefore equal to $\mu_s N/K$. After the initial linear elongation, the spring will oscillate around the elongation ϵ_K with a value of $\mu_k N/K$, and the block will alternate between states of slipping and sticking again.

form solid contacts, due to the high stresses and plastic deformations. Therefore, the tangential force needed to break these solid contacts must overcome a critical shear stress τ_c :

$$F_T = \tau_c S_R . \tag{1.5.3}$$

From eq. 1.5.2, we input the expression for S_R :

$$F_T = \left(\frac{\tau_c}{H}\right) N \ . \tag{1.5.4}$$

If we compare equation 1.5.4 to the familiar Coulomb's law of friction: $f_s = \mu_s N$, then we see that Bowden and Tabor were able to give a microscopic explanation that describes solid friction with the friction coefficient being $\mu_s = \tau_c/H$.

Stick-slip

Stick-slip is a familiar phenomenon: creaking noise of a rusty door or the sound that chalk makes when writing on a blackboard. As evident by the term, the systems that go through stick-slip have two modes. Upon application of a pushing or pulling force, the object does not move and elastic energy is stored in the object when one continues to apply force on the object. After a force threshold is passed, the object is set into motion and slips. But after a while, due to friction, the object will slow down and will eventually stick to the surface again.

A simple model used for stick-slip is shown in Fig. 1.4 (b). A block of mass m on a frictional surface with static and dynamic friction coefficients of μ_s and μ_k accordingly, is connected to a spring with spring constant K, and is pulled at constant velocity v. The block will go through cycles of sticking to the surface due to friction, followed by slipping on the surface, then sticking again. Let us find the elongation of the spring as a function of time $\epsilon(t)$. If X(t) shows the position of the block at time t, then the spring elongation at time t is: $\epsilon(t) = vt - X(t)$. At t = 0, the pulling force F_T , which is equal to the spring force $K\epsilon$, is smaller than the threshold for maximum static friction $f_s = \mu_s N$. Therefore, the block remains stationary at X(t) = 0. The elongation is then simply $\epsilon = vt$ (see the linear portion of the plot in Fig. 1.4 (c)). But as time goes by, the magnitude of the pulling force will increase and will eventually reach the threshold. The block is then set to motion and slips on the surface. When at motion, the friction force applied to the block is equal to the block

$$m\ddot{X} = K\epsilon - \mu_k N . \tag{1.5.5}$$

If we want to find the elongation, we have $\ddot{X} = -\ddot{\epsilon}$ from the equation that connects X and ϵ , given above. Substituting \ddot{X} and performing some rearrangements yields:

$$\ddot{\epsilon} + \frac{K}{m}\epsilon = \frac{\mu_k}{m}N . \qquad (1.5.6)$$

The solution to this differential equation is an oscillatory motion around the mean value $\epsilon_k = \mu_k N/K$ (See Fig. 1.4 (c)) with frequency $\sqrt{K/m}$. As long as the pulling velocity v is larger than $\dot{\epsilon}$, the block stays in this oscillatory motion. Otherwise, the block will stick again to the surface. Note that due to the force balance in the vertical direction, we have: N = mg.

This pattern of stick-slip motion does not only describe the motion behind a screeching door, but is a simple explanation for a plethora of hysteretic phenomena. In the context of geology, this simple system for stick-slip can be used to model earthquakes [80]. In granular materials, this stick-slip pattern can be observed in intermittent flow of granular materials and other type of hysteretic phenomena in granular materials [4].

1.5.3 Van der Waals forces

The van der Waals forces are a set of short-range attractive interactions between the dipole moments of atoms and molecules. The dipole moments can be permanent, but also induced. Therefore, the van der Waals forces exist between polar, as well as nonpolar atoms and molecules. The van der Waals interaction between two molecules at distance r produces a negative potential V(r) that scales like $-1/r^6$. Even though a single van der Waals interaction produces a relatively weak force between atoms and molecules, these forces can accumulate and become significant at the macroscopic scale when two surfaces are separated by distances on the order of nanometers. An example we are all familiar with is cling wraps that we use everyday to pack our lunch or seal bowls [16]. The macroscopic van der Waals force between any two macroscopic objects with different geometries can be calculated by summing the van der Waals force between each two dipole pairs in the two objects. Hamaker [81] has calculated this macroscopic force between two spheres, which is important in the context of the system I work with. The van der Waals force for any two spheres of equal radii Rwith separation distance r is:

$$F_{\rm VdW} = -\frac{AR}{12r^2} ,$$
 (1.5.7)

where A is the Hamaker constant ($A \sim 10^{-19}$ J [82]), which is the reason why van der Waals force is relatively weak and only gains importance in small separation distances r. Let us calculate the order of magnitude of the van der Waals force between a pair of oil droplets in a solution, which is relevant for my experiments. We take the droplet radii to be of the order of 10 μ m. When the droplets are separated by 1 nm, which is not a bad estimation [16], the resulting van der Waals force would be on the order of nano Newtons, which is comparable to the depletion forces that make the droplets cohesive [1].

1.5.4 Electrostatic double-layer repulsion

Electrostatic laws enforce that particles with similar charge type repel each other and follow Coulomb's law of electrostatics. If we have an electrolyte solution, and



Figure 1.5: (a) Yellow circle shows a particle in an electrolyte solution. The negative surface charges of the particle attract the positive ions (counter-ions) in the solution, which screen the negative surface charges of the particle. In turn, the concentration of negative ions (co-ions) drops near the surface of the particle. κ_D^{-1} is the Debye length, where the potential due to the counter-ions drops significantly in distances greater than κ_D^{-1} . (b) The concentration of counter-ions in red and co-ions in blue is plotted versus the multiples of the Debye length. The dashed black line shows the form of the electric potential in the vicinity of the surface of the particle.

dispersed particles with a net charge, these dispersed particles will have a different interaction than expected by the Coulomb's law. Let us assume that we have negatively charged particles in an electrolyte solution of a z-valent salt, as shown in Fig. 1.5 (a). The local concentration of counter-ions (positive in this case, shown in red) will increase in the vicinity of the particles due to the electrostatic field, such that the charge neutrality is preserved and the electric potential due to the negative charges is screened. At the same time, the concentration of co-ions (negative ions in this case, shown in blue) decreases in the vicinity of the charged particles.

Due to the increased local concentration of ions, if two dispersed particles are brought close together, they would still repel each other. However, this interaction is not due to the Coulomb interaction alone, but also entropic in nature. When the particles are brought close, their counter-ions become confined to a smaller space. This restriction reduces the available configurations for the ions, making the arrangement energetically less favorable. Therefore, the particles repel each other and keep a certain distance, so as to maximize the entropy of the system. This interaction is called the double-layer repulsion. We will see how the range of this repulsion can be controlled by changing the concentration of salt in the solution.

Let us consider the simple case, where only the counter-ions are present in the solution. The charge density of counter-ions at distance x from the surface of the particle (or any charged surface) $\rho(x)$ can be found by the Boltzmann distribution:

$$\rho(x) = \rho_{\infty} \exp\left(-\frac{ze\psi(x)}{k_{\rm B}T}\right) . \tag{1.5.8}$$

In the above equation, ρ_{∞} is the charge density of the counter-ion in the bulk solution, away from the charged surface, z is the valency of the counter-ion, e is the charge of the electron, $\psi(x)$ is the electric potential at distance x, $k_{\rm B}$ is the Boltzmann constant and T is the temperature of the solution.

On the other hand, the electric potential follows the Poisson's equation:

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{\rho}{\epsilon \epsilon_0} , \qquad (1.5.9)$$

with ϵ being the relative permittivity of the solution and ϵ_0 , the relative permittivity of vacuum. If we combine equations 1.5.8 and 1.5.9 in the presence of the counter-ions only, we get the Poisson-Boltzmann equation:

$$\frac{\partial^2 \psi}{\partial x^2} = -\left(\frac{\rho_{\infty}}{\epsilon \epsilon_0}\right) \exp\left(-\frac{ze\psi(x)}{k_{\rm B}T}\right) \ . \tag{1.5.10}$$

In the limit of small potential, $\psi(x)$, known as the Debye-Hückel approximation, and in the presence of two ion species, it can be shown that the solution for equation 1.5.10 is [16]:

$$\psi(x) = \psi_{\infty} \exp(-\kappa_D x) , \qquad (1.5.11)$$

where κ_D is essentially:

$$\kappa_D = \left(\frac{2ze\rho_\infty}{\epsilon\epsilon_0 k_{\rm B}T}\right)^{1/2} \,. \tag{1.5.12}$$

The quantity κ_D^{-1} , called the Debye screening length, is the distance beyond which the electric potential due to the counter-ions drops significantly. Therefore, κ_D determines the range of the double-layer repulsion. In an aqueous solution of a monovelanet salt like NaCl with concentration I in mol/L, the Debye length can be calculated by:

$$\kappa_D^{-1} = \frac{0.304}{\sqrt{I}} \quad \text{nm.}$$
(1.5.13)

This means that the range of the double-layer repulsion in solutions is greatly affected by salt concentration.

1.5.5 Hydrophobic interaction

Oil and water are the most familiar examples of two immiscible liquids. We are all familiar with vinaigrette and how we need to keep mixing it before serving, or it will separate into the oil-based and the water-based phases. The unmixing of water and oil is a spontaneous process and entropy driven [16]. While mixing any two species is costly due to both enthalpy and entropy, the interaction of oil and water is especially entropically costly, such that there is a special name for it: the hydrophobic interaction. The high entropic cost of surrounding non-polar molecules, such as oil, with water arises from the disruption of hydrogen bonds. Water molecules are polar and can form strong hydrogen bonds with each other and other polar molecules. However, a non-polar molecule will not form hydrogen bonds with water molecules surrounding it, and therefore, disrupts the network of hydrogen bonds. While water molecules around the hydrocarbon molecule rearrange in such a way to maximize their hydrogen bonds, the water molecules get restricted and lose degrees of freedom, which in turn decreases the total entropy of the system [16]. Therefore, it is energetically favorable to minimize the water-oil interface as much as possible. If the mixture is not agitated or stabilized, the oil and water will separate into two distinct macroscopic phases.

As mentioned in section 1.3.2 on emulsions, surfactants are amphiphilic molecules that consist of a polar head group and a non-polar tail. When surfactants are added to water, it is unfavorable for the non-polar fatty tails to be exposed to water molecules. The hydrophobic interaction then causes the surfactant molecules to migrate either to the water surface or self-assemble into different structures, called micelles, in order to minimize the unfavorable interaction between the polar and non-polar species. Since the ordering of surfactant molecules in micelles is entropically costly, the formation of micelles only starts at concentrations above the critical micelle concentration (CMC). In lower concentrations than the CMC, the surfactant molecules are found individually and do not form micelles. In my experiments, I have an aqueous solution of the surfactant sodium dodecyl sulfate (SDS) above the CMC. Therefore, micelles form in the solutions and the concentration of the SDS molecules in form of micelles in the solution $C_{\rm m}$ can be found by subtracting the CMC concentration $C_{\rm CMC}$ from the total SDS concentration C:

$$C_{\rm m} = C - C_{\rm CMC} \;.$$
 (1.5.14)

1.5.6 Depletion interactions

The depletion interaction is a short-range attractive interaction of entropic origin, which can drive dispersions towards aggregation. This interaction is present in a solution that has two types of dispersed particles with different sizes; smaller particles that are subject to Brownian motion and larger particles (Fig. 1.6). The smaller particles cannot penetrate larger particles or adsorb on their surfaces. Therefore, a depletion zone forms around the larger particles, excluding the smaller particles. This depletion zone reduces the total accessible volume for the smaller particles, which in turn, decreases their total entropy. However, if the larger particles approach each other, such that their depletion zones overlap (Fig. 1.6 (b)), more volume will be available for the smaller particles. Therefore, the entropy of the system will



Figure 1.6: (a) Two particle types (purple and dark blue) exist in a solution (light blue) with one type being smaller than the other. The smaller particles are excluded from a region around the larger particles that is shown with a dashed circle. (b) To minimize their overall excluded region, the smaller particles push the larger particles toward each other, causing the excluded regions overlap. As a result, there is a short-range effective attraction between the larger particles.

increase. Hence, there will be an effective short-range attractive force between the larger particles [16].

The depletion interaction is usually present, when non-adsorbing polymers are dispersed in a solution [16]. In my experiments, the smaller particles are the SDS micelles [1] and the larger particles are the oil droplets with sizes on the order of 10 μ m. Ono-dit-Biot [1] has experimentally measured the strength of the depletion interaction in the same system of oil droplets and SDS micelles and has found that the strength of depletion force F_{adh} between any two droplets of radius r is:

$$F_{\rm adh} \propto r C_{\rm m}$$
, (1.5.15)

where $C_{\rm m}$ is the concentration of SDS micelles.



Figure 1.7: (a) Schematic of dispersed particles coated with polymer chains for stabilization. (b) When particles approach each other, the local concentration of polymer increases and the polymer chains will lose degrees of freedom, which is unfavorable. Therefore, the particles repel each other to maximize the entropy of the system. Steric repulsion is a method used to prevent aggregation in dispersions and colloids.

1.5.7 Steric repulsion

Steric repulsion is a method for stabilizing colloidal particles to prevent aggregation. The steric repulsion is also a force that is entropic in origin. The suspended particles are coated with a polymer as shown schematically in Fig. 1.7. As the particles approach one another, the local concentration of the polymer increases, which is not favorable for the polymers, as their entropy decreases. Therefore, the particles repel each other to maximize the entropy of the system. The range and the strength of steric repulsion could be controlled by the length of the grafted polymer chains and their density [16].

A few consideration that must be taken into account are the interaction of the grafted polymer with the solution. First, the solution should be a good solvent for the polymers. However, the strength of interaction between the solvent and the polymer chains determine the resultant repulsion. Another consideration is the bond between the polymers and the particle. It is not important if the bonds are chemical or physical. Yet, the bond energy should be greater than $k_{\rm B}T$, so that the thermal motions do not detach the polymers from the particles.

Particles that are stabilized using steric repulsion can be considered hard spheres [60, 61, 83] (hard sphere interaction discussed in section 1.5.1) with an effective radius, depending on the particle size as well as the average length of the grafted polymer chains.

