Driven Granular Media

Mixing, Friction & Activity

Marcel Jan Workamp

Propositions

1. The *physics* of granular suspensions is surprisingly sensitive to *chemistry*. (this thesis)
2. The synthesis of macroscopic spherical particles is much more involved than that of their colloidal analogues. (this thesis)
3. The success of fluidity modeling proves that indeed, “panta rhei”.
4. Grant proposals should be judged on the quality of the proposal, rather than the track record of the applicant.
5. Modern day man has lost his “do-it-yourself” skills.
6. Dutch radio is racist.

Propositions belong to the thesis, entitled:
“Driven Granular Media: Mixing, Friction & Activity”
Marcel Jan Workamp
Wageningen, 15 May 2018

Driven Granular Media

Mixing, Friction & Activity

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This research was conducted under the auspices of the Graduate School VLAG (Advanced studies in Food Technology, Agrobiotechnology, Nutrition and Health Sciences).

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Thesis

submitted in fulfilment of the requirements for the degree of doctor
at Wageningen University
by the authority of the Rector Magnificus,
Prof. Dr A.P.J. Mol,
in the presence of the
Thesis Committee appointed by the Academic Board
to be defended in public
on Tuesday 15 May 2018
at 4 p.m. in the Aula.

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Driven Granular Media: Mixing, Friction & Activity
142 pages.

PhD thesis, Wageningen University, Wageningen, the Netherlands (2018)
With references, with summaries in English and Dutch

ISBN: 978-94-6343-747-9
DOI <https://doi.org/10.18174/442126>

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Chapter 1

Introduction

1.1 Granular materials & suspensions

Sand, coffee beans and mud all belong to a class of materials that we call granular materials or granular media. The main constituents of a granular material are discrete, solid particles. Granular materials are abundant not only at the beach and in the coffee shop, but also in industry, where feed stock typically comes in the form of grains, as well as in agricultural settings (grain silo, pelleted feeds). Mud is an example of a granular suspension, a granular material suspended in a liquid. Other examples of suspensions include toothpaste, abrasive cleaning agents and food thickened with corn starch.

Granular materials have two main characteristics. Firstly, the particle size is sufficiently large to neglect thermal fluctuations safely. For dry granular materials, this sets the lower limit on the size of the grains to about $1\text{ }\mu\text{m}$, while it can be considered somewhat bigger in suspensions (approximately $10\text{ }\mu\text{m}$). Secondly, interactions between particles are dissipative, meaning kinetic energy of the particles is irreversibly transferred to thermal energy. Because of these two characteristics, granular materials behave differently from materials composed of molecular entities.

1.2 General features of granular materials

Like materials composed of molecular entities, granular materials can exhibit different phases: solid, liquid and gaseous phases can be identified, depending on the way they are driven [1, 2]. However, these phases display features that are unique to their granular character. Some of the most important features will be discussed below.

A pile of sand is a simple example of the granular solid phase. Due to the combined effect of friction and gravity, a pile of sand holds its shape, as the particles are effectively *jammed*. Unlike in traditional solids, the stresses in a granular solid are not homogeneously distributed, but rather organized in networks of particles that carry a bigger than average load [3–5]. These force networks have been visualized using photoelastic particles [6, 7]. They can also be obtained from the deformation of soft particles [8–10], or by 3D x-ray diffraction [11].

The interparticle forces can be made to fluctuate by applying an external force, liquefying the granular material. Tilting or vibrating are easy ways to achieve this, and so sprinkles flow from their container when tilted, while corn flakes typically need some shaking to make them flow from their box. A flow driven by tilting is an example of a shear flow, which will be described in more detail in Section 1.3.

A characteristic feature of granular materials is dilatancy, which simply means the material expands in volume when deformed. This effect was first described by Osborne Reynolds in the mid 1880s [12, 13]. It occurs because the grains are initially in a close-packed arrangement, without sufficient freedom to move. When a stress is applied, the particles are forced into a less dense state. Dilatancy can be observed while walking on wet beach sand, where the area around footsteps appear to be drier, as the sand below the foot has dilated, and the water has filled

Figure 1.1: Simple shear geometry. Top plate moves a distance x by applying a force F .

the new space formed there.

Even stronger driving can turn a granular material into a gas. In sharp contrast with conventional gasses that tend to spread homogeneously in the available space, particles in a granular gas tend to cluster [1, 14, 15]. This is because energy is dissipated in every collision, which means that particles will have a lower velocity after a collision, so that, on average, their separation distance will decrease. As collisions are more likely within a cluster, the effect is reinforced.

Another striking feature of granular materials can be observed in daily life: *segregation*, also known as the Brazil-nut effect. This effect is common in for example a jar of muesli, where the biggest nuts and chunks rise to the surface, when gently shaking the jar. The precise mechanisms behind this effect are not trivial, but surprisingly, the air pressure also plays a role, as rearrangements of nuts requires air flow [16]. For a review of segregation, and equally important, *mixing* of granular materials, see Reference [17].

Granular materials and suspensions, like colloidal suspensions, foams and emulsions, are structured fluids that exhibit the *jamming transition* [18, 19]. The transition separates the liquid state from the disordered solid state, and occurs when increasing the volume fraction of particles, droplets, or bubbles. The specific volume fraction at which the system jams may depend on many factors, including the shape, frictional properties and polydispersity of the constituents [20–22].

1.3 Rheology

1.3.1 Definitions

The field of quantifying flow properties is called rheology, as *rhei* is Greek for “to stream”. In this section we will identify some of the basic terminology used in the field. Let us consider simple shear: the parallel plate model sketched in Figure 1.1. Here, the top plate is moved by a force F , while the bottom plate is held stationary. We call this type of deformation *shear* and define the shear stress as $\tau = F/A$, with A the area of the top plate. The dimensionless deformation is called the strain,

Figure 1.2: (a) Flow curves $\tau(\dot{\gamma})$ of a shear thickening (blue), Newtonian (red), and shear thinning fluid (yellow). Note that the axes are linear and the origin denotes (0,0). (b) Flow curves of yield stress fluids with the same τ_0 , $n = 1$ and varying values for k . Note that the axes are logarithmic.

which is $\gamma = x/z$, with x the displacement of the top plate and z the gap between the plates. The shear rate or strain rate is then simply the rate at which the strain is applied, and is defined as $\dot{\gamma} = \frac{d\gamma}{dt} = v/z$, with v the velocity of the plate.

We can divide shear rheology into two main categories: continuous shear and oscillatory shear. In oscillatory shear, one typically uses small oscillatory strains, for example by moving the top plate from Figure 1.1 back and forth. This type of rheology is particularly powerful to measure the elastic properties of the materials. As we are interested in the *flow* behavior of granular media, we will not discuss oscillatory rheology in more detail here. As the name suggests, in continuous shear rheology, the shear is continuous in nature. We are typically not interested in transients, but rather in the *steady state*, where τ and $\dot{\gamma}$ are constant over time, or fluctuate around a constant mean value. We can then define the viscosity, $\eta = \tau/\dot{\gamma}$, which is our measure of how easily the material flows.

For simple fluids like water or glycerol, the viscosity is independent of shear rate. Such fluids are typically called “Newtonian”. However, many fluids do not have a constant viscosity and are therefore dubbed “non-Newtonian” fluids. We can distinguish a few different cases. *Shear thinning* fluids have a viscosity that decreases with rate. A classical example is ketchup, which can be hard to dose because of this property. Obviously, *shear thickening* fluids experience an increasing viscosity with shear rate. Such materials are less common, but shear thickening can often be observed in confined dilatant fluids. Another canonical example is a corn starch suspension. Note that the specific type of shear thickening observed in corn starch is usually denoted “discontinuous”, as the viscosity increases significantly in a rather sudden manner, compared to a more smooth increase for regular (“continuous”) shear thickening materials. In Figure 1.2a, we plot typical *flow curves* $\tau(\dot{\gamma})$ of Newtonian, shear thickening and shear thinning fluids.

Figure 1.3: Side views of common geometries used in rheology. (a) Plate-plate geometry. (b) Cone-plate geometry. (c) Couette geometry. The axis on the top is connected to a rheometer, which measures the torque M and rotation rate Ω .

For Newtonian fluids, the fluid will flow at arbitrary low applied stress. This is not the case for so-called *yield stress* fluids, for which there is no flow below a certain threshold stress, known as the yield stress. Indeed, jammed structured fluids typically exhibit such behavior [23–25]. This behavior can be described using the Herschel-Bulkley model [26], which reads:

$$\tau = \tau_0 + k\dot{\gamma}^n, \quad (1.1)$$

where τ_0 is the yield stress, k a proportionality constant and n a power law index. In Figure 1.2b, we plot some examples, showing the role of the different variables. Note that the Herschel-Bulkley model can also capture Newtonian fluids ($\tau_0 = 0$, $n = 1$, $k = \eta$), a special case of yield stress fluids called Bingham plastics ($\tau_0 > 0$, $n = 1$) [27], and “power-law fluids” ($\tau_0 = 0$, $n \neq 1$).

1.3.2 Experimental techniques

An experimental realization of the simple shear geometry described above can only apply a finite amount of strain, insufficient to reach a steady state. To overcome this issue, in simulations, periodic boundaries can be used. However, for experimental work this geometry is impractical. Commercial rheometers rely on rotation to apply shear. Here we describe some of the typical geometries.

The plate-plate geometry uses two circular plates, of which one (usually the top plate) is rotated to provide the shear (Fig. 1.3a). As $v = \Omega r$, with Ω the radial velocity of the plate and r the radius, the shear rate increases linearly with r . Thus, one averages over a large range of shear rates during measurements. A constant shear rate can be achieved using a cone-plate geometry (Fig. 1.3b). By using a cone rather than a plate, the gap z also increases linearly with r , thus resulting in a constant shear rate. For practical reasons, cones are typically truncated and then positioned such that the original tip location coincides with the base plate. Both plate-plate and cone-plate geometries rely on surface tension at the outer edge to keep the fluid between the plates, making these techniques unsuitable for dry granular materials. For suspensions of large particles, the cone-plate geometry is also usually not preferred, as close to the center the gap becomes so small that the

number of particles that fits in the gap approaches zero.

Another often used geometry uses concentric cylinders to shear the system (Fig. 1.3c). This type of shear cell, often called Couette cell, can be used for dry granular materials as well as suspensions (e.g. Refs. [28–31]), and is the geometry used in this thesis. Note that the nomenclature can be somewhat confusing: a Couette flow in fluid dynamics is a flow in between two parallel surfaces moving tangentially relative to one another, which also covers the simple parallel plate model. To differentiate, the type of flow in a Couette cell is often called Taylor-Couette flow, as Taylor studied the stability of such flows [32].