1.6 Capillarity

In this section, we will discuss an important property of liquids: capillarity. Capillarity is the study of interfaces between two immiscible liquids or the interface of a liquid and air. We are all familiar with the flow of liquids and how they take the shape of their container. At the same time, liquids can make various stable shapes according to the surface they are on. As an example, think of how water beads up on a lotus leaf and does not wet this surface, compared to spreading of water on the surface of a clean glass. Each equilibrium shape is a result of interactions at the molecular level between the liquid and the surface underneath. Therefore, water, or any liquid for that matter, changes the shape of its interface to a certain equilibrium shape, in order to minimize the unwanted interactions. In this thesis, I study the collective properties of cohesive, frictionless granular materials. By drawing analogies from concepts in capillarity, such as the *granular capillary length* [1], we aim to better understand the collective properties of these materials. Also, the experiment in paper 1, the granular pendant drop, is inspired by the pendant drop method (sec. 1.6.7), which is a way of determining the surface tension of a liquid.



Figure 1.8: Two immiscible species A and B are shown, where there is an energy cost for A/B interactions. Blue circles represent two A molecules. The molecule on the right is surrounded by A molecules and has all the possible favorable interactions shown by dark blue arrows. The molecule on the left though, is missing half of its favorable interactions, and instead, has costly interactions, represented by the dotted arrows. Adding up the cost of these unfavorable interactions per unit area yields the interfacial tension between A and B.

1.6.1 Surface tension

Surfaces are costly and hard to make! Evidence for this fact can be found in the familiar setting of our kitchens. We use mechanical energy to make a smooth vinaigrette with a high interfacial area between vinegar and oil. More strenuous examples are making whipped cream and meringue. The widespread use of electrical whisks over hand whisks for making whipped cream or meringue highlights the significant energy cost of creating surfaces between two immiscible species.

The energy cost associated with surfaces is due to the difference in the interaction energy between two species at the molecular level. If one of the species is air, then we call this energy cost per unit area, surface tension of that liquid. However, between any two arbitrary species, this energy cost per unit area is called interfacial tension. Let us consider two separate phases of species A and B as an example (Fig. 1.8). We assume that A is a liquid and B is a gas, such that A molecules can freely rearrange and deform the interface to minimize the free energy of the system. We will see how the interfacial tension of A and B, γ_{AB} , is connected to the energy cost due to pairwise interaction of A and B molecules. Let us define the pairwise interaction energy for A molecules as ϵ_{AA} , for B molecules as ϵ_{BB} and for a pair of A and B molecules as ϵ_{AB} . We can introduce an interaction parameter χ , which shows the energy cost associated with the A/B interaction in units of $k_{B}T$:

$$\chi = \frac{z}{2k_{\rm B}T} (2\epsilon_{\rm AB} - \epsilon_{\rm AA} - \epsilon_{\rm BB}) , \qquad (1.6.1)$$

where z is the number of nearest neighbours for each A or B molecules. We can characterize the affinity between A and B molecules through the interaction parameter. If $\chi < 0$, then interaction between A/B molecules is more energetically favorable compared to A/A and B/B interactions. However, if $\chi > 0$, there is an energy cost associated with the A/B interaction. If the average volume occupied by each molecule is v, then according to Jones [16], the interfacial tension between A and B, γ_{AB} is defined as the energy cost of interaction per unit area. So, we can divide the energy cost for a single A/B molecule interaction, which is the actual pairwise energy cost $\chi k_{\rm B}T$, divided by the number of neighbours z, divided by the area of a molecule $v^{2/3}$:

$$\gamma_{\rm AB} = \frac{\chi k_{\rm B} T}{z v^{2/3}} = \frac{1}{2v^{2/3}} (2\epsilon_{\rm AB} - \epsilon_{\rm AA} - \epsilon_{\rm BB}) .$$
(1.6.2)

A point to consider here is that this value for interfacial tension is the maximum possible value for a completely sharp A/B interface. In reality, the free energy will decrease due to the entropic term by TS and the actual surface tension is always lower than the contribution from the interaction energy suggested here. As a result, due to thermal motions, all interfaces are rough, but this roughness bellow the critical point in the phase diagram should be small. At the critical point, the interface should vanish and phases should be highly diffused due to high temperatures [16].

Let us consider the case where $\chi > 0$. In Fig. 1.8, the A molecule on the right, which is surrounded by similar A molecules, has all the z possible favorable interactions with its neighbours. However, the molecule on the left, positioned at the A/B interface is missing half or z/2 of its favorable interactions. Instead, the molecule on the left has z/2 costly, unfavorable interactions with B molecules. These unfavorable interactions add to the energy content of the system. Liquids have deformable surfaces. When $\chi > 0$, the liquids deform in such a way to minimize their surfaceto-volume ratio, in order to minimize the free energy of the system. This is why air bubbles immersed in water are perfectly spherical, as a sphere has the lowest surface to volume ratio. The shape of liquid drops on a surface is also a result of the pairwise interaction, which we will discuss in section 1.6.4 on wetting.

Another way of defining and interpreting surface tension γ is a force per unit length applied on the contact lines. To demonstrate that, we can consider the example of a U-shaped metal frame, made of thin wires, accompanied by a thin perpendicular rod on the open end of the U-shaped frame. The rod is locked in Fig. 1.9 (a) and unlocked in 1.9 (b). Let us imagine that we dip this frame with the locked rod into a bath of soapy water, such that a thin film of relatively stable soapy water forms in the frame. The surface area of this film is large, which is unfavorable as we discussed above. If we then unlock the thin rod (Fig. 1.9 (b)), then the liquid film will rapidly pull the rod to the left to minimize its surface area, and therefore minimize the free



Figure 1.9: Demonstrating the force due to surface tension. (a) A thin soap film (light purple) exists in a closed frame made of a U-shaped frame and a thin rod on the right. The rod is initially locked to the frame, shown by purple crosses. (b) The rod is then unlocked, and due to surface tension, there will be a force that pulls the thin rod to the left, such that the surface area of the soap film is minimized. The magnitude of the pulling force F is proportional to the length of the contact line L and the surface tension of the liquid γ .

energy of the system. The magnitude of this capillary force F is:

$$F = 2\gamma L , \qquad (1.6.3)$$

where L is the length of the contact line of the liquid and the rod, to which the capillary force is applied. The prefactor 2 comes from the fact that the exposed area of the film is on both sides of the frame.

1.6.2 Laplace pressure

The Laplace pressure is an excess pressure inside drops and bubbles, due to surface tension. This pressure difference applies to any curved surface. It is in fact due to the Laplace pressure that the interfaces resist deformation. As mentioned for foams in section 1.3.3, if two bubbles of different sizes are connected to each other, the smaller bubble will empty its gas content into the larger bubble, due to the higher pressure



Figure 1.10: A small surface area between two immiscible liquids. This small fraction is a general surface with radii of curvature R_1 and R_2 and arc lengths of x and y. We are interested to calculate the energy cost of expanding the surface in the z direction by dz, when the arcs x and y are also extended by dx and dy respectively.

of the smaller bubble. By the end of this section, we will derive the dependence of the Laplace pressure on the radii of curvature for a general surface.

Let us assume a small area of a general surface between two immiscible liquids, as shown in Fig. 1.10. In general, any surface can be characterized with two different principal radii of curvature, R_1 and R_2 . The considered area is so small that the principal radii do not change across the chosen surface. We want to calculate the energy cost E due to expanding the surface by a distance dz, shown in Fig. 1.10. First step to determine the change in surface energy is to calculate the increase in the area of the surface dA. The following equations show the initial area A_0 , the area after expansion A_1 and the change in the surface area dA:

$$A_1 = (x + dx)(y + dy) = A_0 + xdy + ydx \qquad \text{area after expansion} \qquad (1.6.5)$$

$$dA = xdy + ydx$$
 change in the area (1.6.6)

Note that we only consider the first order changes in the area, and therefore ignore the second order term, dxdy. Finally, we can calculate the energy cost E to expand the surface by dA:

$$E = \gamma dA = \gamma (xdy + ydx) . \tag{1.6.7}$$

On the other hand, this energy increase needs to be provided to the system by the work done on the surface to expand it. Therefore, based on thermodynamics:

$$W = \Delta p dV = \Delta p(xy) dz , \qquad (1.6.8)$$

where Δp is the pressure difference that occurs when moving from one side of the curved surface to the other. dV is the first order change in volume, due to expansion of the surface, equal to $A_0 dz$.

Now, due to conservation of energy, we have: E = W. Therefore, by equating equations 1.6.7 and 1.6.8, we get:

$$\Delta p(xy)dz = \gamma(xdy + ydx) . \tag{1.6.9}$$

We then rearrange 1.6.9 to find Δp :

$$\Delta p = \gamma \left(\frac{dy}{ydz} + \frac{dx}{xdz}\right) . \tag{1.6.10}$$

Given the small area of the general surface, we can write the following equal ratios in similar triangles:

$$\frac{R_1 + dz}{R_1} = \frac{x + dx}{x} , \qquad \text{therefore} \qquad \frac{dz}{R_1} = \frac{dx}{x} , \qquad (1.6.11)$$

and:

$$\frac{R_2 + dz}{R_2} = \frac{y + dy}{y} , \qquad \text{therefore} \qquad \frac{dz}{R_2} = \frac{dy}{y} . \qquad (1.6.12)$$

Based on equations 1.6.11 and 1.6.12, we can substitute $\frac{dx}{x}$ and $\frac{dy}{y}$ in 1.6.10 to get the Young-Laplace equation:

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \gamma C , \qquad (1.6.13)$$

where $C = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ is the curvature of the surface. The above equation is algebraic and one should put the radii of curvature with the proper sign to get the correct Laplace pressure. Therefore, if we have a concave surface with a negative curvature, the overall pressure difference will be negative. So, in a liquid with a concave surface, the pressure in the liquid underneath the surface will be lower than the pressure outside. This is the basis for capillary bridges discussed in section 1.6.3. In contrast, when the liquid surface is convex, like a drop, the pressure inside the drop is higher than the medium outside. And if a surface is flat, there will be no pressure difference when crossing from one side of the surface to the other.

Droplets as hard spheres

Due to the Laplace pressure, in both experiments presented in this thesis, we consider the oil droplets as hard spheres. Based on equation 1.6.13, we can calculate the over pressure inside an oil droplet. A typical droplet has a radius R of 10 μ m and the interfacial tension of oil and SDS solution is ~ 10 mN/m [84]. These values result in a Laplace pressure of around 20 kPa. We can compare this pressure by the hydrostatic pressure that the droplets experience. If the oil droplets with a density of ~ 800 kg/m³ are immersed at a depth of 1 cm of a liquid with a density of 1000 kg/m³, then the hydrostatic pressure the droplet is subject to is around 20 Pa, which is 1000 times smaller than the Laplace pressure.

1.6.3 Capillary bridges

Capillary bridges form when a small amount of liquid connects two surfaces together. Liquid bridges make the two surfaces adhesive, as the capillary force is keeping the objects together. Everyday examples of the capillary bridges are strands of hair that stick together when wet, or how children are able to make sand castles out of wet sand. Capillary bridges due to interstitial liquid is a classic method for introducing cohesion among granular materials [10–12, 85–87]. Here, we can calculate [82] the magnitude of the capillary force between two flat surfaces, when a drop of liquid with surface tension γ is squeezed between them (Fig. 1.11).

Let θ_E be the angle that the liquid is making with each of the surfaces. This is called the contact angle, and more is discussed on this concept in section 1.6.4. The capillary adhesion is only present if the contact angle $\theta_E < \pi/2$. A capillary bridge can be characterized with its radius R_1 , its surface area $A = \pi R_1^2$ and the separation



Figure 1.11: Dark blue rectangles represent two solid surfaces. The light blue shape with gradient is a liquid with surface tension γ that is squeezed between the two solid surfaces. We consider the 3-dimensional liquid surface with radii of curvature $R_1 > 0$ and $R_2 < 0$. The geometry helps us find R_2 in terms of the contact angle between the liquid and the solid surface θ_E , and the separation distance between the surfaces H.

distance H. In order to find the Laplace pressure, we need to know both the radii of curvature of the capillary bridge. One radius of curvature of the surface is R_1 , and the other is the radius of the arc of the meniscus, R_2 , as shown in Fig. 1.11. If we consider the triangle on the left on Fig. 1.11, we can write $\cos \theta$ in that right triangle to be:

$$\cos \theta_E = \frac{H/2}{R_2}$$
 (1.6.14)

We then rearrange the above equation to R_2 . We then substitute R_2 in the Young-Laplace equation (eq. 1.6.13) to get:

$$\Delta p = \gamma \left(\frac{1}{R_1} - \frac{\cos \theta_E}{H/2}\right) \approx -\frac{2\gamma \cos \theta_E}{H} \,. \tag{1.6.15}$$

The approximation above holds true when $H \ll R_1$. In that case, the adhesive force will be:

$$F = \pi R_1^2 \frac{2\gamma \cos \theta_E}{H} . \qquad (1.6.16)$$

In granular materials that are made adhesive, using a liquid, the adhesive force is

not the same everywhere, as the interstitial liquid can have an uneven local distribution throughout the system. That is why introducing a liquid to a granular system is not the best method for controlling adhesion among the particles.

1.6.4 Wetting

Wetting is a surface property that determines how a certain liquid wets the surface of a solid. The study of wetting and controlling this surface property is of immense importance in various industries and natural phenomena [82]: some examples are chemical industries for manufacturing of ink or paint, automobile industries for pretreating the surface of cars before painting. In food industries, wetting properties of powders can be controlled, such that they are easily dissolvable in liquids. In life sciences, some examples that depend on wetting conditions are: surface properties of vessels in plants that enable water and essential nutrients to be transported. Another example is the role of proteins such as mucins, which coat the eye cornea and transform its surface from highly hydrophobic to hydrophilic. This transformation enables a tear layer of optimal thickness to cover the cornea, ensuring clear vision.

In general, there are two regimes of wetting: total wetting and partial wetting (Fig. 1.12). Total wetting is the condition, where the liquid completely spreads on the surface and the contact angle is zero ($\theta_E = 0$, shown in Fig. 1.12 (a)). Total wetting happens, when the liquid has a high affinity for the surface and total spreading lowers the surface energy of the system. In case of partial wetting, the liquid will have a non-zero contact angle of θ_E at the contact line, where the liquid, air and the solid substrate meet. This contact angle is determined based on the different relative affinities between liquid/air, solid/air and solid/liquid, as we will



Figure 1.12: A drop of liquid on three different surfaces to show different wetting conditions. (a) If the spreading parameter S is positive, then the liquid and the surface have a high affinity to each other. In this case, called "total wetting", the liquid spreads on the surface completely. In the partial wetting condition (b) and (c), the affinity of the surface and the liquid is less strong than the total wetting regime. The drop of liquid in the partial wetting regime makes a non-zero contact angle θ_E with the substrate.



Figure 1.13: A closer look at the edge of a liquid drop on a solid substrate with contact angle θ_E . The forces per unit length, namely surface tension γ , solid/air interfacial tension γ_{SO} and solid/liquid interfacial tension γ_{SL} are shown.

discuss shortly. If the contact angle θ_E is less than or equal to $\pi/2$, we are in the "mostly wetting" regime (Fig. 1.12 (b)), and if $\theta_E > \pi/2$, we are in the "mostly non-wetting" regime (Fig. 1.12 (c)). Similar to surface tension, which represents the relative affinity of liquid molecules towards each other, compared to the ambient air, we can define interfacial tension between a solid substrate and ambient air as γ_{SO} , and interfacial tension between the solid substrate and the liquid as γ_{SL} . These interfacial tensions represent the energy cost for contact between different substances.

The law of Young-Dupré: determining θ_E

As we discussed earlier in section 1.6.1 on surface tension, all interfacial tensions represent a force per unit length. The capillary forces pull on the contact line of the liquid, in order to minimize the surface energy. Due to the capillary forces, a concave or convex meniscus forms. Fig. 1.13 shows a drop on a substrate with $\theta_E < \pi/2$. The interfacial forces on the contact line, normalized by unit length are shown as well.

Based on the law of Young-Dupré, the equilibrium shape of the drop arises from

the horizontal force balance between these three capillary forces:

$$\gamma_{SO} - \gamma_{SL} - \gamma \cos \theta_E = 0 . \qquad (1.6.17)$$

Hence, the contact angle can be found:

$$\cos \theta_E = \frac{\gamma_{SO} - \gamma_{SL}}{\gamma} . \tag{1.6.18}$$

Since the substrate is solid, the vertical component of the capillary force is not strong enough to deform the substrate. However, if the substrate is deformable, such as a soft solid or a liquid, then the surface tension will deform the substrate. In that case, the vertical force balance should hold too.

Wetting condition

Now, let us discuss how we determine the wetting condition of a liquid on a substrate. Essentially, the wetting condition is determined based on the interplay of the three interfacial energies involved. We define a *spreading parameter* S as the difference in energy cost per unit area between a dry substrate and a wet substrate:

$$S = E_{\rm dry} - E_{\rm wet} = \gamma_{SO} - (\gamma_{SL} + \gamma) . \qquad (1.6.19)$$

If the normalized surface energy of the dry substrate is more than the wet substrate, then S > 0 (Fig. 1.12 (a)). In this case, it is energetically more favorable that the liquid spreads and covers the dry substrate fully (total wetting). On the other hand, if the surface energy of the dry substrate is lower than the wet substrate, then S < 0. In this case, we have partial wetting, where the contact angle of the liquid as well as the size of the drop determines how the liquid spreads on the substrate. In case the surface tension and the contact angle are known, the spreading parameter can be determined. Based on the definition of the contact angle, eq. 1.6.18:

$$S = \gamma(\cos\theta_E - 1) . \tag{1.6.20}$$

1.6.5 The capillary length

Many people know about the rise of water in a capillary tube or have seen water making a concave meniscus around the edges in a cup. On a "small" length scales, it seems that water defies gravity. The underlying reason for this peculiar property is the Laplace pressure, which balances out the hydrostatic pressure due to gravity. First, we will see how the pressures balance out, and then, we will have a reference length to define what "small" means.

Here, we consider a liquid that makes a concave meniscus near a wall that perturbs the surface of the liquid (Fig. 1.14). The meniscus diminishes a after a certain length and the surface of the liquid becomes flat. Let us call this length κ^{-1} . z(x) represents the curved shape of the liquid surface. We assume that the container is infinitely long along y direction, normal to the xz plane. Therefore, at any point, the curvature of the liquid surface is simply $-\partial^2 z/\partial x^2$, as the second radius of curvature of the liquid surface is infinite. In the presence of the atmospheric pressure, we write the pressure immediately under the liquid surface at point A. Due to the Laplace pressure in the curved region, we have:

$$p_A = p_{\rm atm} - \gamma \frac{\partial^2 z}{\partial x^2} \,. \tag{1.6.21}$$



Figure 1.14: The meniscus of a liquid near a wall. z(x) shows the height of the meniscus at distance x from the wall. A is an arbitrary point right underneath the surface of the liquid and κ^{-1} is the capillary length, which we interpret as a screening length in this example, after which the perturbation of the liquid due to the wall is mostly diminished.

On the other hand, due to the hydrostatic pressure, the pressure at point A must be:

$$p_A = p_{\rm atm} - \rho g z \ . \tag{1.6.22}$$

Equating the two expressions for p_A , we get:

$$\gamma \frac{\partial^2 z}{\partial x^2} = \rho g z . \qquad (1.6.23)$$

If we then rearrange the equation and solve for z(x), we get:

$$z(x) = z_0 \exp\left(-\sqrt{\frac{\rho g}{\gamma}}x\right) = z_0 \exp(-\kappa x) , \qquad (1.6.24)$$

where the quantity κ^{-1} is defined as:

$$\kappa^{-1} = \sqrt{\frac{\gamma}{\rho g}} \,. \tag{1.6.25}$$

 κ^{-1} is known as the capillary length, which compares capillarity to gravity. In any system, if the characteristic length is smaller than the capillary length κ^{-1} , the capillary effect dominates and gravity can be neglected. But when the considered characteristic length scale is larger than the capillary length κ^{-1} , gravity dominates over capillarity.

As shown in equation 1.6.24, we expect that any deformation in a liquid surface due to an external object or wall to decay exponentially as we move away from the object or the wall. The current solution for the curvature of the meniscus z(x) is not valid for the regions close to the wall. The reader may refer to the book by de Gennes, Brochard-Wyart and Quéré [82] for the exact shape of the meniscus near a wall, according to the specific wetting conditions of the liquid.

1.6.6 Drops on a surface

We have all seen how drops sit on solid surfaces on a rainy day. In the wetting section 1.6.4, we also mentioned the factors that determine the contact angle of a drop. Now, let us see how drops of different sizes spread on a surface. Let us consider drops in the partial wetting regime. If the size of the drop l is smaller than the capillary length, $l < \kappa^{-1}$, then the capillary forces are dominant and the drop will form a spherical cap. Of course, the contact angle of that spherical cap depends on the spreading parameter, based on equation 1.6.20.

As the drops get bigger, the effect of gravity on the drop becomes more pronounced. In case the characteristic size of the drop is much larger than the capillary length, $l >> \kappa^{-1}$, then the drop will spread horizontally due to gravity, while maintaining a constant height e. Pancake batter or a water puddle are familiar examples in this case. However, around the edges, the contact angle θ_E will not change due to the drop size. Let us call this equilibrium shape a puddle and find its height.

Height of a puddle

Fig. 1.15 shows a puddle on a surface with the interfacial tensions as indicated. The puddle makes a contact angle of θ_E with the substrate. We can find the height of the puddle, using the horizontal force balance (per unit length) on a section of the liquid. On the one hand, we have the Young's law, stating that:

$$\gamma_{SO} - (\gamma \cos \theta_E + \gamma_{SL}) = 0. \qquad (1.6.26)$$



Figure 1.15: Edge of a puddle on a solid substrate. The forces per unit length of the contact line are shown. \tilde{P} shows the force per unit length due to the hydrostatic pressure.

On the other hand, we have the force due to the hydrostatic pressure \widetilde{P} which makes the puddle spread:

$$\widetilde{P} = \int_0^e \rho g(e-z) dz = \frac{1}{2} \rho g e^2 . \qquad (1.6.27)$$

Therefore, the force balance equation on a section of the liquid reads:

$$\frac{1}{2}\rho g e^2 + \gamma_{SO} = \gamma + \gamma_{SL} . \qquad (1.6.28)$$

Substituting the definition of the spreading parameter S from eq. 1.6.19, we have the two following equations:

$$S = -\frac{1}{2}\rho g e^2 , \qquad (1.6.29)$$

$$S = \gamma(\cos\theta_E - 1) . \tag{1.6.30}$$

Equating the two top equations leads to:

$$\gamma(1 - \cos \theta_E) = \frac{1}{2}\rho g e^2$$
. (1.6.31)



Figure 1.16: (a)-(c) Progress of a pendant drop toward detachment. (a) a liquid drop is hanging from the tip of a capillary tube. R shows the tube radius and r shows the drop radius in the plane perpendicular to z-axis. The white arrows show the capillary force per unit length γ that applies on the contact line with the length of $2\pi R$. The capillary force keeps the drop attached to the capillary tube, so the direction of the capillary force is opposite to gravitational force. (b) The gravitational force has exceeded the capillary force and the drop elongates to form a neck. (c) The drop and the neck are almost separated with the volume of the separated drop being αV , with $\alpha \sim 0.6$ and V the volume of the drop in (a) just before elongation.

Using the definition of the capillary length, eq. 1.6.25, we have:

$$e^{2} = 2\kappa^{-2}(1 - \cos\theta_{E}), \qquad (1.6.32)$$

which can be simplified into:

$$e = 2\kappa^{-1} \sin \frac{\theta_E}{2} . \qquad (1.6.33)$$

1.6.7 Measuring surface tension: the pendant drop method

One of the simplest ways to measure the surface tension of liquids is the pendant drop method. Imagine a capillary tube filled with a test liquid. As the liquid is pushed out slowly, a small but growing pendant drop forms at the tip of the capillary tube. At low flow rates, the system is in a quasi-equilibrium state. Therefore, the pressures on the drop should balance. The sources of these two pressures are the Laplace pressure and the hydrostatic pressure. If γ is the surface tension of the liquid, C the curvature of the drop at any height z, ρ the liquid density and g the gravitational acceleration, then the balance condition is:

$$\gamma C = \rho g z . \tag{1.6.34}$$

Given that the drop is axisymmetric, and defining $r_z = \frac{dr}{dz}$ and $r_{zz} = \frac{d^2r}{dz^2}$, we can write the curvature in the cylindrical coordinate system as:

$$C = -\frac{r_{zz}}{(1+r_z^2)^{3/2}} + \frac{1}{r(1+r_z^2)^{1/2}}.$$
 (1.6.35)

Optical imaging and image analysis techniques can be used to determine the curvature of the drop with good accuracy, which in turn enables one to determine the surface tension of the liquid, using equation 1.6.34. Note that the density of the liquid should also be known for determining the surface tension.

Another simple method for estimating surface tension is the drop weight method. This technique relies on the balance of gravitational and capillary forces at the moment of drop detachment. By measuring the weight of the detached drop, one can estimate the surface tension. Let us assume that the weight of the drop just before detachment is $W = \rho g V$, where V represents the volume of the drop. The capillary force due to surface tension F keeps the drop attached to the capillary tube and pulls on the contact line along the tube pointing upwards and opposes gravity (Fig. 1.16). Moreover, surface tension gives the drop its characteristic shape. The maximum value for the capillary force is $F = 2\pi R \gamma$, where R is the radius of the capillary tube. The pendant drop can be detached if the gravitational force exceeds the capillary force. Tate [88] has experimentally studied the detached drop method and came up with his law:

$$\alpha \rho g V = 2\pi R \gamma , \qquad (1.6.36)$$

where α is the fraction of the drop that eventually pinches off and its value is usually around 0.6. The reason why the drop weight method only yields an estimation for the surface tension is because only a fraction of the pendant drop will detach, due to the dynamics of pinch off. Right before the drop detaches, a long neck forms, followed by a drop with weight αW (Fig. 1.16 (c)). The rest of the volume of the drop, $(1-\alpha)W$, will remain in the neck. The detached drops are consistent in size [82], given the tube size and the liquid in use are kept constant. The radius of the detached drop r_d can be found from rearranging Tate's law, eq. 1.6.36:

$$r_d = \left(\frac{3}{2\alpha}\kappa^{-2}R\right)^{1/3} . (1.6.37)$$

We have assumed that the detached drop is a perfect sphere to find the radius r_d . The pendant drop method can also be used to determine the interfacial tension between two liquids, for example polymer melts, given that the density of both liquids are known.

In paper 1, the detached drop method is used to study the dripping of a collection of cohesive droplets out of an orifice. The aggregate of droplets extrudes in the form of individual clusters, similar to a dripping faucet. I compare how the volume of the detached cluster scales with the orifice radius and a parameter, which we refer to as the granular capillary length [1], and compare the results to Tate's law. In section 1.3.1, we have discussed some studies on pendant drops, where the pendant drop is not made of a molecular liquid, but from suspensions instead. I refer to these drops as granular pendant drops in paper 1.

1.7 Similarities of particulate materials and liquids

Liquid-like properties of granular materials and dispersions are a familiar sight in everyday life, such as their flow due to an external field. This similarity between liquids and particulate matter is often due to an interstitial fluid in dispersions or immersed granular materials. However, even dry granular materials can flow like a liquid, as seen in the flow of sand through an hourglass. While sand flows like a liquid under gravity, a bed of sand at rest can support compressive stress due to interparticle friction and contact forces. In an interesting experiment, Lohse *et al.* prepared a bed of fluidized sand that could not support compressive stress and instead engulfed a ball introduced to its surface [89], much like a liquid. This unusual behaviour arose from the sand bed preparation, where airflow was used to loosen the sand and weaken the force chains that sustain stresses before the ball was introduced.

1.7.1 Liquid-like instabilities

Even though dry granular materials flow like a liquid, they usually exhibit properties of a fluid in the limit of zero surface tension [90, 91]. As mentioned before, flow properties of bulk granular materials can be varied by changing interparticle forces, packing fraction and grain properties [3, 4, 16]. Therefore, under the right circumstances, it is possible to prepare assemblies of particles that exhibit properties of liquids with surface tension. Parallels of surface tension-related phenomena in particulate materials, such as the Plateau-Rayleigh instability and the Rayleigh-Taylor instability have been observed by different research groups.

The Plateau-Rayleigh instability [82] describes the breakup of a liquid jet due to surface tension into separate drops of a characteristic size. This phenomenon is triggered by fluctuations, such as thermal motion or other sources of noise, and is driven by surface tension. The breakup occurs because the surface-to-volume ratio of a cylindrical jet is higher than that of individual drops. Similar behavior has been observed in freely falling jets of granular materials [92–95], where the jets break up into clusters of particles. While Prado and colleagues [93] attributed the clustering to interactions with the ambient air, the majority of evidence suggests that cohesion between the grains is the primary cause of cluster formation [92, 94–96]. Importantly, the clustering effect is independent of the specific source of cohesion.