To be able to do reliable measurements in a Couette cell it is important that the only significant contribution to the shear stress stems from the fluid in the gap between the vertical walls of the two concentric cylinders. Hence, the bottom of the inner cylinder (often called “bob”), is typically designed such that the shear rates generated between the bottom of the bob and outer part of the cell are negligible (see Fig. 1.3c for one possible solution).

In a Couette cell, the shear stress is not constant, but rather decays with r as [33]:

$$\tau(r) = \frac{M}{2\pi r^2 L} \quad (1.2)$$

where M is the torque measured by the rheometer, and L the length of the cylinders. The average shear stress in a Couette cell with inner cylinder radius r_i and outer cylinder radius r_o can be calculated as $0.5\tau(r_i) + 0.5\tau(r_o)$, which can be written as:

$$\langle \tau \rangle = M \frac{r_i^2 + r_o^2}{4\pi L r_i^2 r_o^2} \quad (1.3)$$

The shear rate in a Couette cell is also not constant. If one assumes the fluid is Newtonian, the shear rate is given by [33]:

$$\dot{\gamma} = \frac{2\Omega}{r^2} \left(\frac{1}{r_i^2} - \frac{1}{r_o^2} \right)^{-1} \quad (1.4)$$

and the average shear rate can be shown to be :

$$\langle \dot{\gamma} \rangle = \Omega \frac{r_i^2 + r_o^2}{r_o^2 - r_i^2} \quad (1.5)$$

However, for a small gap ($r_o \approx r_i$) the shear rate is roughly constant, and Equation 1.4 can be reduced to:

$$\dot{\gamma} = \frac{\Omega r_o}{r_o - r_i} \quad (1.6)$$

1.4 Theory for granular flows

1.4.1 Local rheology

Although the simple Herschel-Bulkley model of Equation 1.1 can capture the rheology of granular materials, it does not provide any insight into the microscopic

origin of the observed behavior. A huge step forward in our understanding of granular flows has been the development of the $\mu(I)$ -rheology [34]. In flows of dry granular materials, we can construct a single dimensionless parameter with the only variables that play a role. This number is the inertial number:

$$I = \frac{\dot{\gamma}d}{\sqrt{P/\rho}} \quad (1.7)$$

where d is the particle diameter, P the local pressure, and ρ the particle density. We can view I as the ratio of two time scales. One of these time scales is macroscopic and set by the (local) shear rate: $t_{macro} = 1/\dot{\gamma}$. The other time scale is less trivial, and related to the time scale at which granular rearrangements take place at the micro scale. Also on dimensional grounds, this time scale is $t_{micro} \propto d/\sqrt{P/\rho}$ [34]. By considering a particle traveling the distance of one particle diameter d , subjected to a force Pd^2 , it can be shown that the pre-factor is of order unity.

If dissipation is frictional, the local shear stress is proportional to the local pressure P :

$$\tau = \mu(I)P \quad (1.8)$$

where $\mu(I)$ is an effective friction coefficient that depends on the inertial number. Empirically, one finds that:

$$\mu(I) = \mu_1 + \frac{\mu_2 - \mu_1}{1 + I_0/I} \quad (1.9)$$

where μ_1 and μ_2 are material dependent parameters and I_0 is typically of order 1. As $I \propto \dot{\gamma}$, one can recognize in Equation 1.9 a structure similar to that of Equation 1.1. Hence, Equation 1.9 is essentially a pressure-dependent Herschel-Bulkley model, where the shear rate has been replaced with the dimensionless I . Indeed, Equation 1.9 is often simplified to:

$$\mu(I) = \mu_c + aI^\alpha \quad (1.10)$$

Although this relation is not much more complex than the Herschel-Bulkley model, we now understand a lot more about the microscopic origin of the observed behavior. In particular, we can ask the question whether the parameters (μ_1 , μ_2 , etc.) depend on microscopic parameters, such as particle stiffness or roughness.

The $\mu(I)$ -rheology can be adapted to grasp the rheology of suspensions [35], where the interstitial fluid plays a role. The rearrangement time $t_{micro} = d/\sqrt{P/\rho}$ is no longer of importance here. If the Stokes number $St = \rho d^2 \dot{\gamma} / \eta_f$ (with η_f the viscosity of the interstitial fluid) is small, the internal time is given by a viscous scaling $t_{micro} \propto \eta_f / P^p$, where P^p is the local confining pressure on the particles [36]. This result can be viewed as a balance of the driving force and the drag force on the particle. A particle first accelerates due to the force Pd^2 , but due to drag forces reaches a final velocity v_∞ , this drag force $F_D \propto \eta_f dv_\infty$ and in this overdamped limit equals the driving force. By defining t_{micro} as the time for a particle with speed v_∞ to travel a distance d , the aforementioned result for t_{micro} is obtained. Note that the porosity of the suspension gives rise to a pre-factor in the

Figure 1.4: Sketch of plastic deformation in a structured fluid. Deformation occurs via elastic deformation, localized plastic events, and nonlocal redistribution of the elastic stress, potentially triggering other plastic events. Reprinted with permission from [37] Copyright (2017) by the American Physical Society.

drag force [36], which depends on the particle size distribution, and is often neglected, as we will do here. Combining the new t_{micro} with our previously defined t_{macro} yields the viscous number I_v :

$$I_v = \frac{\eta_f \dot{\gamma}}{Pp} \quad (1.11)$$

and our local law then reads $\tau = \mu(I_v)P$. The function $\mu(I_v)$ is modeled as the sum of contact and hydrodynamic stresses:

$$\mu(I_v) = \mu_1 + \frac{\mu_2 - \mu_1}{1 + I_0/I_v} + I_v + \frac{5}{2}\phi_m I_v^{1/2} \quad (1.12)$$

where the first two terms represent the contact contribution and the last two terms represent the hydrodynamic contribution, and $\phi_m \approx 0.585$ is the critical volume fraction above which no flow is possible (the viscosity diverges at ϕ_m [35]). Note that I_0 is determined empirically and different values have been used [35, 36]. The local rheologies $\mu(I)$ and $\mu(I_v)$ can be used to predict the flow behavior of granular materials and suspensions, respectively, based on only a few parameters, most notably μ_1 and μ_2 .

1.4.2 Nonlocal rheology

Although the local rheology captures many aspects of the flow behavior of granular materials, there are also features it can not explain. For example, the local rheology predicts that once the local $\mu = \tau/P$ is smaller than μ_c , no flow is possible. This means that in geometries, such as the Couette geometry where τ decreases with r , the flow is localized to a shear band, with a sharp separation between stationary zones and flowing zones. However, in experiments the transition of the flowing to the stationary zone is rather smooth (e.g. Refs. [31, 38–40]). What is causing this?

The origin of this behavior is sketched in Figure 1.4. When deforming the material, stresses are built up, until a localized plastic (irreversible deformation) event occurs, which redistributes the elastic stresses. This may trigger another plastic

Figure 1.5: Local flow curves $\tau(\dot{\gamma})$ and the fluidity model. Reprinted by permission from Macmillan Publishers Ltd: Nature [42], copyright 2008. (a) Local flow curves $\tau(\dot{\gamma})$ of a dense emulsion in wide gap Couette geometry, extracted from the velocity profiles at different driving rates (Inset). Solid black line corresponds to a fit of the Herschel-Bulkley model. (b) Local flow curves of the same emulsion in a small microchannel, for various pressure drops over the channel. The local flow curves do not collapse onto the same Herschel-Bulkley fit (solid black line), yet can be accurately predicted (dashed lines) using the fluidity model of Equation 1.13. Inset shows the velocity profiles used to obtain the flow curves, where solid lines are predictions from the fluidity model.

event somewhere else in the material. Hence, even though the region outside of a shear band may appear stationary, it is still affected by the flow. This can be made apparent by placing a high-density ball on top of a container filled with granular materials, which can be driven from below. In the absence of driving, the granular material acts like a solid and the ball stays in position. However, when the granular material is driven, even when the shear band does not reach the top surface, the grains in the top layers are fluidized by nonlocal effects, causing the ball to sink [41].

Nonlocality is a relevant physical mechanism that plays a role in a variety of disordered systems; emulsions [42] and foams [43] also display nonlocal behavior. Nonlocality is not just important to understand the liquefaction of regions outside the shear zone (such as the ball sinking in the sheared bucket), but is also essential to predicting the local flow of structured fluids accurately. When the stress field is known and the flow profile is measured, one can determine the flow curve $\tau(\dot{\gamma})$ locally. When no nonlocal effects are present, this yields overlapping flow curves for flows at different driving rates (Fig. 1.5a). If nonlocal effects are present, the local flow curves do not collapse, see Figure 1.5b.

To accurately predict the local flow of an emulsion in a small microchannel, a fluidity model was introduced [42]. In this model, the fluidity f is defined as

$f = \dot{\gamma}/\tau$, i.e. proportional to the inverse viscosity. In absence of nonlocal effects, $f = f_{loc} = \dot{\gamma}(\tau)/\tau_{loc}$, where τ_{loc} is the local stress, and $\dot{\gamma}(\tau)$ is an “inverted” form of the usual constitutive equation $\tau(\dot{\gamma})$. The fluidity field can be described using the following law:

$$f = f_{loc} + \xi^2 \nabla^2 f \quad (1.13)$$

where ξ is the flow cooperativity length scale which depends on a fitting parameter commonly referred to as the “nonlocal amplitude” [44], the size of the particles, as well as the distance of the local stress to the yield stress [37, 44–46]. This model captures the local flow of emulsions accurately [42, 47]. It can be adapted to granular materials by incorporating pressure dependence, such that the granular fluidity g is defined as $g = \dot{\gamma}/\mu$, and the local law is the $\mu(I)$ -rheology [45]. The granular fluidity model accurately predicts the flow profiles of granular materials in complex geometries [46].

1.5 Role of particle properties in granular flows

In Section 1.4, we discussed how local and nonlocal modeling can accurately capture flow of granular materials. These modeling efforts are successful, however provide little insight into the microscopic mechanism that provide their success. This lack of microscopic understanding also limits their broader implementations. In particular, the role of particle properties, which govern the microscopic interactions, remains poorly understood. In this Section, we highlight some of the properties that play a role in the rheology of granular materials, and discuss the work done in this regard.

1.5.1 Particle stiffness

Granular materials in industry and nature typically consist of hard particles, hence the effect of particle stiffness on granular or suspension flows is poorly studied experimentally, in contrast to their colloidal analogues (e.g. Refs. [48–50]). Reference [51] investigates the role of thermal motion in soft particle suspensions using hydrogel particles in both the colloidal and granular size range. They find that the elastic properties of dense suspensions are qualitatively similar, while the flow curves are different, arguing that in the thermal system particles remain separated by a thin solvent layer, while friction plays a role in the granular case. Soft particles can also be used to elucidate force networks in static packings, as the force can be deduced from the deformation of the particle, using imaging with refractive index matching techniques [8–10].