Another fluid-like instability that can be observed in particulate materials is the Rayleigh-Taylor instability [82]. This instability occurs, when a film of more dense fluid is placed on top of a bulk of less dense fluid. In this case, surface tension is the stabilizing force, working against generation of new interfaces, while gravity drives the instability by pulling the high density materials downwards. The result is a film with an array of hanging drops with a characteristic size and spacing. Everyday examples of this instability is the condensation film on the ceiling of a fridge. Analogues of the Rayleigh-Taylor instability have been seen in both granular [97, 98] and colloidal systems [99].

These examples show that the hydrodynamic framework can be applied to study liquid-like properties in particulate systems. Therefore, there are many studies which replicate the classic fluid dynamics experiments with particulate materials. These experiments help explore the similarities and differences between discrete and continuum systems. In paper 1, we perform the pendant drop experiment, using cohesive aggregates of droplets instead of a molecular liquid. Our question is how well does this system replicate the features of a molecular liquid, and if not, what are the main differences between these two systems.
Chapter 2

Experimental details

Experimental details for each specific experiment are discussed in the corresponding manuscript. In this chapter, I will present the experimental procedures in greater details, such that the experiments can be easily reproduced. I start with the details of the experimental chamber in section 2.1. Then, I will discuss preparing aggregates of droplets in section 2.2. In section 2.3, details on imaging, edge detection and data analysis are given.

The overall procedures of both experiments are quite similar. I fill a cuvette with an aqueous solution of sodium dodecyl sulfate (SDS) and 1.5% (w/w) NaCl. A 3Dprinted holder holds a glass pipette (inner diameter ~ 1 mm) vertically, that is sealed at the top with a 3D-printed lid. In paper 1, this pipette is actually a custom-made glass funnel. However, in paper 2, a plain cylindrical pipette is used as a reservoir for droplets. A micropipette filled with oil is inserted in the chamber and makes oil droplets *in situ* that directly float into the vertical pipette/funnel due to buoyancy, and aggregate at the top. Front-view images are taken with an optical microscope and processed using ImageJ and custom python scripts. Note that in this section, I will simply refer to the bigger pipette/funnel as a "funnel" for both experiments 1 and 2, to avoid any ambiguity with the micropipette.

2.1 Experimental chamber

In this section, I provide details on different parts of the experimental chamber. But before delving into the details, I provide a general overview to clarify how these parts are related and work together for a typical experiment.

The whole experiments take place in a cuvette (BRAND, Germany) with outer dimensions: $12.5 \times 12.5 \times 45$ mm³, shown as a black frame in Fig. 2.1 (a). The funnel holder is custom designed and 3D-printed (polylactic acid - PLA), such that it holds funnels of different sizes and has an opening on the right for the micropipette to be positioned under the funnel for droplet production. The funnel is glued to the funnel holder, using caulking. Once the funnel holder and the micropipette are placed in the cuvette, the cuvette is filled with an aqueous solution of SDS and NaCl and topped by a thick layer of mineral oil to prevent evaporation and ensure constant concentration of both SDS and NaCl throughout the whole experiment. The cuvette is exchanged for each experiment. However, the micropipette, the funnel and its holder are washed thoroughly, to ensure that the chamber is free of dust and unwanted particles. The cleaning procedure is as follows. Given that the micropipette is fragile, I spray it with ethanol, until visually clean and let it air dry. The funnel and its holder are washed using Sparkleen cleaning solution, then rinsed with filtered and deionized water, followed by spraying thoroughly with ethanol. I then dry the funnel and its holder with 99.9% ultrapure nitrogen gas.



Figure 2.1: (a) A schematic diagram showing the experimental chamber. A funnel is held in place via a 3D printed funnel holder and sealed at the top by a lid. A micropipette is bent to 90° at two points and positioned under the funnel. The micropipette is filled with oil and a small reservoir (not shown in picture) supplies the cuvette needed to produce oil droplets. The pipette is filled with an aqueous solution of SDS and NaCl and is topped with oil to ensure constant solution concentration. The top dashed box shows the region of interest for experiment 1 and the lower dashed box shows the region of interest for experiment 2. (b) An optical microscopy image of the tip of the funnel and a cluster of oil droplets, floating upwards due to buoyancy. (c) An optical microscopy image of a pipette/funnel filled with droplets. The aggregate of droplets forms a conical pile with an angle of repose θ . The scale bars are shown on the images.

2.1.1 Micropipettes

Micropipettes are used for producing oil droplets (discussed in section 2.2). Capillary tubes (World Precision Instruments, USA, outer diameter 1 mm, inner diameter 0.58 mm) are pulled using a pipette puller (PN-31, Narishige, Japan) such that the inner diameter is around 20 μ m. The active part of the puller is a wide platinum ribbon that is connected to an electrical circuit. When the capillary tube is placed in position for pulling, the ribbon is set close to the glass. As current passes through the ribbon, it gets hot, which causes the glass to locally melt. Then, electromagnets are used for pulling the pipette from one side, while the other side remains fixed. As a result of this heat-pulling, a micropipette forms. The ribbon temperature and the strength of the electromagnets can be manipulated to achieve different results. However, to change the diameter of the micropipettes, I did not change these parameters on the puller. The details of adjusting the tip size is discuss bellow.

The pulled pipette is tapered, getting thicker further from the tip. Therefore, the pipette tip could be cut at a point, where the tip has a diameter compared to the desired droplet size. Barkley *et al.* [100, 101] have shown that the diameter of the tip determines the size of the produced droplets. If one needs diameters smaller than the tip of the originally pulled pipette, one can perform the double-pulling technique developed by Carmen Lee, a previous member of our group. The technique is discussed in details in her Ph.D. thesis [102].

After pulling and getting the desired tip size, the micropipette is bent to 90° at two different points, such that the produced droplets float directly into the funnel (See micropipette in Fig. 2.1 (a)). We bend pipettes using a heated platinum wire that is connected to an electric circuit. This platinum wire gets hot as electric current passes through it. The micropipette (controlled with translation stages) is placed in contact with the platinum wire and locally melts as the wire gets hot. We use a pair of tweezers or another wire to carefully bend the fragile micropipette to 90°. The wire temperature should be adjusted properly through modulating the electric current, so that the pipette neither melts completely nor breaks from being too stiff while bending.

2.1.2 Preparing funnels

For cluster production in paper 1, we need a slow flow of the droplet aggregate through the orifice. If the flow rate is too high, there will be a jet of the droplets extruding from the orifice. To restrict the extrusion rate of aggregates, I made funnels with a dome-shaped geometry. I used a capillary tube (Kimble, USA, outer diameter: 1.8 mm, inner diameter: 1.5 mm) and hand-pulled it on an alcohol burner. I then cut the pulled tube at a place, where the slope of the pipette tapering is the most, such that we are left with a piece without a long narrow neck (Fig. 2.2 (a)). I then carefully heat the tip again in a uniform way, such that the orifice closes and the formed dome is axisymmetric (Fig. 2.2 (b) and (c)). Next, I use sand paper (grit 600 up to 1000) to grind the tip of the funnel and make an orifice of desired size (Fig. 2.2 (c) and (d)). I use an optical microscope to check the orifice size and the levelness of the tip (meaning that the plane of the orifice is perpendicular to the main axis of the funnel). An important consideration for making the tip is that the orifice is the narrowest part in the funnel's cross-section (as shown in Fig. 2.2 (d)) and a neck does not exist.



Figure 2.2: The procedure of making dome-shaped funnels out of glass pipettes. (a) I hand-pull a pipette over an alcohol lamp. Then cut the long tip, using tweezers. (b) I then heat the tip uniformly using an alcohol lamp until the tip of the funnel is closed, therefore a dome forms. (c) Using sand paper, I grind and polish the tip of the funnel, until an orifice of desired diameter D forms.



Figure 2.3: A 3D image of the pipette holder. The top part shows the hole for the funnel/cylinder on the left. On the right, there is an opening for the micropipette to be positioned under the funnel/cylinder. The posts have relatively wide feet to help with stability and prevent tilting.

2.1.3 Other custom parts

The holder

The holder is custom-designed to: first, fit perfectly in the cuvette; second, hold the funnel vertically in place; and third, allow the micropipette to reach the bottom of the funnel through an opening. Fig. 2.3 illustrates the design of the holder. This part is 3D-printed using PLA. The funnel is glued to the holder by caulking.

The lid

In order to prepare a dense aggregate of droplets, the orifice should be closed when the droplets are being collected in the funnel. Therefore, I custom-designed a lid to seal the top of the funnel. This part is also 3D-printed using PLA. Furthermore, caulking is applied to the tip of the lid to ensure a perfect seal. The position of the lid is precisely controlled using 3 translation stages. When enough droplets are produced for each experiment, I slowly remove the lid.

2.2 Aggregate of droplets

In this section, I discuss the aqueous solution of NaCl and the surface active agent SDS. In addition, I will discuss how the droplets are produced and some tips regarding the snap-off technique. However, before getting into the details, I will give an overview of the interplay of the solution and the droplets.

For both projects, we require a stabilized system of cohesive, frictionless particles that are uniform in size. In our laboratory, we make these particles out of oil droplets. Since the oil/water interface has a roughness on the order of a nanometer at room temperature [103, 104], we assume the oil droplets are smooth and effectively frictionless. Uniformity of the droplets is ensured by using the snap-off technique, which is a reliable method for making highly monodisperse droplets [100, 101]. The stability of the droplets, as well as their cohesive interactions is achieved by adding sodium dodecyl sulfate (SDS), a micelle-forming surface active agent (*i.e.* surfactant) to the solution (more on surfactants in section 1.3.2). The surfactant molecules reduce the interfacial tension between oil and water [103, 104], therefore improve the stability of the oil droplets against coalescence. Furthermore, SDS molecules form micelles as discussed in sections 1.3.2 and 1.5.5. Thereby, the micelles, subject to Brownian motion will act as depletants, and will generate an effective short-range cohesive interaction among the oil droplets (see section 1.5.6 on depletion interaction), which can be controlled by the concentration of the depletants, *i.e.* SDS micelles. Given

that SDS is an anionic surfactant, and adsorbs on the surface of the oil droplets, NaCl is added to the solution to screen the surface charges due to SDS molecules (see section 1.5.4 on double-layer repulsion).

2.2.1 Preparing solutions

Solutions are prepared using filtered deionized water, sodium dodecyl sulphate (Bio-Shop) and NaCl (Caledon). In order to calculate the depletion force properly, the effect of NaCl on SDS micelle formation should be considered. It has been shown that the critical micelle concentration (CMC) of SDS reduces as NaCl is added to the solution [105, 106]. While CMC of SDS in pure water is 8 mM, CMC drops to less than 1 mM for $C_{\text{NaCl}} = 260$ mM. This means that at higher NaCl concentrations, fewer SDS molecules remain in the solution, as most of them exist in the micellar form. As mentioned in section 1.5.5, the concentration of micelles C_{m} is found as follows:

$$C_{\rm m} = C_{\rm SDS} - C_{\rm CMC} \;.$$
 (2.2.1)

Therefore, the strength of the depletion force F_{adh} between two droplets of radius r can be found according to the C_m , based on the experimental work of Ono-dit-Biot *et al.*. [1], by the following formula:

$$F_{\rm adh} \propto r C_{\rm m}$$
 . (2.2.2)

For paper 1, the concentration of SDS ranges between 0.68% to 5.00% (w/w) $(C_{\rm m} \sim 23 \text{ mM} \text{ to } 173 \text{ mM})$ with NaCl concentration kept constant at 1.50% (w/w) (260 mM) $(C_{\rm CMC} = 1 \text{ mM}$ and the Debye screening length: $\kappa_D^{-1} \sim 0.6 \text{ nm}$).

For paper 2, the concentration of NaCl is 260 mM for SDS concentrations between 0.3% (w/w) to 8% (w/w) ($C_{\rm m} \sim 10$ mM to 278 mM). However, to explore ultra-low SDS concentrations, 0.03% (w/w) to 0.1% (w/w) ($C_{\rm m} \sim 0.0$ to 1.5 mM), I lowered the concentration of NaCl to 0.5% (w/w) (85.5 mM). Lowering NaCl concentration increased the CMC and consequently lowered the micelle concentration, therefore minimized the depletion interaction, while maintaining droplet stability. When the concentration of NaCl is 260 mM, even a very small amount of SDS will form micelles, resulting in an effective cohesion. Therefore, at high NaCl concentrations, getting the right amount of SDS to stabilize the oil droplets without having micelles is challenging. But at lower NaCl concentrations, more SDS molecules will be present in the molecular form in the solution and less in the micellar form. This lower NaCl concentration is enough to screen the charges due to the anionic SDS molecules ($\kappa_D^{-1} \sim 1$ nm for the lower NaCl concentration).

2.2.2 Producing droplets

The droplets are produced using the snap-off method, which is a reliable way of producing highly uniform (or monodisperse) droplets. This method was developed in our laboratory and details of this method and its underlying mechanism are given in the two articles by Solomon Barkley *et al.* [100, 101]. In this section, I briefly touch upon the overall way of producing droplets, followed by some experimental tips, regarding the snap-off technique. I also provide the rationale for the tips, based on the principles of the snap-off instability.

We start with a syringe, filled with a liquid of choice for making the dispersed phase, *i.e.* the droplets. The liquid of choice in my experiments was light paraffin oil (Sigma-Aldrich). The syringe needle is connected to a plastic tubing (inner diameter: 1/32")(Tygon S3, formula E-3603), which is subsequently filled with oil. This tubing is then connected to the prepared micropipette (pulled and bent by 90° at two places as explained in section 2.1.1). Paraffin oil is then pushed by the syringe to fill the entire micropipette. The micropipette is then positioned in the solution (*i.e.* the continuous phase) under the funnel. While monitoring the tip of the micropipette, we pull the plunger slightly back, such that some aqueous solution wets the inner part of the micropipette tip. This step is essential to initiate the snap-off instability. We then slightly increase the oil pressure, such that droplet production starts. As long as the extrusion pressure remains constant, droplet production can run smoothly for days.

To maintain constant extrusion pressure, we detach the needle from the syringe and secure it at a height, where the droplet production is not interrupted. The snap-off instability is influenced by the oil flow rate and consequently the extrusion pressure. By fixing the needle (which has a small reservoir) and exposing it to air pressure, we ensure a nearly constant extrusion pressure. As the droplets are small, there will be a negligible change in the oil level in the reservoir, even after days of droplet production.

A few practical recommendations are presented here, such that the snap-off technique runs smoothly: The snap-off instability works based on the backflow of the continuous phase into the micropipette to pinch off the dispersed phase. Therefore, if the tip of the micropipette is broken in an irregular shape and not flat, backflow runs more smoothly [101]. Furthermore, due to the spontaneous backflow of the continuous phase, unwanted particles from the chamber might move into the micropipette and even block the tip entirely, which disrupts the droplet production. Therefore, cleanliness of the whole experimental chamber is of immense importance.

Another point is that the droplet production usually stops after around 7 days. If one needs to salvage the micropipette, the first step this author suggests is to change the tubing. We suspect that the tubes leach into the oil and change the viscosity of the dispersed phase. While this point is not scientifically proven, we have observed swelling of the tubing upon a few days of exposure to paraffin oil.

Lastly, it is insightful to mention a point about liquid of choice for droplets. We chose light paraffin oil (Sigma-Aldrich), which has a lower viscosity compared to mineral oil (used by most laboratory members previously). Barkley *et al.* have shown [100] that upon increasing the flow rate of oil, there is a distinction between lower viscosity and higher viscosity liquids. When increasing flow rate of a more viscous liquid, the size of the droplets increases. Whereas for a less viscous liquids, the droplet size does not change significantly for the same increase in flow rate. Instead, the rate of droplet production increases with a negligible change in size. Therefore, light paraffin oil allows for a more reliable way of producing smaller droplets at a relatively high rate.

2.3 Imaging and data analysis

All the images were taken using optical microscopy. A 4x objective (Nikon), accompanied by a camera (ThorLabs, USB2.0 Digital Camera) captured front-view images, similar to the viewpoint shown in Fig. 2.1 (a). The areas of interest for the first and second experiments are highlighted using boxes in Fig. 2.1 (a), followed by the microscopy images in Fig. 2.1 (b) and (c). In order to capture high quality images, a good light source is needed. I used a light sheet (Advanced Illumination, Side-fired Backlight) to uniformly illuminate the cuvette from behind.

For experiment 1, the data extracted from the images was the volume of the droplet clusters. For experiment 2, we were interested in finding the angle of repose of the conical pile.

The criteria for choosing the proper clusters for experiment 1 is fully explained in paper 1. After deciding which clusters make it to the analysis, the images are cropped, such that only one cluster per image remains in frame, and no other object or isolated droplet exists in the image. Image pre-processing was done manually using Fiji ImageJ [107]. Next, we find the coordinates of the edge of the cluster, using an edge-detection script, based on the Sobel filter [108] from scikit-image [109] package in Python. The Sobel filter operates by calculating the intensity gradient of an image in both horizontal and vertical directions. By applying a threshold to these gradients, edges can be identified. To find the volume of the clusters, we assume that the clusters are axisymmetric, as the orifice they extrude from is circular and does not put any directional bias on the clusters. Therefore, we find the cluster volume from the area of the 2D projection of the cluster. More details are given in paper 1.

For experiment 2, we extract the angle of repose of the pile from the images. Given the limited number of images, image processing was done manually using Fiji ImageJ [107]. More details are given in paper 2.

Chapter 3

Paper 1: The pendant drop experiment for aggregates of cohesive granular particles

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3.1 Paper introduction

In this paper, we investigate the extrusion of densely packed aggregates of oil droplets in an aqueous solution from an orifice. The droplets are monodisperse and frictionless with controlled cohesion. The flow of particles through the orifice is slow, such that the system is in a quasistatic state. We observe that an aggregate flows out of the tube and remains dangling, until it grows to a certain size, after which a cluster detaches due to the buoyant force, overcoming the interparticle cohesion. This observation is similar to the pendant drop experiment, except that instead of a molecular liquid, we have an aggregate of densely packed droplets. We vary the cohesion among the droplets, the droplet size as well as the orifice size and find that the average volume of the clusters is proportional to the area of the orifice, as well as the *granular capillary length*, which compares the effects of cohesion and buoyancy. This finding is in contrast to the liquid pendant drop, as the volume of the drop is proportional to the perimeter of the orifice and not the area.

The idea for this project and initial experimental setup came from Jean-Christophe Ono-dit-Biot. He gathered preliminary data and performed image analysis to find the volume of the granular pendant drops. I changed the setup, with help from Kari Dalnoki-Veress to a great extent to improve the overall robustness of the experiments and to restrict the aggregate flow, such that individual clusters can form, and the whole aggregate does not readily flow out of the orifice. All of the data used in this paper was obtained by me. I took the core piece of the code for edge detection from Carmen Lee (one of the group members at the time) and expanded upon that to develop a system for data analysis and taking insights from the data. The base idea for how to find the volume of the clusters was given by Kari Dalnoki-Veress and Jean-Christophe Ono-dit-Biot. The theory was collaboratively developed by myself and Kari Dalnoki-Veress. I prepared the first draft of the manuscript, which was edited by other contributors.

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The pendant drop experiment for aggregates of cohesive granular particles^{\dagger}

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The pendant drop experiment can be used to study the interfacial tension of a liquid. Here we perform a similar experiment for a granular system. When a dense aggregate of cohesive particles extrudes from an orifice, a cluster of particles detaches, similar to the detachment of a liquid drop. We investigate the volume of the clusters formed from close-packed cohesive oil droplets in an aqueous solution. Our findings reveal that the volume of the clusters depends on the size of the orifice as well as the cohesion strength. Interestingly, we observe that the droplet size does not significantly impact the average cluster volume. We establish a scaling law that governs the size of a granular cluster which differs from that of a classic pendant drop. We propose that the key difference between continuum and granular systems is the constraints on rearrangements within the cohesive particles that prevent the clusters from adopting a minimal surface structure, as is the case for a classic pendant drop.

Introduction

The contrast between pouring ketchup slowly from a bottle and water dripping from a faucet raises the question: what determines the size of drops in these distinct cases? While the answer to this question is solved for simple molecular liquids by Tate in 1864¹, the answer is not so obvious for the case of complex fluids, cohesive granular materials, suspensions and emulsions. Extrusion of dense aggregates of cohesive particles and foams is commonplace. Of particular interest is the size of clusters of dense drop-like aggregates as they extrude from an orifice due to gravity or other driving forces. These granular aggregate 'drops' are relevant to many industrial applications, such as spraying, ink-jet printing and the food industry^{2–4}. In addition, clusters of granular particles and suspensions play a vital role in advanced technologies such as drug delivery⁵ and bioprinting^{6,7}, where precise control over cluster size is paramount.

The classic pendant drop experiment is a simple method for studying the surface or interfacial tension of liquids⁸. Typically a needle, connected to a reservoir, is filled with a liquid. The liquid is slowly pushed through the needle such that the system remains in a quasi-static state, and a drop of liquid forms at the tip of the needle. The capillary force stabilizes the drop against

gravity. As the pendant drop grows, gravity eventually overcomes capillarity and the drop detaches from the needle. The volume of the detached drop V is obtained from a simple force balance between the gravitational and capillary forces, as determined experimentally by Tate in 1864, and commonly referred to as Tate's Law¹.

Multiple studies have shown that the presence of cohesive forces in granular materials can lead to properties which are reminiscent of liquids with surface tension. For example, the breaking up of a jet of granular particles into drop-like clusters downstream⁹⁻¹², is strikingly similar to the Plateau–Rayleigh instability seen when a thin jet of water breaks up into drops. Cohesive forces are the primary origin of cluster formation, regardless of the source of cohesion: be it capillary bridges, van der Waals forces, or even both^{9,11,12}, surface charges, and even geometrical constraints between particles¹³. Collectively, one can conclude that the interparticle cohesion in granular materials can result in effects that are analogous to the capillary forces of molecular liquids.

The pendant drop experiment can be used to study drop formation of complex fluids like suspensions, dispersions, and cohesive granular materials. In the granular version of the pendant drop experiment, an aggregate of cohesive particles or a suspension with desired particle density is slowly pushed through an orifice. Gravity pulls on the aggregate and the cohesion among the particles stabilizes the formation of a drop-like cluster, similar to the role of surface tension in liquids. The cluster grows until a certain size is reached, after which the cluster detaches from the orifice. However, due to the athermal nature of some suspensions

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and granular materials, the particles do not readily rearrange and the stress must be large enough to cause a wholesale rearrangement for the detachment of a cluster. Considering the yield stress characteristics of such amorphous materials, it is instructive to investigate how drop-like clusters form in these systems¹⁴.

While drop formation and pinch-off of simple liquids has been studied extensively¹⁵, formation of drop-like clusters, or 'granular drops' is not fully understood. Unlike a drop of liquid with the number of molecules approaching Avogadro's number, granular drops may be composed of tens to a few thousand particles. Given the relatively low particle number, heterogeneities, like local variations in packing fraction, as well as specific local rearrangements are important. The formation of granular drops has been studied over the years, using different granular systems, and with suspensions of varying particle densities. Current studies on granular pendant drops mostly focus on the effect of granular-ity on the dynamics of pinch-off^{16–20}. The ability to control the volume of the granular drops is especially critical for advanced applications, such as drug delivery⁵ and bioprinting^{6,7}.

Here we use densely packed oil droplets with controlled cohesion in an aqueous solution. The effect of gravity on the buoyant oil droplets causes the aggregate to extrude slowly from an orifice, while the cohesive interaction stabilizes the growing granular drop. We characterize the volume of the detached clusters, while varying the cohesion strength, the orifice size, and the droplet size. We find that the average volume of the clusters is proportional to the orifice area, which is in contrast with the case of the classic liquid pendant drop experiment where the volume depends linearly on the orifice perimeter. Moreover, the volume depends on a parameter that emerges from a balance between the cohesion strength and the effective buoyancy, termed the granu*lar capillary length*, δ^{21} . Note that for brevity we refer to *effective* buoyancy and imply the contribution of both the force of gravity (dependent on the density of the droplet), and the buoyancy (dependent on the density of the aqueous solution). We conclude that the overall properties of our cohesive granular system is reminiscent of viscoplastic materials under tensile stress²², and that the volume of the granular drop remains, on average, self-similar, despite the nuances due to granularity.

Methods

The experimental setup

A schematic diagram of the experimental setup is shown in Fig. 1 (a). The experiment is carried out in a cuvette (BRAND, Germany), which is filled with an aqueous solution of a surfactant, sodium dodecyl sulfate (SDS)(BioShop), and NaCl (Caledon). A layer of mineral oil is added on top of the solution, to prevent evaporation and ensure a constant concentration.

The surfactant serves two purposes. First of all, SDS stabilizes the oil droplets against coalescence. Second, since SDS forms micelles above the critical micelle concentration (CMC), the SDS induces a tuneable short-range cohesion due to the depletion interaction. The SDS micelle concentration, $C_{\rm m}$, is then simply achieved by deducting the value of the CMC, $C_{\rm CMC}$, from the SDS concentration, C: $C_{\rm m} = C - C_{\rm CMC}$. Ono-dit-Biot *et al.*²¹ have



Fig. 1 (a) Schematic of the experimental setup. A cuvette is filled with an aqueous solution. i) is the funnel, where droplets accumulate, ii) is the funnel holder. iii) is the lid that seals the funnel. iv) is the micropipette that produces the droplets and v) is an oil layer that prevents any evaporation. (b) An optical microscopy image, showing the tip of the funnel at the bottom and a cluster of oil droplets. The cluster rises because of buoyancy. The specific parameters in (b) are: $C_{\rm m} = 104$ mM, $R = 44 \ \mu {\rm m}$ and $r_{\rm d} = 12.6 \ \mu {\rm m}$. The scale bar on the right is 250 $\ \mu {\rm m}$. The edge of the cluster is shown in blue. The cluster height $h_{\rm max}$ and width of the cluster at height z, w_z are shown.

experimentally shown that the cohesive force, $F_{\rm adh}$, is linearly proportional to the micelle concentration, as well as the droplet size, $r_{\rm d}$: $F_{\rm adh} \propto r_{\rm d}C_{\rm m}$. The SDS micelle concentration ranges from ~ 23 mM to 173 mM. Based on previous experiments²¹, this range of SDS concentration gives rise to cohesion strengths, $\mathcal{A} = F_{\rm adh}/r_{\rm d}$, of 2.87 μ N/m to 21.62 μ N/m. As SDS is an ionic surfactant, NaCl is added to the solution to screen electrostatic interactions among SDS molecules. The NaCl concentration is held constant at ~ 260 mM (1.50% (w/w)) for all the experiments. It has been shown that the presence of NaCl in an aqueous solution of SDS decreases the CMC from 8 mM for SDS in pure water, to ~ 1 mM for the NaCl concentration that we work with^{23,24}. Therefore, $C_{\rm CMC} = 1$ mM is used to obtain $C_{\rm m}$

The droplets are made, using a micropipette. To prepare the micropipettes, we pull glass capillary tubes with an outer diameter of 1 mm, and an inner diameter of 0.58 mm (World Precision Instruments, USA), using a pipette puller (Narishige, Japan), so that a long tapered end forms (Fig. 1 (a)), with a tip opening in the range of tens of micrometers. We then bend the micropipette with heat to 90° at two points. With the micropipette located appropriately within the experimental chamber, the droplets are produced and fill a capped funnel as shown in Fig. 1 (a)). Light paraffin oil (Sigma-Aldrich) is pushed through the micropipette via a tubing (inner diameter 1/32"; Tygon S3, formula E-3603) that is connected to a reservoir open to atmospheric pressure. The height of the reservoir controls the the pressure at the pipette tip and determines the rate of droplet production via the snap-off instability^{25,26}. When the pipette is immersed in the solution, droplets are produced at a frequency of about 1 Hz. Once the droplet production starts, it can continue for days. This method is a reliable way of making highly monodisperse droplets²⁵. We note that the degree of polydispersity is bounded by the uncertainty of droplet size measurement²⁵, which is approximately 0.4 μ m in this study. Barkley et al.²⁵ have shown that the size of the droplets produced by the snap-off method is proportional to the size of the micropipette tip. We control the droplet size by controlling the size of the micropipette tip and use droplets with radius, r_d , that ranges from ~ 5.0 μ m to 13.5 μ m.

The funnel is manually made by heating a glass pipette over an alcohol burner (outer diameter: 1.8 mm, inner diameter: 1.5 mm)(Kimble, USA), then pulling it. We cut the pulled glass at a certain length with desired width, then heat it again, so that the glass gently melts to form a small and smooth circular orifice, without the orifice closing. The tip is then polished so that the orifice is flat and perpendicular to the pipette using sandpaper (grit 600 up to 1000). This process can be used to fine-tune the orifice size. Here we use three different funnels with orifice radii, R, of 44 μ m, 70 μ m and 93 μ m. The funnel is covered by a removable lid that is 3D printed using PLA, so an aggregate of droplets can form. When the aggregate is big enough to produce ~ 200 clusters, we remove the lid and start the experiment. A microscope, consisting of a camera (ThorLabs, USB2.0 Digital Camera) equipped with an objective (4x, Nikon) records images, as shown in Fig. 1 (b). A video of a typical experiment can be found in the ESI[†].