Clearly, numerical results for the effect of particle stiffness in granular flows do exist. In Reference [52], μ was found to depend on the dimensionless stiffness $k_n/\rho d^3 \dot{\gamma}$, with k_n a spring constant. However, more recent work suggests that a rescaled particle stiffness $S = k_n/P$ does not matter for the $\mu(I)$ scaling parameter α (Eq. 1.9), and μ_c depends on S only very weakly [53]. Thus, from experiments as well as simulations, the precise role of particle stiffness remains unclear.

1.5.2 Frictional properties

Since interactions in granular materials are generally frictional in nature, understanding the role of the frictional properties of the particles on the rheology of the ensemble is of key importance. Because it is not trivial to determine the frictional properties of individual particles in experiment, much of the literature on the subject is based on computer simulations. One particularly important finding is that for dry, *frictionless* particles, the macroscopic friction coefficient $\mu(I)$ remains finite [54]. Furthermore, it is generally accepted that when the friction coefficient of the particles μ_m is larger than about 0.5, the rheology does not change much more. For example, the dependence on I (the exponent α) becomes constant around this value in dry granular materials [53], and in suspensions, μ_c was also shown to be roughly constant for such large μ_m [55]. Reference [44] studies the effect of μ_m on a fitting parameter of the granular fluidity model, the “nonlocal amplitude”, and found a weak effect. Although much can be learned from such simulations, they have a number of limitations. In particular, simulations can typically capture behavior over a relatively small range of time and length scales, which may cause important physical mechanisms to be suppressed. Hence, experimental work is crucial to provide a perspective for numerical studies.

For suspensions the situation is very similar. Since it is usually difficult to control (let alone measure) the granular or fluid pressure in a dense suspension, experimental data for the role of friction or other material properties in the $\mu(I_v)$ -rheology is limited. In the original paper describing the $\mu(I_v)$ -rheology [35], a truncated cone-plate geometry is used where the top plate is porous, so that the pressure P^p is a pressure exerted only on the particles. This is an elegant solution, but the geometry has several drawbacks. One is that it is very large, such that any heterogeneity in the local volume fraction, leading to large variations in local normal stresses, may cause serious damage to the rheometer, due to torques generated perpendicular to the rheometer axis. Importantly, the authors find a single function $\mu(I_v)$ to fit the rheological data of both poly(methyl methacrylate) and polystyrene particles suspended in a density matching fluid, which suggests there is at least *some* universality to the $\mu(I_v)$ -rheology. Reference [56] simulated particles with and without friction and found $\mu(I_v)$ to be constant, in sharp contrast to the more recent numerical work of Reference [55]. As such, the role of friction in dense suspension rheology remains poorly understood.

In some suspensions at volume fractions well below ϕ_m , such as in corn starch suspensions [57], “discontinuous” shear thickening is observed, where the viscosity suddenly increases significantly to enormous values when a critical amount of stress is reached [58]. The effect can be so strong, that one can easily run across a pool of corn starch suspension, while one sinks almost instantaneously when walking slowly. Understanding this phenomenon has been a long quest. Although long thought to be related to hydrodynamic clusters [59] or shear-induced melting of a partially ordered state [60], recent theoretical work proposed the transition to be a frictional one [61], where frictional contacts arise when repulsive forces are overcome at some critical stress. Recent experimental work confirms this picture [62–64].

Discontinuous shear thickening is typically observed in suspensions of colloidal

particles or granular particles with particle diameters well below $100\text{ }\mu\text{m}$, while for larger particles it does not exist. This is reasonable, as for such small particles, electrostatic or other repulsive forces are still of importance. If these repulsive forces are absent, for example when corn starch is suspended in ethanol rather than in water, the phenomenon is absent [65]. It is noteworthy that Reference [66] already describes that the onset stress of discontinuous shear thickening depends on the roughness of the (colloidal) particles, years before References [61–65] appeared.

1.5.3 Other particle properties

Many other particle properties play a role in granular flows, here we will name just a few. Although most of the literature of granular materials deals with spherical particles, in nature, particles are generally not spherical, which may have consequences for the flow properties. Here, we shall give a few examples. Elongated particles tend to align [67], an effect that can also be observed when pouring sprinkles or rice grains from their containers. Interestingly, contrary to convex particles, non-convex particles, such as 3D stars, can be used to create stable columns [68]. Reference [69] shows that μ depends on the angularity of 2D polygonal particles. Another particle interaction that may be important is attraction. When particles are attractive, this has consequences for their collective flow behavior: the flow curve may have a “dip” [70, 71]. This dip means the flow is unstable; a consequence is that there is range of stresses for which the flow can have two shear rates. Which of the two is picked depends on the history of the flow.

1.6 Active granular matter

Colonies of bacteria, microtubule assemblies, as well as schools of fish display interesting collective phenomena in which the activity plays a crucial role. Understanding how such collective behavior is induced has been one of the main reasons to study these active materials. In recent years, active matter has developed into a trend in the soft matter community, highlighted by well-cited papers in high-impact journals (e.g. Refs. [72–76]), as well as a number of reviews [77–79]. In active matter systems, the “particles” are self-driven, meaning they move by means of a force that acts on the individual particle. Active materials can be studied at many length scales: molecular motors [72], microtubules [73], and birds [74] display interesting collective phenomena.

As a granular gas needs continuous driving to keep it in the gaseous state, one can argue that there is little difference between a granular gas and an active granular material. A granular gas however, does not have particles that inject energy to the system locally, rather the energy is injected to the system globally. In a typical granular gas experiment, the particles are confined to a horizontal plane, which is shaken in the vertical direction. If the particles have some chirality [80, 81], or are even just rod-like [82], interesting collective phenomena may occur.

Of particular relevance to this thesis is the work presented in Reference [83]. In

this numerical work, a 2D assembly of rotating particles (“spinners”) was studied. The spinners consist of four peripheral disks attached to a central, larger disk and have a finite torque. The authors find that in mixtures of particles spinning clockwise or anti-clockwise, at sufficiently high volume fractions, the spinners phase separate based on chirality, and may even form phase separated crystals. Not surprisingly, at low driving torques, the ensemble freezes.

1.7 Outline of this thesis

In this introduction, the recurring theme is that the role of material properties in the behavior of driven granular materials is poorly understood. This thesis aims to address this issue, using innovative experimental systems. The thesis consists of two parts:

In **Part I: Soft Spere Suspensions** we will investigate the rheology of soft particle suspensions. In **Chapter 2**, we devise a method to produce monodisperse, millimetre-sized hydrogel particles with tunable size, using a droplet dispensing technique combined with a coaxial air flow. We propose a simple model that can predict the droplet size. We use the described method to synthesize particles of cross-linked gelatin and polyacrylamide. In **Chapter 3**, we describe an experimental system to probe the origin of granular fluidity. We use the particles made in Chapter 2, and show that we can image stress fields using the photoelasticity of gelatin particles in a custom Couette cell. We also compare the flow profiles of the gelatin suspension to that of a polyacrylamide hydrogel suspension. We observe qualitatively different behavior, and use both rheometric and optical methods to look at relaxation of the suspension after suddenly stopping shear, which highlights the differences between gelatin and polyacrylamide particle suspensions once more. In **Chapter 4** we examine the rheology of the soft sphere suspensions in more detail. We measure the friction coefficient of the materials using a custom-made tribometer, and link these to the rheology of the suspensions. We find a flow instability for gelatin particles, which is absent for polyacrylamide particle suspensions. We find that the friction coefficient of the materials relates directly to the suspension friction coefficient μ , provided the material friction coefficient exceeds a critical value.

In **Part II: Driven Granular Systems** we look at granular materials that are not sheared in a classical way, yet somehow mechanically driven. In **Chapter 5**, we demonstrate that friction also plays a crucial role in the collective behavior of a model active matter system. The system consists of disks similar in design to those used in Reference [83], rotating within a circular boundary, and we investigate the effect of the surface roughness of the disks in their collective motion. We also test if such an active granular gas can be modeled using theory for atomic gases. Finally, in **Chapter 6**, we use a recent finding in suspension rheology, shear induced diffusion [84, 85], to design an efficient microfluidic mixer. The mixer chip features two inlets and a single mixing chamber, in which particles are driven by a magnet. We will compare mixing chips with and without particles, and investigate the mixing efficiency as a function of the driving rate of the magnet.

The thesis is concluded with a **general discussion** and a **summary**.

References

- [1] H. M. Jaeger, S. R. Nagel, and R. P. Behringer, “Granular solids, liquids, and gases,” *Reviews of Modern Physics*, vol. 68, no. 4, p. 1259, 1996.
- [2] Y. Forterre and O. Pouliquen, “Flows of dense granular media,” *Annual Review of Fluid Mechanics*, vol. 40, pp. 1–24, 2008.
- [3] D. W. Howell, R. Behringer, and C. Veje, “Fluctuations in granular media,” *Chaos: An Interdisciplinary Journal of Nonlinear Science*, vol. 9, no. 3, pp. 559–572, 1999.
- [4] R. Hartley and R. Behringer, “Logarithmic rate dependence of force networks in sheared granular materials,” *Nature*, vol. 421, no. 6926, pp. 928–932, 2003.
- [5] J. H. Snoeijer, W. G. Ellenbroek, T. J. Vlugt, and M. van Hecke, “Sheared force networks: anisotropies, yielding, and geometry,” *Physical Review Letters*, vol. 96, no. 9, p. 098001, 2006.
- [6] T. S. Majmudar and R. P. Behringer, “Contact force measurements and stress-induced anisotropy in granular materials,” *Nature*, vol. 435, no. 7045, pp. 1079–1082, 2005.
- [7] A. Amon, P. Born, K. Daniels, J. Dijkstra, K. Huang, D. Parker, M. Schröter, R. Stannarius, and A. Wierschem, “Preface: focus on imaging methods in granular physics,” *Review of Scientific Instruments*, vol. 88, no. 5, p. 051701, 2017.
- [8] N. Brodu, J. A. Dijkstra, and R. P. Behringer, “Spanning the scales of granular materials through microscopic force imaging,” *Nature Communications*, vol. 6, 2015.
- [9] D. M. Walker, A. Tordesillas, N. Brodu, J. A. Dijkstra, R. P. Behringer, and G. Froyland, “Self-assembly in a near-frictionless granular material: conformational structures and transitions in uniaxial cyclic compression of hydrogel spheres,” *Soft Matter*, vol. 11, no. 11, pp. 2157–2173, 2015.
- [10] J. A. Dijkstra, N. Brodu, and R. P. Behringer, “Refractive index matched scanning and detection of soft particles,” *Review of Scientific Instruments*, vol. 88, no. 5, p. 051807, 2017.
- [11] R. Hurley, S. Hall, J. Andrade, and J. Wright, “Quantifying interparticle forces and heterogeneity in 3d granular materials,” *Physical Review Letters*, vol. 117, no. 9, p. 098005, 2016.
- [12] O. Reynolds, “Lvii. on the dilatancy of media composed of rigid particles in contact. with experimental illustrations,” *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, vol. 20, no. 127, pp. 469–481, 1885.
- [13] O. Reynolds, “Experiments showing dilatancy, a property of granular material, possibly connected with gravitation,” *Proceedings of the Royal Institution of Great Britain*, vol. 11, no. 354363, p. 12, 1886.
- [14] I. Goldhirsch and G. Zanetti, “Clustering instability in dissipative gases,” *Physical Review Letters*, vol. 70, no. 11, p. 1619, 1993.
- [15] J. Eggers, “Sand as maxwell’s demon,” *Physical Review Letters*, vol. 83, no. 25, p. 5322, 1999.
- [16] M. E. Möbius, B. E. Lauderdale, S. R. Nagel, and H. M. Jaeger, “Brazil-nut effect: size separation of granular particles,” *Nature*, vol. 414, no. 6861, pp. 270–270, 2001.
- [17] J. Ottino and D. Khakhar, “Mixing and segregation of granular materials,” *Annual Review of Fluid Mechanics*, vol. 32, no. 1, pp. 55–91, 2000.
- [18] A. J. Liu and S. R. Nagel, “Nonlinear dynamics: jamming is not just cool any more,” *Nature*, vol. 396, no. 6706, pp. 21–22, 1998.
- [19] A. O. Siemens and M. Van Hecke, “Jamming: a simple introduction,” *Physica A: Statistical Mechanics and its Applications*, vol. 389, no. 20, pp. 4255–4264, 2010.
- [20] A. Kyrilyuk, A. Wouterse, and A. Philipse, “Percolation and jamming in random heterogeneous materials,” *Progress in Colloid and Polymer Science*, vol. 137, p. 29, 2010.
- [21] L. E. Silbert, “Jamming of frictional spheres and random loose packing,” *Soft Matter*, vol. 6, no. 13, pp. 2918–2924, 2010.
- [22] S. Chialvo, J. Sun, and S. Sundaresan, “Bridging the rheology of granular flows in three regimes,” *Physical Review E*, vol. 85, no. 2, p. 021305, 2012.
- [23] J. A. Dijkstra, *Granular media: flow & agitations*. Granular and Disordered Media, Leiden Institute of Physics, Faculty of Science, Leiden University, 2009.
- [24] J. A. Dijkstra, E. Wandersman, S. Slotterback, C. R. Berardi, W. D. Updegraff, M. van Hecke, and W. Losert, “From frictional to viscous behavior: three-dimensional imaging and rheology of gravitational suspensions,” *Physical Review E*, vol. 82, no. 6, p. 060301, 2010.

- [25] M. Dinkgreve, J. Paredes, M. Michels, and D. Bonn, “Universal rescaling of flow curves for yield-stress fluids close to jamming,” *Physical Review E*, vol. 92, no. 1, p. 012305, 2015.
- [26] W. H. Herschel and R. Bulkley, “Konsistenzmessungen von gummi-benzollösungen,” *Kolloid-Zeitschrift*, vol. 39, pp. 291–300, Aug 1926.
- [27] E. C. Bingham, “An investigation of the laws of plastic flow,” *Bulletin of the Bureau of Standards*, vol. 13, pp. 309–353, 1916.
- [28] R. Khosropour, J. Zirinsky, H. Pak, and R. Behringer, “Convection and size segregation in a couette flow of granular material,” *Physical Review E*, vol. 56, no. 4, p. 4467, 1997.
- [29] D. M. Mueh, “Measurements of particle dynamics in slow, dense granular couette flow,” *Physical Review E*, vol. 67, no. 1, p. 011304, 2003.
- [30] N. Huang and D. Bonn, “Viscosity of a dense suspension in couette flow,” *Journal of Fluid Mechanics*, vol. 590, pp. 497–507, 2007.
- [31] H. De Cagny, A. Fall, M. M. Denn, and D. Bonn, “Local rheology of suspensions and dry granular materials,” *Journal of Rheology (1978-present)*, vol. 59, no. 4, pp. 957–969, 2015.
- [32] G. I. Taylor, “Stability of a viscous liquid contained between two rotating cylinders,” *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character*, vol. 223, pp. 289–343, 1923.
- [33] J. W. Goodwin and R. W. Hughes, *Rheology for chemists: an introduction*. Royal Society of Chemistry, 2000.
- [34] GDR-MiDi, “On dense granular flows,” *European Physical Journal E*, vol. 14, no. 4, 2004.
- [35] F. Boyer, É. Guazzelli, and O. Pouliquen, “Unifying suspension and granular rheology,” *Physical Review Letters*, vol. 107, no. 18, p. 188301, 2011.
- [36] C. Cassar, M. Nicolas, and O. Pouliquen, “Submarine granular flows down inclined planes,” *Physics of Fluids*, vol. 17, no. 10, p. 103301, 2005.
- [37] L. Bocquet, A. Colin, and A. Ajdari, “Kinetic theory of plastic flow in soft glassy materials,” *Physical Review Letters*, vol. 103, no. 3, p. 036001, 2009.
- [38] P. Coussot, J. Raynaud, F. Bertrand, P. Moucheron, J. Guilbaud, H. Huynh, S. Jarny, and D. Lesueur, “Coexistence of liquid and solid phases in flowing soft-glassy materials,” *Physical Review Letters*, vol. 88, no. 21, p. 218301, 2002.
- [39] G. Ovarlez, S. Rodts, A. Ragouilliaux, P. Coussot, J. Goyon, and A. Colin, “Wide-gap couette flows of dense emulsions: local concentration measurements, and comparison between macroscopic and local constitutive law measurements through magnetic resonance imaging,” *Physical Review E*, vol. 78, no. 3, p. 036307, 2008.
- [40] P. Schall and M. van Hecke, “Shear bands in matter with granularity,” *Annual Review of Fluid Mechanics*, vol. 42, no. 1, p. 67, 2009.
- [41] K. Nichol, A. Zanin, R. Bastien, E. Wandersman, and M. van Hecke, “Flow-induced agitations create a granular fluid,” *Physical Review Letters*, vol. 104, no. 7, p. 078302, 2010.
- [42] J. Goyon, A. Colin, G. Ovarlez, A. Ajdari, and L. Bocquet, “Spatial cooperativity in soft glassy flows,” *Nature*, vol. 454, no. 7200, pp. 84–87, 2008.
- [43] G. Katgert, B. P. Tighe, M. E. Möbius, and M. van Hecke, “Couette flow of two-dimensional foams,” *EPL (Europhysics Letters)*, vol. 90, no. 5, p. 54002, 2010.
- [44] K. Kamrin and G. Koval, “Effect of particle surface friction on nonlocal constitutive behavior of flowing granular media,” *Computational Particle Mechanics*, vol. 1, no. 2, pp. 169–176, 2014.
- [45] K. Kamrin and G. Koval, “Nonlocal constitutive relation for steady granular flow,” *Physical Review Letters*, vol. 108, no. 17, p. 178301, 2012.
- [46] D. L. Henann and K. Kamrin, “A predictive, size-dependent continuum model for dense granular flows,” *Proceedings of the National Academy of Sciences*, vol. 110, no. 17, pp. 6730–6735, 2013.
- [47] P. Jop, V. Mansard, P. Chaudhuri, L. Bocquet, and A. Colin, “Microscale rheology of a soft glassy material close to yielding,” *Physical Review Letters*, vol. 108, no. 14, p. 148301, 2012.
- [48] N. Koumakis, A. Pamvouxoglou, A. Poulos, and G. Petekidis, “Direct comparison of the rheology of model hard and soft particle glasses,” *Soft Matter*, vol. 8, no. 15, pp. 4271–4284, 2012.
- [49] A. Ikeda, L. Berthier, and P. Sollich, “Unified study of glass and jamming rheology in soft particle systems,” *Physical Review Letters*, vol. 109, no. 1, p. 018301, 2012.