Cluster characterization

Image analysis is performed using custom-written code and direct length measurements were done on Fiji ImageJ²⁷. The occupied volume of the clusters is found as follows. Fig. 1 (b) shows a raw image of a sample cluster. The edge of each cluster is detected, using a code, based on the Sobel filter^{28,29}. Knowing the coordinates of the edge, we determine the width of the cluster, w_z , at any vertical coordinate z. Using the edge detection results, we also find the maximum height of the cluster, h_{max} .

Since we image along one projection and the funnel is axisymmetric, we assume that the clusters do not have a directional bias and are thus axisymmetric as well. As a result, the cross section of the cluster is estimated as a circle with diameter w_z , and the volume element will be a disc with the diameter w_z and the thickness dz, which is one pixel: $dV = \pi (w_z/2)^2 dz$. To find the apparent volume of the cluster, V_{app} , we simply do a discreet integration of the volume of each disc dV, over the height of the cluster:

$$V_{\rm app} = \int dV = \frac{\pi}{4} \int_0^{h_{\rm max}} w_z^2 dz. \tag{1}$$

The relevant parameter here is the occupied volume of the cluster rather than the apparent volume, as it is the oil droplets that generate the buoyant force. To find the occupied volume, we multiply the apparent volume, V_{app} , by the packing fraction ϕ , $V = \phi V_{app}$. For simplicity, we assume that ϕ is constant. The value for the packed aggregate is a number between random close packing and hexagonal close packing, ranging from 0.64 to 0.74. For all the results shown in this article, we have chosen the packing fraction to be 0.7. We stress that all volume values presented are the



Fig. 2 (a) Volume of the clusters plotted for an experiment in chronological order. The red line shows the average volume and the black line shows the moving average over a window of 20 clusters. Despite the high number of clusters (N = 187), no meaningful change is observed in cluster volume. In this particular experiment, the parameters are: $C_{\rm m} = 156$ mM, $R = 70 \,\mu$ m, and $r_{\rm d} = 10.2 \,\mu$ m. (b) Volume distribution, from which an average volume can be extracted.

occupied cluster volume, V, and not the apparent volume V_{app} .

Cluster selection

To promote cluster formation rather than extrusion of droplets in a jet, we maintain a low flow rate for aggregates exiting the orifice with Reynolds number, Re ~ 0.01 (this is obtained using the speed at which the cluster forms, not the motion of the cluster in the solution). This low flow rate is controlled by two factors: first, the dome-shaped geometry of the funnel, which restricts the flow³⁰, and second, limiting the number of droplets in the funnel to reduce the hydrostatic pressure exerted by the aggregate in the funnel.

We choose a time-window of each experiment for analysis based on two criteria: first, we select clusters from the later stages of the experiment because the lower hydrostatic flow results in slow cluster production; second, we plot the cluster volume time series for each experiment and ensure that the volume of clusters does not meaningfully change. This approach provides enough clusters for a reliable statistical analysis while minimizing the effect of hydrostatic pressure on cluster size and ensuring that we are in a quasi-static regime for cluster pinch-off.

An example is shown in Fig. 2 (a), where we plot the volume of the clusters in chronological order for a typical experiment. To show the long-term trends in the cluster volume, we smooth the data by plotting the simple moving average (SMA) for 20 consecutive clusters. The total average cluster volume is shown as a reference. The moving average shows that the volume fluctuates around a mean value and is not impacted by the small hydrostatic pressure acting on the aggregate in the funnel. The volume distribution is shown in Fig. 2 (b), and the volume fluctuation is in part due to the granular nature of the system, which affects the dynamics of cluster pinch off²⁰. For each experiment, we take the average cluster volume as the characteristic volume and the standard deviation as the 'error'.

Another consideration in cluster selection is the formation of small satellite clusters, which can be seen in Fig. 3. These are the smaller clusters that occasionally form when the main cluster



Fig. 3 The formation of a cluster. The droplets rearrange to form a long neck, similar to homogeneous liquids 31,32 . The cluster forms a neck, which can break up at multiple points to form a satellite cluster. The time interval between any two consecutive image is 0.25 seconds. The parameters for this particular experiment are: $C_{\rm m}=173$ mM, $R=93~\mu{\rm m}$ and $r_{\rm d}=4.9~\mu{\rm m}.$

is pinching off. Due to rearrangement of the droplets in the thin neck, packing fraction varies locally, leading to break up at multiple points and leaving a smaller cluster trailing the main cluster. Since the size of these small clusters is not set by balance between cohesion and the effective buoyancy, which is the focus of this work, we exclude the small fragments of satellite clusters.

Results and discussion

In a pendant drop experiment for a molecular liquid (continuum liquid), the volume of a detached liquid drop, V, is given by Tate's Law and obtained from a simple force balance between the gravitational and capillary forces^{1,33}. The detached drop volume is $V \propto R \frac{\gamma}{\rho g}$, where γ is the surface tension, ρ is the density of the liquid, R is the orifice radius, and g is the gravitational acceleration. The capillary length is a length scale that characterizes the importance of gravity compared to surface tension, and is given by $\kappa^{-1} = \sqrt{\gamma/\rho g}^{33}$. We can then rewrite the volume of the detached drop as $V \propto R(\kappa^{-1})^2$.

Although classic and granular pendant drops share similarities, they differ significantly in particle rearrangement. In the classic pendant drop, the liquid molecules rearrange rapidly compared to the time scale of drop formation. This rapid reorganization, driven by thermal motion, enables the liquid to minimize surface area through capillary forces. As a result, a spherical drop with minimum surface-to-volume ratio forms upon detachment. In contrast, the particles in the granular pendant drop studied here do not rearrange rapidly because they are athermal. Furthermore, the cohesive, monodisperse droplets in the granular case form relatively stable crystalline structures upon aggregation. For wholesale rearrangement to occur, bonds between neighbouring droplets must break, requiring an external stress on the aggregate. When stresses remain below a threshold determined by the macroscopic cohesion strength³⁴, the aggregate retains its shape. Ono-dit-Biot and colleagues studied the rearrangement of a single layer of monodisperse oil droplets under compression, observing that the aggregate withstands compressive stress up to a yield point³⁵, after which a wholesale rearrangement occurs. This resistance to rearrangement influences the shape of the resulting cluster. In the present study, dense aggregates extrude from a circular orifice. Therefore, the aggregate adopts a near-cylindrical shape as it exits. Due to lack of sufficient compressive stress in the vertical direction, the cluster retains its shape. As the cluster detaches, a long neck starts to form, due to the tension in the vertical direction and gives rise to the spindle-like shape of the cluster shown in Fig. 3.

A total of 36 experiments are carried out with eight different values of the micelle concentration, three funnel opening sizes, and droplet sizes ranging from ~ 5.0 μ m to 13.5 μ m. For each experiment we obtain the average volume of the clusters, $\langle V(C_{\rm m}, r_{\rm d}, R) \rangle$, as described above and shown in Fig. 2. Just as gravity opposes the capillary force for the classic pendant drop experiment, we assume that the forces that affect the cluster volume are the cluster cohesion and the effective buoyancy. We further assume that the quasi-static experiments minimize the contribution of viscous dissipation. Furthermore, the droplets can be treated as frictionless since we can assume no friction at liquid interfaces^{21,35–37}.

We first qualitatively investigate the role of cohesion strength and funnel orifice size on the cluster volume. Fig. 4 (left box) shows typical clusters from two experiments in which the droplet size and orifice size are kept constant, while the SDS micelle concentration is varied. We observe that higher cohesion leads to larger clusters. This observation makes sense in the light of our assumptions: with R and r_d held constant, the number of droplets in contact at the orifice area is the same between the two experiments. However, with a higher cohesion the effective buoyant force needed for a cluster to detach must be larger, resulting in the formation of a larger cluster.

Next we turn to the qualitative dependence of the cluster size on the orifice size, while keeping the cohesion strength and droplet size constant. As can be seen in Fig. 4 (right box), we observe that a larger orifice results in a larger cluster when compared to the smaller orifice. This correlation is consistent with the assumptions: even though the cohesive force remains unchanged, as we increase the orifice size, the cross-sectional area, and hence the number of droplets in contact at the orifice area increases. Therefore, a higher effective buoyant force is required to form a cluster emerging from a larger orifice.

The results for all the experiments are shown in Fig. 5 (a), where the average occupied volume of the clusters, $\langle V \rangle$ is plotted as a function of the SDS micelle concentration, $C_{\rm m}$. The data show that increasing cohesion results in larger cluster volumes.

We can develop a simple model for the the dependence of the average cluster volume as a function of the experimental parameters. In the experiments, an aggregate of oil droplets experiences an upwards body force due to the effective buoyancy which depends on the density difference $\Delta \rho$ between the oil droplets and the aqueous solution. Just as capillary forces in the classic pendant drop experiment, here the forming cluster is stabilized by the cohesive force $F_{\rm adh}$ between the droplets, which prevents the droplet particles from emerging one by one. The cohesion strength in the granular pendant drop is defined as $\mathcal{A} = F_{\rm adh}/r_{\rm d}$, and dimensionally, this is a force per unit length²¹. This cohesion strength is analogous to the surface tension of the liquid γ in the classic pendant drop. In analogy with the definition of the capil-



Fig. 4 Left box: The effect of micelle concentration on the cluster size. Both the orifice size and droplet size are kept constant at $R = 44 \ \mu m$ and $r_d = 13 \ \mu m$. Cohesion strength among the droplets is lower in (a) than in (b). As a result, clusters in (a) are smaller than in (b). Right box: The effect of orifice size on the cluster size. Both the micelle concentration and droplet size are kept constant at $C_m = 104 \ \mu m$ and $r_d = 13 \ \mu m$. Orifice size is smaller in (c) than in (d). As a result, clusters in (c) are smaller than in (d).

lary length for simple liquids, $\kappa^{-1} = \sqrt{\gamma/\rho g}$, we can define the granular capillary length, δ , as²¹:

$$\delta = \sqrt{\frac{\mathcal{A}}{\Delta \rho g}} \,. \tag{2}$$

The granular capillary length sets a natural length scale for our system of droplets 21,36 , since it results from a balance between the effect of cohesion among the droplets and the effective buoyancy.

In order to formulate a quantitative description for the volume of the granular pendant drop, we use a simple scaling argument. There are three natural length scales in our system: the droplet radius, r_d , the orifice radius, R, and the granular capillary length, δ . Given the relatively large number of droplets in each cluster, we assume that the packing fraction is independent of the size of the droplets, and hence, the cluster size is also independent of the size of the droplets, *i.e.* r_d does not affect the volume of oil in the clusters which causes the effective buoyancy. As will be shown below, this assumption is validated by experiments. In 3D we can then write that $V \propto R^{3-\alpha}\delta^{\alpha}$. The vertical scale of the cluster depends on the balance between the effective buoyancy and adhesion, given by δ , suggesting a linear dependence of the volume on δ with $\alpha = 1$. We conclude then that the occupied cluster volume can be written as:

$$V = \xi R^2 \delta , \qquad (3)$$

with ξ a constant of proportionality of order 1. We note that the R^2 dependence of the cluster volume is intuitive: The droplets are cohesive and the aggregate takes on and maintains the shape of the orifice – the cross-sectional area of the cluster is set by the area of the orifice and the aggregate has paste-like properties. The clusters do not adopt a spherical shape, as one would expect for a simple liquid, but take on a spindle-like shapes as they extrude from the circular orifice, similar to viscoplastic materials, such as mayonnaise and toothpaste²².

We can test the proportionality relation of eqn 3 by plotting the average occupied volume $\langle V \rangle$ first versus δ for an intermediate



Fig. 5 (a) Average cluster volume plotted versus the micelle concentration. The error bars in all the plots represent the standard deviation of the data. (b) Average cluster volume is plotted versus δ to show an intermediate collapse in accordance with eqn 3, where the data from any orifice falls on the same line. Darkest line corresponds to the smallest orifice and lightest corresponds to the largest orifice. (c) Average cluster volume as a function of $R^2\delta$ as suggested by eqn 3 with $\xi=2.58\pm0.15.$ (d) Normalized cluster volume versus droplet radius. The line of best fit shows a negligible correlation with a slope of -0.06 \pm 0.04 .

collapse and then versus $R^2\delta$. The results are shown in Fig. 5 (b) and (c). We see an excellent collapse of the data for the 36 experiments. The best fit lines are given by eqn 3 with $\xi = 2.58 \pm 0.15$. We note that as expected from the model, ξ is a constant of order 1. Lastly, above we made the assumption that r_d does not play a role in determining the average cluster volume. We can test this assumption by plotting the normalized volume $\langle V \rangle / R^2 \delta$ versus r_d . The results in Fig. 5 (d) show that the data is consistent with no dependence of the cluster volume on the droplet size; if there is a dependence, the dependence is clearly weak.

Conclusion

In conclusion, we have developed an experimental setup to replicate the pendant drop experiment for dense aggregates of cohesive droplets. We have studied the resultant cluster size as a function of cohesion strengths, orifice, and droplet sizes. We find that the volume of the cluster is proportional to the orifice area multiplied by the granular capillary length, a characteristic length of the system that emerges from a balance of cohesion and buoyancy, $\delta = \sqrt{A/\Delta\rho g}$. The emergence of the granular capillary length as a critical parameter has appeared in other works as well^{21,36}. The scaling law in this cohesive and frictionless granular system, $V \propto R^2 \delta$, is different from that of the classic pendant drop, where Tate's Law shows that $V \propto R(\kappa^{-1})^2$. The crossover from the linear dependence on R for a molecular liquid, to the dependence on R^2 for the granular system, is due to the wholesale rearrangements of particles required in the athermal system and the paste-like response of the droplet aggregates. Thus we find a difference in the shape of the granular pendant drop and the scaling law, when compared to molecular liquids. We expect that as one decreases the size of particles that make up the granular aggregate and reduces the cohesion, thermal effects become important enabling rearrangements within the system. One would expect a crossover from a square dependence on the orifice size to a linear dependence when the system becomes thermalized, akin to the molecular system.

Conflicts of interest

There are no conflicts to declare.