- [50] L. Mohan, C. Pellet, M. Cloitre, and R. Bonnecaze, “Local mobility and microstructure in periodically sheared soft particle glasses and their connection to macroscopic rheology,” *Journal of Rheology*, vol. 57, no. 3, pp. 1023–1046, 2013.
- [51] P. Menut, S. Seiffert, J. Sprakel, and D. A. Weitz, “Does size matter? elasticity of compressed suspensions of colloidal-and granular-scale microgels,” *Soft Matter*, vol. 8, no. 1, pp. 156–164, 2012.
- [52] C. S. Campbell, “Granular shear flows at the elastic limit,” *Journal of Fluid Mechanics*, vol. 465, pp. 261–291, 2002.
- [53] A. F. de Coulomb, M. Bouzid, P. Claudin, E. Clément, and B. Andreotti, “Rheology of granular flows across the transition from soft to rigid particles,” *Physical Review Fluids*, vol. 2, no. 10, p. 102301, 2017.
- [54] P.-E. Peyneau and J.-N. Roux, “Frictionless bead packs have macroscopic friction, but no dilatancy,” *Physical Review E*, vol. 78, no. 1, p. 011307, 2008.
- [55] M. Trulsson, E. DeGiuli, and M. Wyart, “Effect of friction on dense suspension flows of hard particles,” *Physical Review E*, vol. 95, no. 1, p. 012605, 2017.
- [56] S. Gallier, E. Lemaire, F. Peters, and L. Lobry, “Rheology of sheared suspensions of rough frictional particles,” *Journal of Fluid Mechanics*, vol. 757, pp. 514–549, 2014.
- [57] A. Fall, N. Huang, F. Bertrand, G. Ovarlez, and D. Bonn, “Shear thickening of cornstarch suspensions as a reentrant jamming transition,” *Physical Review Letters*, vol. 100, no. 1, p. 018301, 2008.
- [58] E. Brown and H. M. Jaeger, “Shear thickening in concentrated suspensions: phenomenology, mechanisms and relations to jamming,” *Reports on Progress in Physics*, vol. 77, no. 4, p. 046602, 2014.
- [59] X. Cheng, J. H. McCoy, J. N. Israelachvili, and I. Cohen, “Imaging the microscopic structure of shear thinning and thickening colloidal suspensions,” *Science*, vol. 333, no. 6047, pp. 1276–1279, 2011.
- [60] R. Hoffman, “Discontinuous and dilatant viscosity behavior in concentrated suspensions. ii. theory and experimental tests,” *Journal of Colloid and Interface Science*, vol. 46, no. 3, pp. 491–506, 1974.
- [61] M. Wyart and M. Cates, “Discontinuous shear thickening without inertia in dense non-brownian suspensions,” *Physical Review Letters*, vol. 112, no. 9, p. 098302, 2014.
- [62] J. R. Royer, D. L. Blair, and S. D. Hudson, “Rheological signature of frictional interactions in shear thickening suspensions,” *Physical Review Letters*, vol. 116, no. 18, p. 188301, 2016.
- [63] J. Comtet, G. Chatté, A. Niguès, L. Bocquet, A. Siria, and A. Colin, “Pairwise frictional profile between particles determines discontinuous shear thickening transition in non-colloidal suspensions,” *Nature Communications*, vol. 8, p. 15633, 2017.
- [64] C. Clavaud, A. Bérut, B. Metzger, and Y. Forterre, “Revealing the frictional transition in shear-thickening suspensions,” *Proceedings of the National Academy of Sciences*, p. 201703926, 2017.
- [65] L. O. Gálvez, S. de Beer, D. van der Meer, and A. Pons, “Dramatic effect of fluid chemistry on cornstarch suspensions: linking particle interactions to macroscopic rheology,” *Physical Review E*, vol. 95, no. 3, p. 030602, 2017.
- [66] D. Lootens, H. Van Damme, Y. Hémar, and P. Hébraud, “Dilatant flow of concentrated suspensions of rough particles,” *Physical Review Letters*, vol. 95, no. 26, p. 268302, 2005.
- [67] T. Börzsönyi, B. Szabó, G. Törös, S. Wegner, J. Török, E. Somfai, T. Bien, and R. Stannarius, “Orientational order and alignment of elongated particles induced by shear,” *Physical Review Letters*, vol. 108, no. 22, p. 228302, 2012.
- [68] Y. Zhao, K. Liu, M. Zheng, J. Barés, K. Dierichs, A. Menges, and R. P. Behringer, “Packings of 3d stars: stability and structure,” *Granular Matter*, vol. 18, no. 2, p. 24, 2016.
- [69] E. Azéma, N. Estrada, and F. Radjai, “Nonlinear effects of particle shape angularity in sheared granular media,” *Physical Review E*, vol. 86, no. 4, p. 041301, 2012.
- [70] E. Irani, P. Chaudhuri, and C. Heussinger, “Impact of attractive interactions on the rheology of dense athermal particles,” *Physical Review Letters*, vol. 112, no. 18, p. 188303, 2014.
- [71] E. Irani, P. Chaudhuri, and C. Heussinger, “Athermal rheology of weakly attractive soft particles,” *Physical Review E*, vol. 94, no. 5, p. 052608, 2016.
- [72] R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. Bastiaansen, D. J. Broer, and B. L. Feringa, “Molecular machines: nanomotor rotates microscale objects,” *Nature*, vol. 440, no. 7081, pp. 163–163, 2006.

- [73] T. Sanchez, D. T. Chen, S. J. DeCamp, M. Heymann, and Z. Dogic, “Spontaneous motion in hierarchically assembled active matter,” *Nature*, vol. 491, no. 7424, pp. 431–434, 2012.
- [74] W. Bialek, A. Cavagna, I. Giardina, T. Mora, E. Silvestri, M. Viale, and A. M. Walczak, “Statistical mechanics for natural flocks of birds,” *Proceedings of the National Academy of Sciences*, vol. 109, no. 13, pp. 4786–4791, 2012.
- [75] L. Berthier and J. Kurchan, “Non-equilibrium glass transitions in driven and active matter,” *Nature Physics*, vol. 9, no. 5, pp. 310–314, 2013.
- [76] S. C. Takatori, W. Yan, and J. F. Brady, “Swim pressure: stress generation in active matter,” *Physical Review Letters*, vol. 113, no. 2, p. 028103, 2014.
- [77] S. Ramaswamy, “The mechanics and statistics of active matter,” *Annual Review of Condensed Matter Physics*, vol. 1, pp. 323–345, 2010.
- [78] M. C. Marchetti, J.-F. Joanny, S. Ramaswamy, T. B. Liverpool, J. Prost, M. Rao, and R. A. Simha, “Hydrodynamics of soft active matter,” *Reviews of Modern Physics*, vol. 85, no. 3, p. 1143, 2013.
- [79] A. M. Menzel, “Tuned, driven, and active soft matter,” *Physics Reports*, vol. 554, pp. 1–45, 2015.
- [80] J.-C. Tsai, F. Ye, J. Rodriguez, J. P. Gollub, and T. Lubensky, “A chiral granular gas,” *Physical Review Letters*, vol. 94, no. 21, p. 214301, 2005.
- [81] C. Scholz and T. Pöschel, “Velocity distribution of a homogeneously driven two-dimensional granular gas,” *Physical Review Letters*, vol. 118, no. 19, p. 198003, 2017.
- [82] V. Narayan, S. Ramaswamy, and N. Menon, “Long-lived giant number fluctuations in a swarming granular nematic,” *Science*, vol. 317, no. 5834, pp. 105–108, 2007.
- [83] N. H. Nguyen, D. Klotsa, M. Engel, and S. C. Glotzer, “Emergent collective phenomena in a mixture of hard shapes through active rotation,” *Physical Review Letters*, vol. 112, no. 7, p. 075701, 2014.
- [84] D. Pine, J. P. Gollub, J. Brady, and A. Leshansky, “Chaos and threshold for irreversibility in sheared suspensions,” *Nature*, vol. 438, no. 7070, pp. 997–1000, 2005.
- [85] B. Metzger, O. Rahli, and X. Yin, “Heat transfer across sheared suspensions: role of the shear-induced diffusion,” *Journal of Fluid Mechanics*, vol. 724, pp. 527–552, 2013.

Part I

Soft Sphere Suspensions

Chapter 2

Production of millimeter-sized spherical hydrogel particles

In this chapter, we describe a method to produce millimeter-sized hydrogel particles, which we will use in following chapters to elucidate the role of material properties in suspension flows. We disperse aqueous droplets in an oil using a nozzle and subsequently solidify them. We show that we can vary the size of the particles using an air flow along the nozzle. The resulting particle size can be well predicted by a simple model where a drag force generated by the air flow, adds to the weight pulling the droplet from the nozzle. Particles produced using this method have diameters ranging from 0.7 to 2.3 mm. Production rates up to 0.5 ml/min per nozzle have been achieved, which compares favorably to standard microfluidic techniques, which do not allow for synthesis of particles over a few hundred μm . Our particle production method can be used to produce both physical and chemical gel particles and is thus highly universal.

This chapter is based on:

M. Workamp, S. Alaie and J.A. Dijkman, *Coaxial air flow device for the production of millimeter-sized spherical hydrogel particles*, Review of Scientific Instruments 87(12) (2016), 125113.

2.1 Introduction

Hydrogel particles are of interest in many scientific fields, owing to their unique properties. For example, their porous structure renders them useful for drug delivery, as solutes in the gel are released slowly [1, 2]. Drug release rates can be tuned since the gel pore size, governing the diffusion of solutes, often depends on ionic strength and pH, and can be tuned by adjusting the chemistry of the gel. Furthermore, many hydrogels have non-trivial frictional properties [3], such as very low friction coefficients, making them interesting materials to study fundamental questions in the physics of granular materials and suspensions (e.g. Ref. [4]). Obtaining spherical hydrogel particles in sufficient quantities is therefore of great interest for many fields. One way of synthesizing hydrogel particles is by solidifying pre-made droplets. However, making monodisperse droplets with sizes around 1 mm is challenging. In this chapter we describe how to make large amounts of such large particles.

Standard emulsification using high energy input devices, such as dispersers and homogenizers, yields highly polydisperse droplets [5], where resulting size distributions can span several decades. Alternatively, microfluidic devices can be employed to produce highly monodisperse droplets; for a review see Reference [6]. In most microfluidic droplet generating chips, shear forces break up a continuous stream into small droplets, using a perpendicular flow (T-junction) [7], focusing flow [8] or shear flow [9]. Although such methods are usually well-understood and the droplet size can often be tuned, they are typically suited for production of droplets with diameters up to a few hundred μm [6], and thus unsuitable for our purposes. Furthermore, in practice it is often difficult to keep such devices operating for the several hours necessary to produce large amounts of particles.

Another difficulty arises when making millimeter-sized particles: while surface tension has the tendency to keep droplets spherical, gravity can cause droplets to become non-spherical while the submersed particles are solidifying in their immiscible liquid environment. One can quantify the relative importance of gravity with respect to surface tension by calculating the Bond number (also called Eötvös number) [10]:

$$Bo = \frac{\Delta\rho g l^2}{\Gamma} \quad (2.1)$$

where $\Delta\rho$ and Γ are the density difference and the surface tension between the two phases, g is the gravitational acceleration, and l is a characteristic length scale, typically the diameter of the droplet. When droplets are small, Bo is small, surface tension dominates and droplets are spherical. It is therefore essential to adjust experimental parameters to ensure $Bo < 1$ in our context of the production of large particles. As l is an important parameter in Bo , controlling the droplet size is of

key importance.

Here we present a simple technique to produce spherical hydrogel particles while also controlling their size. We use a nozzle to disperse droplets of a solution in oil and subsequently solidify them. By making droplets one at a time, the production process is reproducible, resulting in monodisperse particles. Furthermore, using cheap and easy to use syringe pumps, a relatively high production rate (in terms of volume) can be achieved. Additionally, by adding a coaxial air flow to the nozzle, we obtain excellent control over the particle size. Although using a coaxial air flow is not new [11–15], to the best of our knowledge, a quantitative description relating droplet size to the air flow rate is still lacking. We show that a simple theoretical description of this droplet production process can predict the particle size. Conjointly, we extend the method to allow for production of both physical and chemical gels.

2.1.1 Drop detachment

In the quasistatic limit, a drop of liquid will detach from a blunt nozzle when the weight F_g just exceeds the maximum capillary force $F_\Gamma^{max} = 2\pi r\Gamma$, where r is the radius of the nozzle (Fig. 2.1). This is known as Tate’s law [16], $F_g = f_{HB}F_\Gamma^{max}$ or

$$\Delta\rho\frac{\pi}{6}d^3g = 2f_{HB}\pi r\Gamma. \quad (2.2)$$

Here, f_{HB} is a constant smaller than unity, known as the Harkins-Brown correction factor [17], which accounts for the liquid that remains attached to the nozzle after drop detachment. As indicated by Equation 2.2, by suspending the nozzle in air rather than in oil, $\Delta\rho$ is maximized at formation of the droplet and the droplet diameter d is decreased. In our setup, this small droplet subsequently falls in oil to minimize $\Delta\rho$ during the solidification process. Immersion of the liquid droplet in oil reduces Bo , keeping the drop spherical. We can reduce d further by choosing smaller nozzles (decreasing r), but as $d \propto r^{\frac{1}{3}}$, this provides only limited control. Furthermore, reducing r has a tremendous effect on the pressure drop ΔP over the nozzle, as $\Delta P \propto r^{-4}$ [18], leading to increasing difficulties in maintaining high production rates.