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Chapter 4

Paper 2: Angle of repose in aggregates of confined frictionless cohesive particles

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4.1 Paper introduction

In this paper, we work with a monodisperse system of oil droplets in an aqueous solution. The droplets are frictionless and their cohesion can be precisely controlled. Upon slow accumulation in a vertical tube, the aggregate forms a conical pile, resembling a sand pile. This is surprising, as previous studies on spreading of similar oil droplets against an infinite barrier [1, 32] show that the aggregate grows to a certain height then spreads horizontally, similar to a liquid puddle. Therefore, we conclude that the formation of a conical pile is a consequence of geometrical constraints on the aggregate, due to the tube walls. In addition, we observe that the pile does not go through avalanches, but collapses: a pile of dry granular material goes through intermittent avalanches, where particles flow on the edge of the pile. In our system of frictionless cohesive droplets, a small heap will form on top of the conical pile, which collapses periodically into the pile. We vary the droplet size, the cohesion strength and the diameter of the tube and measure the angle of repose of the conical pile. Based on the Coulomb's friction criterion, we find that the angle of repose is directly proportional to the *granular capillary length*, which captures the effect of cohesion among the droplets, and inversely proportional to the droplet size. We also find that the angle of repose is independent of the tube size. Another interesting observation is a non-zero angle of repose, where the cohesion due to depletion forces is effectively zero. While simulations like [34] have already established a non-zero angle of repose in lack of cohesion and friction, the value of the angle of repose that we find is larger than the predicted values. Therefore, we suggest that attractive van der Waals forces are at play in the absence of depletion interaction.

The idea of this experiment was inspired by my observations in experiment 1, presented in paper 1. When droplets accumulated in the funnel, they formed a perfectly conical pile, which was intriguing. I then pursued this observation and made it into a project with encouragement from Kari Dalnoki-Veress. I planned and conducted all the experiments and collected all the data. In addition to data analysis, I developed the theory and prepared the first draft of the manuscript.

Angle of repose in aggregates of confined frictionless cohesive particles[†]

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While spreading of conventional granular materials onto a surface results in a conical pile due to interparticle friction, spreading of frictionless cohesive particles (specifically oil droplets) against an infinite barrier results in a puddle-like structure. We have performed spreading experiments with frictionless cohesive oil droplets in a confined tube, and surprisingly, the aggregate takes a conical shape with a distinct angle of repose, deemed as effective friction. The barrier's presence gives rise to an effective friction, which increases with increasing interparticle cohesion and decreasing particle size. We observe that the collapsing dynamic differs from an avalanche in conventional granular materials. Using the Coulomb's friction criterion, we find the dependence of the effective friction on the relevant parameters. Our theory also suggests that the effective friction is independent of the tube size, in line with experiments. The reason is that particles can slide on the walls without friction. Our findings emphasize how the presence of edges fundamentally change the bulk properties of granular materials.

INTRODUCTION

From migration of giant sand dunes in deserts [1, 2] to flow of drug powders in pharmaceutical facilities [3], flow and spreading of dense granular materials are common in various settings and across vast length scales. Therefore, characterizing the flow properties of granular materials is essential, not only from a fundamental point of view, but also for designing material handling equipment to avoid flow problems, such as obstruction and flooding.

Upon slow accumulation against a boundless surface, dry granular materials form distinct conical piles, characterized by the base angle θ , termed the angle of repose [4–6]. Measuring the angle of repose of a pile of granular matter is a simple way to characterize the effective friction of the material μ [7]. Internal friction, material flowability, and the angle of repose are closely connected [7]. For a heap of frictional granular material, less friction between particles results in greater flowability and a shallower angle of repose.

Fundamentally, the bulk properties of granular materials depend on their packing fraction and interparticle forces [4, 5, 8]. In a dry sand pile, the interparticle forces are mainly frictional, and the pile is subject to gravity. As the grains spread, the interplay of gravity and friction creates an equilibrium state—a conical pile.

However, in many naturally occurring systems, both friction and cohesion from various sources (Van der Waals forces, capillary bridges, electrostatic forces, etc.) are present. Multiple studies [9–11] have shown that introducing cohesion among frictional particles via an interstitial liquid results in a pile, with a steeper angle of repose.

The reason is that cohesive forces contribute to the material strength, as reflected in the Coulomb failure criterion for cohesive materials [12].

To isolate the effect of cohesion, we should study an assembly of non-frictional granular particles, where cohesion is the only interparticle force. However, controlling cohesive interactions experimentally has been challenging, as capillary bridges are often the primary source of cohesion in most experiments. But recent studies on cohesive granular materials have achieved good control over the cohesive force [13, 14]. Despite this, interparticle friction is still present in these systems. Although achieving a perfect model system of cohesive frictionless particles with conventional granular materials remains challenging, our research group has pioneered in the development of such model, using oil droplets in an aqueous solution [15, 16]. The droplet size can be tuned, such that a crystalline or an amorphous systems can be explored [17–20].

Spreading experiments on systems of frictionless cohesive particles have been conducted by Ono-dit-Biot [18] and Hoggarth [20]. The results show that the droplet aggregate grows to a certain height, after which it spreads only horizontally, similar to a liquid puddle. As more droplets are added, the buoyancy of the central stream of oil droplets pushes the aggregate outward in all directions. Since the droplets can move against the surface without friction, the aggregate cannot withstand shear force, preventing the formation of a conical pile. In contrast, the presence of friction between a rough surface and a pile of frictional granular matter, the grains at the bottom are pinned to the surface. This friction gives enough support to the pile to sustain shear force up to the point of yielding. We will now discuss how confining non-frictional granular material within edges can provide a support for emergence of a conical pile.

The effect of edges on the flow of granular materials

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is often overlooked, yet edges are relevant in diverse settings. Examples include the flow in confined spaces like hoppers or silos, the effect of mechanical confinement on the early development of organisms [21], and even the spreading rate of cancer cells [22], which depends on the viscosity of the environment. A limited number of studies have investigated how the presence of boundaries affects granular flow [23–25]. However, these studies primarily focus on the effect of wall friction on flow [25], the velocity profile of surface flow [23, 25], or restricted flow in tight channels [24], rather than on spreading properties.

Studies focusing on the role of geometrical constraints show that the combination of confinement and contact forces gives rise to a small but non-zero angle of reposeor angle of internal friction, where applicable [26]—in assemblies of non-frictional, non-cohesive particles [27– 31]. A closely related experimental work to the present study was conducted by Shorts and Feitosa [29] on the spreading of air bubbles in a soapy solution, where the spreading region was confined to a tube. Upon constant replenishment of air bubbles, a non-zero angle of repose $(\theta_{\text{avg}} = 3.75^{\circ})$ was observed. However, due to the unstable nature of air bubbles, the pile was meta-stable and flattened as the flow of the bubbles stopped. Consequently, it remains unclear whether the formation of a conical pile is flow-driven, as in the study by Ortiz et al. [30], or a result of confinement within the tube.

We aim to investigate the static angle of repose of stable droplets confined to a tube, focusing on how the presence of walls influences the spreading pattern of the droplet aggregate. Additionally, we explore how varying cohesive strength between droplets affects their spreading properties.

Specifically, we examine the spreading of frictionless, monodisperse oil droplets in an aqueous solution, where effective interparticle cohesion arises from depletion interactions, giving us precise control over the cohesive force. The experiment is conducted in a tube closed at the top, and we observe that the tube walls provide sufficient support for the frictionless droplets to form a conical pile. However, the tube size does not affect the resultant angle of repose. Even in the absence of cohesion, a non-zero angle of repose is observed, confirming the role of confinement in pile formation. As the cohesive strength increases, the angle of repose becomes steeper

EXPERIMENT

The experiment is conducted within a cuvette (BRAND, Germany), containing an aqueous solution of sodium dodecyl sulfate (SDS)(BioShop) and NaCl (Caledon). A layer of mineral oil is applied atop the solution to prevent evaporation, such that the concentration of both SDS and NaCl remain constant. The concentration of NaCl is constant, but we change the SDS concentration to control the cohesion interaction among the droplets. The droplets are produced from a micropipette and ac-



 $250\,\mu{
m m}$

FIG. 1. (a) The experimental setup inside a cuvette. The cuvette is filled with an aqueous solution of SDS and NaCl. i) shows the confining tube, where the droplets accumulate. ii) is the tube holder and iii) shows the lid that seals the tube. iv) is the micropipette that produces the droplets. The oil droplets float in the aqueous solution and accumulate in the tube. v) is the oil layer to cover the solution and prevent any evaporation. The dashed box shows the field of view of the microscope and the region of interest. (b) An optical microscopy image of the region of interest. The angle of repose θ is shown to guide the eye and does not specifically mean the side from which the angle of repose is extracted. For a full description of measurement, refer to the last paragraph of section "Spreading in a tube".

iv)

(a)

 F_B

iii)

cumulate in a tube, that is sealed at the top with a lid. As the droplets slowly accumulate in the tube, the aggregate forms a conical pile and we measure the angle of repose of the pile at different stages of the experiment. FIG. 1 (a) shows the experimental setup.

SDS has two roles in the system. First, SDS stabilizes the oil droplets by reducing the interfacial tension between water and oil. Secondly, due to the micelleforming nature of SDS, the addition of this surfactant to water above a specific threshold—known as the critical micelle concentration (CMC)—induces a controllable short-range cohesion among the droplets through the depletion interaction. Ono-dit-Biot et al. [18] have experimentally demonstrated that the cohesive force $F_{\rm c}$ is directly proportional to both the depletant concentration $C_{\rm m}$ and the droplet radius $(F_{\rm c} \propto rC_{\rm m})$. The concentration of SDS micelles (depletant) $C_{\rm m}$ is determined by subtracting the CMC value from the SDS concentration C: $C_{\rm m} = C_{\rm SDS} - C_{\rm CMC}$. In our experiments, $C_{\rm m}$ values range from 0.0 to 278.2 mM. Within this concentration range, and the results from previous experiments [18] we conclude that cohesion strength due to depletion $(\mathcal{A} = F_{\rm c}/r_{\rm d} \propto C_{\rm m})$ varies from 0.00 to 34.78 μ N/m. However, direct force measurements[32] show that even at $C_{\rm m} = 0.0$ or even slightly below, there is a cohesive interaction among the droplets, comparable to the Van der Waals force between two spheres. We will get back to this point in the discussion section to address the inAs SDS is an ionic surfactant, NaCl is introduced to the solution to mitigate the electrostatic interaction among SDS molecules. The concentration of NaCl is approximately 260.0 mM for the experiments with SDS micelle concentrations from 34.0 to 278.2 mM, and 85.5 mM for $C_{\rm m}$ from 0.0 to 2.5 mM. When calculating $C_{\rm m}$, one needs to consider that the presence of NaCl reduces the CMC [33, 34]. Less NaCl enables us to explore the system in the absence of depletion interaction, without compromising the stability of the oil droplets. For the exact SDS concentrations, as well as a discussion on the effect of NaCl on the effective cohesion, see ESI[†].

We use micropipettes to produce the droplets. We prepare micropipettes by pulling glass capillary tubes (outer diameter: 1 mm, inner diameter: 0.58 mm)(World Precision Instruments, USA) with a pipette puller (Narishige, Japan). Due to heat-pulling, a long, tapered micropipette will form with a tip opening in the range of tens of micrometers. We then heat-bend the micropipettes to 90° at two points, such that the droplets are produced directly into the tube (FIG. 1 (a)).

The droplets are made, using the snap-off technique [15, 16], which produces highly monodisperse droplets (polydispersity < 0.5% [15]) [35]. This method involves extruding oil from a micropipette into a surfactantcontaining solution. Barkley et al. [15] showed that droplet size depends on the micropipette tip size. Therefore, by cutting the micropipette to the right length, where the tip diameter compares to the desired droplet size, one can produce droplets of the desired size. The droplet radius in our study, r, varies from 5.3 to 24.2 μ m. Light paraffin oil (Sigma-Aldrich) is propelled through the micropipette via tubing (inner diameter: 1/32")(Tygon S3, formula E-3603) connected to a reservoir open to the atmospheric pressure. The height of the reservoir controls the oil flow rate, which in turn affects the droplet production rate, typically around 1 Hz once initiated. This droplet production can continue for several days.

The droplets float due to buoyancy into a tube, which is a glass pipette (outer diameter: 1.8 mm, inner diameter: 1.5 mm)(Kimble, USA). A 3D-printed lid (PLA) covers the tube to ensure droplet aggregation, and can be removed after an experiment is done to empty the tube. After the layer of droplets is almost twice as thick as the unevenness of the lid, the droplets form a conical pile. We use a microscope system comprising a camera (ThorLabs, USB2.0 Digital Camera) equipped with a 4x objective (Nikon), to capture images of the pile. The dashed line in FIG. 1 (a) shows the region of interest. FIG. 1 (b) show an optical microscopy image from the region of interest.

Spreading in a tube

As the droplets accumulate against the horizontal barrier, they slide without friction to the highest possible point, due to the buoyant force. However, a small heap forms at the point where the stream of droplets reaches the aggregate (FIG. 3 (a)). This small heap grows and periodically collapses into the aggregate of interconnected droplets and forces the aggregate to spread horizontally (For a video of collapsing events, see ESI^{\dagger}). Before the aggregate touches the edges of the tube, the aggregate grows horizontally with a constant height, as seen in experiments with infinite barrier, conducted by Ono-dit-Biot [18] and Hoggarth [20]. However, shortly after the aggregate reaches the edges, the spreading is restricted and the height of the aggregate must increase. Therefore, the aggregate takes a conical shape with a well-defined angle of repose, due to the presence of the wall. The edges give enough support for the pile to sustain a conical shape, similar to pinning of frictional dry granular materials to the surface underneath, which supports the conical pile. It takes about two hours for the pile to reach a quasi-equilibrium state, where the angle of repose will fluctuate around an average value. We monitor the pile for 24 hours in each experiment. A video of a typical experiment can be found in ESI^{\dagger} .

In order to see how the angle of repose depends on the system parameters, we change the SDS micelle concentration $C_{\rm m}$, to change the cohesive strength, and the droplet radius r, to change the cohesive force $F_{\rm c}$, as $F_{\rm c} \propto rC_{\rm m}$. We also change the tube size R to see how the angle of repose changes. Furthermore, similar to the work of others in this specific system of cohesive droplets [18–20], we assume that the only relevant forces in this system are cohesion and buoyancy, and ignore viscous dissipation and friction; the droplets are added slowly to the system, so that viscous dissipation due to droplet rearrangements does not play a significant role. Moreover, the liquid interfaces are smooth and do not have friction against each other or the walls. Therefore, the relevant parameters to change in this system are the SDS micelle concentration, as well as the droplet size.