We can however add another force to stimulate droplet detachment at small drop sizes. By placing the nozzle in a downward air flow, air drag on the growing droplet will promote early drop detachment. The air flow imposes a drag force F_D on the droplet, which contributes to the downward force. For droplet detachment, we must have:

$$F_g + F_D > f_{HB}F_\Gamma^{max}. \quad (2.3)$$

Figure 2.1: Schematic of the droplet detachment process. Air (dashed arrows) flows along a nozzle with diameter $2r$. This generates a drag force F_D on the droplet that adds to its weight F_g . The droplet detaches from the nozzle when $F_g + F_D$ exceeds the maximum capillary force F_{Γ}^{max} .

Generally, the drag force can be computed as [18]:

$$F_D = 0.5C_D A u^2 \rho, \quad (2.4)$$

in which u and ρ are the velocity and density of the flowing liquid respectively, C_D is the drag coefficient and A is the cross-sectional area of the obstacle. For our droplet, we take $A = \frac{1}{4}\pi d^2$. During pumping, d will gradually increase until $F_g + F_D > f_{HB} F_{\Gamma}^{max}$. We will show that the droplet size can be well predicted by Equation 2.3.

2.2 Materials & methods

2.2.1 Gelatin particles

As an example of physical gels we use a common household polymer: gelatin. Well known in the food industry, gelatin solutions are highly sensitive to temperature: at high temperatures they are fluids, while at low temperatures they form gels [19, 20], as hydrogen bonds cross-link the strands reversibly, making gelatin an example of a “physical gel”. We can use gelatin’s temperature responsiveness to produce particles, by dispersing drops of hot gelatin solution in a low temperature oil bath. As bonds are reversible, we prevent the gel particles from slowly

dissolving in an aqueous solvent by cross-linking the particles chemically with glutaraldehyde [21]. Glutaraldehyde is not the only available cross-linker for gelatin; many others are known in the literature [22–24]. We dissolve 10 wt% gelatin (from porcine skin, type A, Bloom 300, Sigma-Aldrich) in hot water. Note that the exact type of gelatin is of importance: fish gelatin has very different properties than porcine or bovine gelatin and is much less suitable for our purposes [20, 25].

The solution is dispersed using a standard syringe pump equipped with tubing and a nozzle (Nordson EFD, Prod. Nr. 7005008), with an internal diameter of 200 μm and length of 12.7 mm. To ensure the solution remains liquid, the syringe pump is located in a heated box. The box is heated by a small heat exchanger attached to a thermal bath circulating 50°C water. Two 12V fans blow air through the heat exchanger into the box. The box reaches a temperature of over 45°C, well above the melting point of gelatin [19, 20].

The flow rate of the gelatin solution should not matter for the resulting droplet size as long as the fluid does not influence the drop detachment process. We keep the flow rate constant at 500 $\mu\text{L min}^{-1}$. Higher flow rates are not fundamentally impossible to achieve, but tend to result in experimental issues, such as leakage at the tubing connectors, as the pressure drop is increased. We dispense the gelatin solution into a funnel (PP, RS Pro) connected to a hose (PVC, RS Pro, ID = 10 mm, OD = 13 mm) filled with oil (decane, >99%, TCI Chemicals), which is immersed in a second tube filled with circulating 5°C water. Droplets detach from the nozzle and fall into the cold oil, solidifying them during their settling to the base of the tube, where a reservoir collects the particles. It is essential that the hose is sufficiently tall so that droplets are partially solidified before reaching the bottom, thereby preventing coalescence of the droplets. We find that for the largest droplets, a tube of approximately 2 meters is sufficient. As smaller droplets cool faster, a plastic beaker with a height of 15–20 cm is sufficient for the smallest droplets. Note that the funnel, hose and beaker are made of hydrophobic materials (PP, PVC) to prevent droplets from sticking to the walls.

To produce small particles, air is focused along the nozzle using a simple 3D-printed holder (Fig. 2.2). The plastic (Luer lock) part of the nozzle fits tightly in this holder, thereby centering the nozzle in the 3.2 mm exit. This design makes the nozzle stick out from underneath the holder by 2.5 mm. We did not vary this length scale as we assume it is of minor importance for the prefactor in Equation 2.4. The air flows through four holes in the sides of the holder. The holder is glued to the cap of a 50 mL centrifuge tube. We drill two holes in the centrifuge tube; one to let the air flow in, another for the tubing connecting the syringe pump to the nozzle. To prevent droplets from drying during formation, the air flows through a gas-washing bottle, which contains water. Without this air humidification step,

Figure 2.2: (a) 3D drawings of the nozzle holder. Four holes in the sides of the holder allow air to flow through. The arrows indicate the direction of the air flow. (b, c) The Luer-Lock (1) of the nozzle fits tightly in the holder (2) glued to the cap of a 50 mL centrifuge tube (3). The tip of the nozzle (4) is centered in the 3.2 mm exit and distanced 2.5 mm from the holder.

filaments of gelatin are formed, presumably due to local drying of the gelatin. The filaments make the droplet production process erratic. For a schematic overview of the set-up, see Figure 2.3. The air flow rate Q is set using a Cole-Parmer valved acrylic flow meter (100 mm Scale for Air, 2-20 LPM). We produce particles at six different values of Q , ranging from 0 to 6 L min⁻¹. Higher air flow rates are not investigated, as the required air pressure approaches the maximum operating pressure of the gas-washing bottle.

After particle generation, we add 1.5 mL of a 50 wt% glutaraldehyde solution (Sigma-Aldrich) to 10 mL of particles suspended in 100 mL of decane. The particles are left in this mixture for 1 hour, while shaking thoroughly to avoid particles from cross-linking to each other. After this step, we wash the particles repeatedly with ethanol and water to ensure all decane is removed. The particles obtain a slight brown/orange color by treatment with glutaraldehyde, and do not melt in hot water as a result of the chemical cross-links present on the gelatin network after this treatment.

2.2.2 Polyacrylamide particles

Our coaxial air flow droplet generator is also suitable for making chemical gel beads, that cross-link irreversibly. Polyacrylamide (PAAm) gel beads have many uses, even though they are not food grade. For example, they are utilized in extraction processes [26], and can be functionalized to prepare biochemical adsor-

Figure 2.3: Schematic overview of the device used to produce particles. A thermally insulated box is heated by fans blowing through a heat exchanger (1). The box holds a syringe pump (2) equipped with a syringe with the solution. Air flows through a gas-washing bottle (3) to moisturize the air. The air flow is focused around the nozzle (4) which produces droplets falling into a plastic hose with cold oil (5). The air flow rate is set using a valved flow meter (6).

bents [27]. They are generally made by co-polymerization of acrylamide (AAM) and N,N'-methylenebisacrylamide (BIS). The reaction is started using an initiator such as ammonium persulfate (APS). Additionally, a catalyst can significantly enhance the reaction rate at room temperature. We prepare an aqueous solution of 20 wt% AAM (>98%, Sigma-Aldrich), 1 wt% BIS (99%, Sigma-Aldrich) and 1 wt% APS (BIO-RAD). We use the method described above to generate particles. There are a few differences however: the PAAm components are liquid at room temperature, and the cross-linking reaction does not require low temperatures. Rather, we dissolve 2 wt% of catalyst (tetramethylethylenediamine (TEMED), ultra pure grade, VWR) in the oil phase (kerosene, purum, Sigma-Aldrich), to allow for quick gelation of the droplets. After particle generation, the particles are washed with ethanol and water to remove the oil and unreacted materials.

2.3 Results & discussion

To determine the particle size resulting from our production technique, we record the droplet production at the nozzle with a high speed camera, while illuminating

Figure 2.4: Diameter d as function of air flow rate Q , for two different materials. Error bars are deduced from a peak width estimate in the droplet production frequency as obtained from video recordings – see text. Also shown is the outcome of our simplified force balance model.

with an LED lamp from a 90° angle. By monitoring the time dependence of the mean intensity of an array of pixels below the nozzle, we find the frequency of droplet generation by taking the Fourier transform of the intensity signal. As we know the rate at which the solution is pumped ($500 \mu\text{L min}^{-1}$), the volume and diameter of the droplets can subsequently be calculated. In Figure 2.4, we plot the diameter as function of the air flow rate Q for both materials. The error bars correspond to the lower and upper bounds of the peak in the Fourier transform of the video intensity signal. As we image a finite amount of time (about 10 s), the number of recorded drop detachments increases with Q , leading to smaller errors.

We compare our measured diameters with the outcome of the simple force balance picture given in Equation 2.3. We employ Equation 3 and 7 from Reference [28] to find f_{HB} using only Γ and $\Delta\rho$ as input parameters. We use $\Gamma \approx 0.06 \text{ N/m}$, in agreement with literature values for gelatin solutions [29] and we measured the surface tension of the acrylamide solution in a drop tensiometer to be 0.057 N/m . Assuming the density difference $\Delta\rho \approx 10^3 \text{ kg/m}^3$, we find $f_{HB} \approx 0.88$, leading to a droplet with diameter $\approx 2.35 \text{ mm}$ at $Q = 0$, in agreement with our droplet size determination. Note that after the droplets are submersed in the oil bath, $Bo \approx 0.25$ for these droplets, suggesting that surface tension between the oil and water/gel phase is dominant over gravity, resulting in spherical particles, in agreement with our observations.

Using Equations 2.2 and 2.4, we calculate the three forces acting on the

Figure 2.5: Examples of particles made using our technique. Gelatin particles made without air flow (a) and at 3 and 6 L min⁻¹ (b, c). PAAm particles made without air flow (d) and at 3 and 6 L min⁻¹ (e,f). Grid size is 1 mm. Note that the magnification is different in each column. (g) Particle size distribution of gelatin particles made at 3 L min⁻¹.

droplet. The gray area in Figure 2.4 denotes a regime where the total downward force on the droplet exceeds the maximum capillary force, whereas in the white area the capillary force exceeds the downward force. Drop detachment is expected at the boundary. We find good agreement between our data and the model using $C_d \approx 1.2$. Although C_d for a sphere at these intermediate Reynolds numbers ($Re \approx 10^3$) is about a factor of 3 lower according to literature [18], we attribute this to the non-sphericity of the pendant drop, as well as the possible influence of the nozzle and air flow geometry around the nozzle.

In Figure 2.5a-f, we show examples of particles produced using our technique. We also image a layer of particles to obtain the particle size distribution. The imaged area is around 5 x 5 cm. The image is analyzed with MATLAB, using a circular Hough transform to find the circles and calculate their radius R . We plot the particle size distribution of gelatin particles made at 3 L min⁻¹ in Figure 2.5g, showing that particles are highly monodisperse. We find the standard deviation of the radius σ_R to be 22 μ m, resulting in a polydispersity $\sigma/R \approx 0.03$. This is equivalent to the polydispersity achieved in a microfluidics setting [9].

As the droplet detachment is highly reproducible, droplets are monodisperse. However, after formation of the droplets and submersion in the oil, droplets may still merge before being fully solidified. This becomes increasingly likely when the frequency of drop formation increases. We believe this to be the origin of the observed polydispersity in Figure 2.5f, where some particles have twice the volume

($\sqrt[3]{2} \approx 1.26$ times the diameter) of other particles. We have used the funnel and tube described in our experimental section to produce these particles. To avoid droplets from merging, a larger diameter tube or beaker could be used. We did not test if our method can be used to produce smaller particles using higher air flow rates than 6 L min^{-1} . We expect that, as the Reynolds number increases, the method will start to resemble atomization processes such as those used in spray drying, where particle size distributions are much broader [30].

2.4 Conclusion

We presented a simple method to produce millimeter-sized gel spheres using a macroscopic technique. We used an air flow along the nozzle to tune the size of the particles. Particles produced using this method have diameters ranging from 2.3 to 0.7 mm, as evidenced by Figure 2.4 and 2.5. This size can be easily predicted using a simple force balance picture. The method can be used to produce both physical and chemical gels and is hence highly universal. For example, it has already been used to produce alginate particles [31], and could also be used to make temperature sensitive poly(N-isopropylamide) particles.

References

- [1] R. Cortesi, C. Nastruzzi, and S. Davis, "Sugar cross-linked gelatin for controlled release: microspheres and disks," *Biomaterials*, vol. 19, no. 18, pp. 1641–1649, 1998.
- [2] T. T. Lau, C. Wang, and D.-A. Wang, "Cell delivery with genipin crosslinked gelatin microspheres in hydrogel/microcarrier composite," *Composites Science and Technology*, vol. 70, no. 13, pp. 1909–1914, 2010.
- [3] J. P. Gong, "Friction and lubrication of hydrogels: richness and complexity," *Soft Matter*, vol. 2, no. 7, pp. 544–552, 2006.
- [4] D. M. Walker, A. Tordesillas, N. Brodu, J. A. Dijksman, R. P. Behringer, and G. Froyland, "Self-assembly in a near-frictionless granular material: conformational structures and transitions in uniaxial cyclic compression of hydrogel spheres," *Soft Matter*, vol. 11, no. 11, pp. 2157–2173, 2015.
- [5] T. Mason and J. Bibette, "Shear rupturing of droplets in complex fluids," *Langmuir*, vol. 13, no. 17, pp. 4600–4613, 1997.
- [6] S.-Y. Teh, R. Lin, L.-H. Hung, and A. P. Lee, "Droplet microfluidics," *Lab on a Chip*, vol. 8, no. 2, pp. 198–220, 2008.
- [7] T. Thorsen, R. W. Roberts, F. H. Arnold, and S. R. Quake, "Dynamic pattern formation in a vesicle-generating microfluidic device," *Physical Review Letters*, vol. 86, no. 18, p. 4163, 2001.
- [8] L. Yobas, S. Martens, W.-L. Ong, and N. Ranganathan, "High-performance flow-focusing geometry for spontaneous generation of monodispersed droplets," *Lab on a Chip*, vol. 6, no. 8, pp. 1073–1079, 2006.
- [9] P. Umbanhowar, V. Prasad, and D. Weitz, "Monodisperse emulsion generation via drop break off in a coflowing stream," *Langmuir*, vol. 16, no. 2, pp. 347–351, 2000.
- [10] W. H. Hager, "Wilfrid Noel Bond and the bond number," *Journal of Hydraulic Research*, vol. 50, no. 1, pp. 3–9, 2012.
- [11] T. Reh, C. Dorger, and P. C. Chau, "Application of an atomizer in producing small alginate gel beads for cell immobilization," *Biotechnology Letters*, vol. 8, no. 2, pp. 111–114, 1986.
- [12] D. B. Seifert and J. A. Phillips, "Production of small, monodispersed alginate beads for cell immobilization," *Biotechnology Progress*, vol. 13, no. 5, pp. 562–568, 1997.
- [13] M. Albarghouthi, D. A. Fara, M. Saleem, T. El-Thaher, K. Matalaka, and A. Badwan, "Immobilization of antibodies on alginate-chitosan beads," *International Journal of Pharmaceutics*, vol. 206, no. 1, pp. 23–34, 2000.
- [14] S. Koch, C. Schwinger, J. Kressler, C. Heinzen, and N. Rainov, "Alginate encapsulation of genetically engineered mammalian cells: comparison of production devices, methods and microcapsule characteristics," *Journal of Microencapsulation*, vol. 20, no. 3, pp. 303–316, 2003.
- [15] Nisco Engineering AG. http://www.nisco.ch/var_j1.html.
- [16] T. Tate, "Xxx. on the magnitude of a drop of liquid formed under different circumstances," *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, vol. 27, no. 181, pp. 176–180, 1864.
- [17] W. D. Harkins and F. Brown, "The determination of surface tension (free surface energy), and the weight of falling drops: the surface tension of water and benzene by the capillary height method.," *Journal of the American Chemical Society*, vol. 41, no. 4, pp. 499–524, 1919.
- [18] T. E. Faber, *Fluid dynamics for physicists*. Cambridge University Press, 1995.
- [19] A. G. Ward and A. Courts, *Science and technology of gelatin*. Academic Press, 1977.
- [20] A. Simon, Y. Grohens, L. Vandanjon, P. Bourseau, E. Balnois, and G. Levesque, "A comparative study of the rheological and structural properties of gelatin gels of mammalian and fish origins," *Macromolecular Symposia*, vol. 203, no. 1, pp. 331–338, 2003.
- [21] L. O. Damink, P. Dijkstra, M. Van Luyn, P. Van Wachem, P. Nieuwenhuis, and J. Feijen, "Glutaraldehyde as a crosslinking agent for collagen-based biomaterials," *Journal of Materials Science: Materials in Medicine*, vol. 6, no. 8, pp. 460–472, 1995.
- [22] R. De Carvalho and C. Grosso, "Characterization of gelatin based films modified with transglutaminase, glyoxal and formaldehyde," *Food Hydrocolloids*, vol. 18, no. 5, pp. 717–726, 2004.
- [23] C. Vichasilp, K. Nakagawa, P. Sookwong, O. Higuchi, F. Kimura, and T. Miyazawa, "A novel gelatin crosslinking method retards release of mulberry 1-deoxynojirimycin providing a prolonged hypoglycaemic effect," *Food Chemistry*, vol. 134, no. 4, pp. 1823–1830, 2012.

- [24] A. Bigi, G. Cojazzi, S. Panzavolta, N. Roveri, and K. Rubini, "Stabilization of gelatin films by crosslinking with genipin," *Biomaterials*, vol. 23, no. 24, pp. 4827–4832, 2002.
- [25] A. Karim and R. Bhat, "Fish gelatin: properties, challenges, and prospects as an alternative to mammalian gelatins," *Food Hydrocolloids*, vol. 23, no. 3, pp. 563–576, 2009.
- [26] E. Cussler, M. Stokar, and J. Varberg, "Gels as size selective extraction solvents," *AIChE Journal*, vol. 30, no. 4, pp. 578–582, 1984.
- [27] J. K. Inman and H. M. Dintzis, "Derivatization of cross-linked polyacrylamide beads. controlled introduction of functional groups for the preparation of special-purpose, biochemical adsorbents," *Biochemistry*, vol. 8, no. 10, pp. 4074–4082, 1969.
- [28] Y. H. Mori, "Harkins-brown correction factor for drop formation," *AIChE Journal*, vol. 36, no. 8, pp. 1272–1274, 1990.
- [29] H. Sato and K. Ueberreiter, "Surface tension of aqueous gelatin solutions, 1. concentration dependence," *Die Makromolekulare Chemie*, vol. 180, no. 3, pp. 829–835, 1979.
- [30] A. Lefebvre, *Atomization and sprays*, vol. 1040. CRC press, 1988.
- [31] M. N. Corstens, C. C. Berton-Carabin, P. T. Elichiry-Ortiz, K. Hol, F. J. Troost, A. A. Masclee, and K. Schroën, "Emulsion-alginate beads designed to control in vitro intestinal lipolysis: towards appetite control," *Journal of Functional Foods*, vol. 34, pp. 319–328, 2017.

Chapter 3

Shear banding and relaxation in soft sphere suspensions

In this chapter, we describe a method to investigate the microscopic origin of granular fluidity. We probe the flow of suspensions of soft hydrogel particles, using a Couette cell with transparent bottom and lid. We produce the particles using the method described in Chapter 2. As gelatin is photoelastic, we have access to local stress fluctuations. We also use particle image velocimetry to measure the flow profiles of the suspension. We compare the profiles of the gelatin suspension to that of a polyacrylamide hydrogel suspension, to assess robustness of observed phenomenology. With the exquisite control that our setup provides, we have the unique ability to combine optical and rheological measurements. How do our suspensions flow? We focus on the flow profiles during shear, as well as the relaxation of the suspension after the flow is suddenly stopped. We find that the flow profiles for both types of hydrogel are different; gelatin suspensions feature narrower shear bands. Also in the relaxation behavior the gelatin suspensions are less dynamic; using optical and rheological methods, we find that the gelatin suspensions show less relaxation compared to the polyacrylamide case. We speculate on the origin of the observed differences by considering the frictional properties of the hydrogels.

This chapter is based on:

M. Workamp, S. Alaie and J.A. Dijksman, *What is fluidity? Designing an experimental system to probe stress and velocity fluctuations in flowing suspensions*, EPJ Web of Conferences 140 (2017), 03020.