In a series of experiments, we change the cohesive strength by changing the SDS micelle concentration, while keeping the droplet size constant, and see that the stronger the cohesive strength among the droplets, the steeper the angle of repose will be (FIG. 2 (a)-(c)). This observation makes sense; as the cohesive strength increases, the mechanical strength of the aggregate as a whole increases too, and a larger aggregate with a steeper angle of repose can be supported. Furthermore, while keeping $C_{\rm m}$ constant, we changed the droplet size to see how this parameter affects the angle of repose. We see that the smaller the droplet size, the steeper the angle of repose (FIG. 2 (d)-(f)). All the measurements for the angle of repose while varying $C_{\rm m}$, r and the tube size are



FIG. 2. Top row:(a)-(c) shows three experiments to study the effect of the micelle concentration, *i.e.* the effective cohesion, on the angle of repose of the pile. The droplet radius is similar for all three experiments at $r = 18 \ \mu\text{m}$. Bottom row: In (d)-(f) we demonstrate how droplet size affects the angle of repose. $C_{\rm m}$ is kept constant at 243.2 mM. The angle of repose shown in purple is to guide the eye. All images have the same scale. The white scale bar shown on image (d) is 250 μm .



FIG. 3. (a) A heap, outlined in black with a cylinder on the verge of collapse: the normal stress of the heap $\sigma_{\rm N}$ with height h has overcome the macroscopic strength of the pile σ_c . In this case, the heap pushes inwards and applies a shear stress τ outwards to make space for the heap that is wedging in, and σ_c works against τ . The dotted line shows where the pile fails. (b) The pile has failed and opened up shown by the two dotted lines. The heap, shown with a small black cone deforms from a cylinder on (a) and wedges in. The white arrows show the direction of the pile moving away. The white scale bar on the top right is 250 μ m.

shown in FIG. 4 (a). To measure the angle of repose, we measure the angle of the vertex of the cone, subtract it by 180° and divide the result by two, to find and average angle of repose of the right and the left side. To find the variation in the angle of repose, we take 10 to 20 images from the beginning, middle part and the end of each experiment, and the standard deviation of the measurements are represented as the error bars in FIG. 4 (a).

Collapsing events

We observe that the dynamic that gives rise to the conical shape of the pile is different from frictional granular materials, where intermittent avalanches [25, 36, 37] occur that involve flow of particles on the free surface of the cone. In the case of frictionless cohesive droplets, we observe the formation of a small central heap atop the bigger conical pile (FIG. 3 (a)), due to cohesion, followed by collapsing of the heap due to buoyancy into the network of interconnected droplets (FIG. 3 (b)). This distinct dynamic, which is very different than avalanche of conventional dry granular materials has been also observed in the experiment on air bubbles by Shorts and Feitosa [29], as well as spreading experiments by Ono-dit-Biot [18] and Hoggarth on frictionless oil droplets [20]. To explain the origins of this difference, let us consider a conical pile with no heap on top. Due to the short-range cohesion in the system, the aggregate as a whole has a macroscopic strength that we call σ_c . This strength is proportional to the cohesive force over the area of a droplet [5]:

$$\sigma_{\rm c} \propto \frac{F_{\rm c}}{r^2} \,.$$
 (1)

Any stress beyond this critical amount can make the aggregate collapse. If one droplet is added to the pile and the normal stress due to the buoyancy of the droplet is smaller than the macroscopic strength of the pile σ_c , the droplet will simply remain on the surface of the conical pile. In this case, if we continue adding droplets to the pile, a heap of droplets will form atop the pile, which is indeed what we consistently see in the experiments (FIG. 3 (a)). We assume that this heap is axisymmetric, as no direction is preferred over the other in the horizontal plane. Eventually, with enough droplets on the heap, the normal stress due to buoyancy overcomes the macroscopic strength of the pile and the heap will collapse into the pile (FIG. 3 (b)). This periodic formation of heaps and collapsing events is observed consistently in our experiments, as well as spreading experiments by Hoggarth [20].

The collapsing aggregate breaks the bonds between the droplets immediately below the heap to wedge in, while the network of droplets away from the heap changes minimally, specifically, the network close to the edges. Hence, the angle of repose of the pile remains will fluctuate briefly around an average value upon periodic collapsing (see error bars in FIG. 4 (a)). We hypothesize that the height of the heap results from a balance between cohesion strength $\mathcal{A} = F_{\rm c}/r \propto C_{\rm m}$ (\mathcal{A} defined in analogy with surface tension, a force per unit length) and buoyancy, similar to a natural length scale of the system, called the granular capillary length δ [18, 20], which results from the same balance, as following:

$$\delta = \sqrt{\frac{\mathcal{A}}{\Delta \rho g}} , \qquad (2)$$

where $\Delta \rho$ is the density difference between the oil and the aqueous solution and g is the gravitational acceleration.

We assume that the maximum height of the heap just before collapse is proportional to the granular capillary length δ with a geometrical factor of order one: $h \approx \delta$. This assumption has been tested in previous works done in this system of cohesive droplets [18, 20].

Coulomb criterion for stability

Let us consider the system on the verge of collapse. The normal stress due to the buoyancy of the heap σ_N is proportional to the hydrostatic pressure of the heap with height δ :

$$\sigma_{\rm N} \propto \Delta \rho g \delta$$
 . (3)

To identify how the angle of repose depends on the system parameters, we can write the Coulomb criterion for stability [5, 12] at the critical point as:

$$\tau = \mu \,\sigma_{\rm N} \,, \tag{4}$$

where τ is the applied shear stress on the material, μ is the friction coefficient of the material. In order to write eq. 4, we ignore any changes in the packing fraction during the collapsing events. In addition, we write eq. 4 for the horizontal plane with the normal vector pointing upwards, along the buoyant force.

The shear force τ is applied by the heap that pushes the droplets in the pile away in all directions to make space for the intruding heap. However, the strength of the pile due to cohesion σ_c opposes the shear stress applied by the heap τ (FIG. 3 (a)). Therefore, the value of the shear stress is equal to the value of pile strength due to cohesion: $|\sigma_c|=|\tau|$. σ_c is also called the macroscopic cohesion of the pile.

Moreover, it can be shown that the friction coefficient μ and the angle of internal friction of the aggregate α have the following relation: $\mu = \tan \alpha$ [5]. Since the aggregate is relatively close-packed, we can consider the angle of internal friction to be the same as the angle of repose [26]. Therefore, we have $\mu = \tan \theta$.

Based on the last two arguments, we can write the Coulomb criterion for stability as:

$$\sigma_{\rm c} = \tan \theta \, \sigma_{\rm N} \, . \tag{5}$$

Note that σ_c and σ_N have the same sign, as they are both compressive stresses; σ_N compresses the heap against the pile, and macroscopic cohesion σ_c holds the pile together by resisting against the shear stress. If we then substitute σ_c and σ_N from before (eq. 1 and 3), and isolate tan θ , we have:

$$\tan\theta \propto \frac{F_{\rm c}}{\Delta\rho g \delta r^2} \,. \tag{6}$$

As mentioned at the end of the "Collapsing events" section, F_c/r can be written as \mathcal{A} , the cohesion strength, resulting in:

$$\tan\theta \propto \frac{\mathcal{A}}{\Delta\rho g \delta r} \,. \tag{7}$$



FIG. 4. (a) The measured angle of repose for all experiments versus the SDS micelle concentration. The symbols are larger than the error bars, where the error bars are absent in all three plots. (b) $\tan(\theta)$ *i.e.* the effective friction versus the square root of SDS micelle concentration, while varying the tube size, micelle concentration and droplet size. This plot shows an intermediate collapse. (c) shows $\tan(\theta)$ *i.e.* the effective friction by the theory (See eq. 8). All the data collapse on a single line. For discussions on the intercept, look at the last paragraph of section "Coulomb criterion for stability".

Using the definition of the granular capillary length δ , we can combine eq. 2 and 7, then simplify to get:

$$\tan\theta \propto \frac{\delta}{r} . \tag{8}$$

This equation means that by increasing cohesive strength (controlled by increasing the SDS concentration), or decreasing the droplet size, the angle of repose increases. To check the dependence of $\tan \theta$ separately on the SDS micelle concentration, we can plot $\tan \theta$ versus $\sqrt{C_{\rm m}}$. The result is shown in FIG. 4 (b), where the data from any specific droplet size (shown by distinct color) fall on a line. Then, to verify the combined dependence (eq. 8), we plot $\tan \theta$ versus δ/r in FIG. 4 (c). We see that all the data collapse onto a single line, which shows that the data indeed follows our theoretical dependence in eq. 8. This theory confirms that the angle of repose is independent of the tube size, in line with the experiments. The reason that the angle of repose is independent of the tube size is that the droplets have no friction towards the wall, and that droplets are much smaller than the tube size (r < R/25).

The intercept in FIG. 4 (c), corresponds to $\theta = 8.0^{\circ}$. This value shows the angle of repose with no effective depletion interaction. The presence of an angle of repose in frictionless, non-cohesive particles is indeed observed previously in both simulations [27, 31] and experiments [28, 29]. However, the value that we find is slightly larger than the value reported by these studies. We can justify this, using two arguments. First, the droplets used in our experiments are highly monodisperse, which can cause interlocking of droplets in crystalline packing and reduce the overall flowability of the pile. Second, this discrepancy in the angle of repose can be attributed to the van der Waals force between droplet pairs. See ESI[†] for calculations.

CONCLUSION

In conclusion, we have explored the spreading of frictionless cohesive oil droplets in a tube and observed that, unlike the spreading of the same droplets in an infinite barrier, the droplets form a conical pile in the tube. This is surprising, as the non-zero angle of repose implies a non-zero effective friction for the aggregate of frictionless cohesive droplets. The effective friction coefficient

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provide useful insights for designing meta-materials with

a controlled effective friction coefficient using frictionless,

cohesive particles.

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Chapter 5

Conclusion

In this thesis, I have explored bulk properties of cohesive, frictionless granular aggregates as an ideal model system for cohesive granular materials.

In paper 1, we studied the quasistatic extrusion of cohesive aggregates of oil droplets from an orifice into an aqueous bath, the granular analogue of the pendant drop experiment. Specifically, we explored how the volume of the detached clusters of droplets depends on the cohesion among the droplets, the orifice size and the droplet size. We find that the average volume of the clusters is proportional to the area of the orifice, times a characteristic length of the system, called the *granular capillary length*. The granular capillary length is a measure that compares the strength of cohesion against buoyancy, in analogy with the capillary length, which compares the strength of surface tension against gravity. It is interesting that the volume of the granular clusters depends on the area, similar to extrusion of a soft solid, in contrast to the classic pendant drop, using molecular liquids, where the volume depends on the perimeter of the orifice. Our findings serve as an example of how subtle changes in the type and range of interparticle forces affect the bulk properties of amorphous

materials. Altering interparticle forces in particulate materials opens the door to investigating a wide range of systems and designing novel materials.

In paper 2, we conducted a spreading experiment of aggregates of frictionless, cohesive oil droplets in a confined geometry. Interestingly, the aggregate spreads into a conical pile due to the geometrical constraint put on the aggregate. The conical structure and non-zero angle of repose can be interpreted as an effective friction of the aggregate as a whole. We study how the angle of repose of the pile depends on the interparticle cohesion, the droplet size and the confinement (tube) size. The results show that the angle of repose is proportional to the granular capillary length divided by the droplet size. We also find that the angle of repose is independent of the confinement size within the tested range. Another interesting observation is how the dynamic of the pile is different compared to dry frictional granular materials *e.g.* sand. While sand grains roll down the surface of a pile during an avalanche, cohesive frictionless droplets form a small heap over the conical pile, which collapses into the pile after a critical heap size is reached. The results of this study highlight the role of geometrical constraints in determining the bulk properties of frictionless particulate materials.

Particulate materials are simple, yet rich systems, which I am happy to have had the chance to work with. While many possibilities exist to explore these systems for specific applications outside my expertise, I merely suggest some directions to go that are closely related to the research that I have conducted.

• It would be useful to find ways to pin droplets to a substrate with a controllable strength. This will be the base requirement for some of the following suggestions. A practice that comes to mind is silanization of the glass substrate, such that oil droplets have more affinity to the silanized glass, compared to other droplets. The density of the grafted polymer chains could be modulated to adjust the stickiness of the glass.

- Spreading of granular particles against a substrate is affected by the boundary conditions of the substrate. It would be interesting to control the roughness of the substrate and see how the boundary conditions affect the spreading against an infinite barrier. A controlled roughness could be introduced to a substrate in 3D systems by using pinned droplets, as mentioned above. In 2D systems, where the substrate is 1-dimensional, the substrate can be the edge of a thin SU-8 film, and patterns can be generated on the edge of the thin film (saw tooth, alternating squares, etc.), using photolithography.
- An interesting configuration to test the bulk properties of cohesive, frictionless droplets is pulling a dense droplet raft apart, using two micropipettes parallel to the plane that the droplet raft exists. The challenge for this experiment is adhesion of the droplets to the micropipettes, which can possibly be solved by silanization. The results of this experiment provide insights into the relatively broad volume distribution observed in the granular pendant drop experiment (paper 1) compared to a molecular liquid. Irregularity in cluster pinch-off during the paper 1 experiment results in the production of satellite clusters and clusters of varying volumes—more so for certain parameter sets than others. Therefore, understanding the pinch-off of dense aggregates might result in better control over cluster volume, as well as satellite clusters, which are considered a nuisance in the printing industry. The pulling experiment could be conducted in both 2D and 3D system. While 3D systems can be more rich and different in some ways,

a 2D system has the benefit of transparency, where the motion of every particle could be observed and analyzed. However, a 3D aggregate must be density matched, so that buoyancy does not affect the aggregates. Yet, matching the density of oil droplets to the aqueous solution is a challenge of its own in our system.

- Another simple experiment which can be done is a quasistatic shearing of a 2Draft of droplets at the interface of oil and water, such that buoyant force does not affect the droplets. Given that shearing experiment can yield an effective friction coefficient for the aggregate, the results can be cross-checked with the results from the experiment in paper 2.
- A natural extension for paper 1 is using a polydisperse system for the granular pendant drop experiment. The hypothesis is that polydispersity makes the aggregate more mobile and facilitates rearrangements of the droplets. More mobility might result in an aggregate that is more similar to simple liquids. This hypothesis can be verified by studying the dependence of the volume of the clusters on the orifice size: if the volume depends on the perimeter of the orifice, this means that the aggregate is liquid-like. One can also study how the volume distribution, as well as emergence of satellite droplets compare between the monodisperse and polydisperse systems.

While other avenues exist to explore, I conclude this thesis by saying that the world of particulate materials is a rich, interdisciplinary field that contributes to both manufacturing applications, as well as fundamental research. Studying particulate materials enrich our comprehension of diverse phenomena at virtually every length scale.

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