3.1 Introduction

The flow behavior of dry granular materials and dense suspensions can generally be viewed as consisting of two regimes. In the slow flow limit or quasi-static regime, grain-to-grain interactions are frictional and the shear stress is rate-independent or at best weakly rate-dependent [1], because dry friction is generally considered rate-independent. At higher driving rates, the material becomes more fluid-like: inertia or the viscosity of the interstitial fluid starts to play a role and the stress increases are well described by a power law originating from collisional or viscous energy loss in this flow regime. Such behavior can be captured by the Herschel-Bulkley (HB) model that is widely used to describe yield-stress fluids:

$$\tau = \tau_0 + k\dot{\gamma}^n, \quad (3.1)$$

where τ denotes the shear stress, τ_0 the yield stress, $\dot{\gamma}$ the shear rate, k a proportionality constant and n a power law index. The HB model is very effective in capturing the macroscopic flow response of structured fluids including granular materials, suspensions, emulsions and foams. There are several avenues of active research that aim to improve its descriptive power and deepen the knowledge of its microscopic origin. Such efforts focus on conditions in which the HB model fails to capture the flow behavior of yield stress fluids. For example, it is well-known that the *local* flow behavior of yield stress fluids is poorly captured. In particular, it is established that HB fluids can form shear bands (for a review see Ref. [2]), especially when a spatially inhomogeneous stress field is applied. One way to apply such a stress field is in a Couette geometry, where a cylinder rotates coaxially in a, usually static, second cylinder. The shear stress τ in such a system decays as $\tau(r) \sim 1/r^2$, with r the radius. Although, based on the HB model, one may expect the flow to stop abruptly where the local stress drops below the bulk yield stress (at $r(\tau < \tau_0)$), the flow profile for a yield stress fluid is smooth [2–5].

Recently, models have been developed to predict such smooth flow profiles, relying on the notion of *nonlocality* (see Section 1.4.2). These models are based on the so-called fluidity field, which is proportional to the rate of plastic rearrangements [6], which govern the nonlocal effects. The local fluidity is proportional to the inverse viscosity [6], i.e. $f_{loc} = \dot{\gamma}(\tau)/\tau_{loc}$. The fluidity field f in its most general form is given by:

$$f = f_{loc} + \xi^2 \nabla^2 f \quad (3.2)$$

where ξ is a length scale that depends, amongst others, on the distance of the local stress to the yield stress [7–10]. The second, diffusive, term ensures the smoothness of the flow profiles. Fluidity modelling, originally proposed for emulsions [6],

can be adapted to granular flows by incorporating pressure dependence [8]. Although fluidity modelling successfully predicts flow profiles in different geometries with few fitting parameters [9], the microscopic meaning of the fluidity field remains subject of debate. The fluidity field somehow models fluctuations present in a slowly flowing granular material, yet are these fluctuations of velocities, stresses, or something else?

Here we propose and construct an experimental environment in which we can probe the role of local stress and velocity fluctuations in the flow behavior of a three-dimensional suspension. We perform experiments in Couette flows of gelatin particles, made using the methods described in Chapter 2. The gap of the Couette cell is approximately 10 particle diameters wide (see Section 3.2), resulting in a highly heterogeneous stress field, making nonlocal effects probable. To probe stress fluctuations, we need access to local stress information. This is traditionally done with photoelastic materials. As gelatin is photoelastic [11], the gelatin particles we described in Chapter 2 can be used to obtain local stress measurements, by imaging the particles in transmission mode. As the particles are transparent but not refractive index matched, we also have access to the velocity profiles of the particles.

In this chapter we will demonstrate that we can indeed optically resolve an average local stress field inside a flowing suspension. Because particle image velocimetry (PIV) of granular materials is typically done by imaging only a surface, it is not evident that transmission mode imaging can also resolve flow fields. We show here that we can indeed obtain velocity measurements from transmission imaging. To see how universal the flow profiles of the gelatin suspension are, we then compare them to those of another typical hydrogel, polyacrylamide (PAAm). We find that PAAm suspensions have wider shear bands, and their width depends less on the driving rate. We perform additional experiments to find out how the two suspensions are mechanically different. By looking at the relaxation processes in the suspension after suddenly stopping the flow, we obtain another measure for the fluctuations that may play a role in the rheology. Again, the PAAm suspension shows much more mobility than the gelatin suspension. We speculate the origin of the observed differences to be related to the frictional properties of the particles.

Figure 3.1: (a) Schematic of the Couette cell. The inner cylinder diameter $d_i = 50$ mm, while the outer cylinder diameter $d_o = 90$ mm. The height of the shear cell $h = 20$ mm. (b) Schematic overview of the experimental setup. A pressure sensor is mounted to the lid of the cell. We image the suspension in transmission mode using an LED lamp and diffuser, and an 8-bit camera.

3.2 Materials & methods

3.2.1 Setup

We use a custom Couette geometry with fixed volume to drive the flow of a hydrogel particle suspension. The inner cylinder and outer wall are 3D-printed. The inner cylinder diameter $d_i = 50$ mm, while the outer cylinder diameter $d_o = 90$ mm (Fig. 3.1a). To avoid slip, both inner and outer walls are made rough with vertical grooves of approximately 2.5 mm, similar in size as the particles (see Section 3.2.4). The height of the shear cell $h = 20$ mm, while the height of the inner cylinder is 19 mm, so that it freely rotates between the bottom and top plate (lid), which are made of smooth acrylic plastic. The bottom plate is glued to the outer wall of the cell using two component glue (Bison Kombi Snel), while the top plate is held in position using a ring that is bolted down to the rest of the shear cell. Additional particles can be added through a small hole in the lid, which is sealed with a cap that is flush with the lower surface of the lid, so that the particle/fluid flow along the lid surface is not disturbed.

We measure the vertical confining pressure using a calibrated load cell on part of the top plate (denoted “pressure sensor” in Fig. 3.1a). To avoid capillary effects in the small spacing between the part of the lid connected to the load cell and the rest of the lid, we submerge the entire lid with a layer of water, and correct for buoyancy. We provide power to the load cell (Futek LSB210, 2 lb, submersible)

Figure 3.2: (a) Example of an image made using linear polarizers, showing the photoelastic response of the gelatin particles. Stresses are anisotropic and point against the direction of shear (inner cylinder rotating clockwise). (b) Image of a suspension without polarizers. (c) Same as (b) after transforming the coordinate system from Cartesian to polar.

using a standard laboratory power supply set to 5.0 V, and we record the voltage difference using a USB I/O device (National InstrumentsTM USB-6211), interfaced with LabVIEW (National InstrumentsTM).

We use a stress-controlled rheometer (Anton-Paar MCR 300) to drive the inner cylinder at a fixed rotation rate. We set the CSR value, which controls the feedback between the applied shear stress and obtained shear rate, to its maximum to ensure a constant rotation rate; at low CSR value, or in automatic mode, stick-slip behavior is observed at low driving rates (i.e. the applied rate is not constant). This is probably because the CSR then creates a too flexible effective coupling between the rheometer motor and the driving cylinder. We image the suspension from below with an 8-bit camera (Basler avA1000-120km), while illuminating from the top using an array of LEDs and a diffuser (Fig. 3.1b). We can add polarizers to image the photoelastic response of the gelatin particles, of which we show an example in Figure 3.2a.

3.2.2 Protocol

We perform experiments in suspensions at fixed volume fraction, characterized by the pressure exerted on the top plate. We measure this confining pressure at a low rotation rate of the inner cylinder ($\Omega_i = 6.3 \times 10^{-3}$ rad/s) and make sure all experiments are carried out at the same pressure $P^p \approx 2 \times 10^2$ Pa. As the particles are porous and their swelling depends on the solvent, density matching of these particles is challenging. Because the particles are composed of *hydrogel*, we use water as the interstitial fluid. The maximum hydrostatic pressure resulting from the density difference $\Delta\rho$ between the particles and water can be estimated $P_g = \Delta\rho gh \approx 20$ Pa. The pressure due to the density mismatch is always much smaller than any applied confining pressure, so we assume we can neglect the role of P_g .

Before our measurements, we pre-shear the suspension at $\Omega_i = 63$ rad/s for 10 seconds. After waiting for 30 seconds, we then start driving the suspension at a fixed Ω_i ranging from 6.3×10^{-3} rad/s to 6.3 rad/s, spanning three decades in driving rate. To obtain flow profiles, we image the suspension for 10 seconds at 119 frames/second, the maximum frame rate of the camera system. To ensure that we measure in the steady-state, we start recording only after the inner cylinder has made about one full rotation at the set driving rate.

3.2.3 Image analysis

We first convert our recorded images (without polarizers) such that the coordinates are transformed from Cartesian to polar, see Figure 3.2b+c. This allows for finding the intensity as a function of the angle θ at given radius r , corresponding to a row of pixels. Typical for particle image velocimetry (PIV), we find the correlation between intensity profiles to get an estimate of the velocity at given r . Note that PIV is usually done on surface deformations, and it is not clear that this approach also works on a depth-averaged signal as obtained here in transmission imaging. However, we can still find significant correlation between intensity profiles; an example is shown in Figure 3.3. By finding the shift of the signal for different time steps Δt , we find the angular velocity $\Omega(r)$ – this is the standard method to do PIV.

Figure 3.3: Intensity profiles of a row of pixels at two distinct times, showing that the signals are correlated. The profile at later time is shifted to the right.

3.2.4 Particle characterization

We synthesize spherical hydrogel beads of mean diameter $d = 2$ mm to perform the experiments. We use the method described in Chapter 2 to produce particles of 10% cross-linked gelatin and polyacrylamide (PAAm). We make the particles in two sizes (around 1.9 and 2.3 mm), creating a bidisperse mixture that avoids crystallization. To characterize the stiffness of the particles, we measure the elastic modulus of the particles by uni-axial compression. We squeeze the particle between two submersed plates and measure the resulting normal force F_n as a function of the gap z between the two plates. By starting the measurement 200-300 μm above the particle, F_n can be easily corrected for the buoyancy of the top plate. To obtain the Young's modulus of the particles we apply Hertz's law [12]:

$$F_n = \frac{4}{3} E^* R^{1/2} \delta^{3/2} \quad (3.3)$$

with R the particle radius and $\delta = \frac{1}{2}(2R - z)$ the overlap corrected for the symmetry of the problem. The contact modulus E^* is given by:

$$E^* = \frac{E}{1 - \nu^2} \quad (3.4)$$

where E is Young's modulus and ν is Poisson's ratio. By assuming $\nu = 0.5$ (the value for an incompressible material), we can obtain E from our experimental data. In Figure 3.4, we plot F_n as function of the overlap δ . Indeed, the hydrogels are well described by Hertz's theory, as $F_n \propto \delta^{3/2}$. We measure the elastic moduli of 5 particles per material. For PAAm, the measured moduli range from 0.29 MPa

Figure 3.4: Typical results of uni-axial compression tests of hydrogel particles. Normal force F_n as a function of overlap δ . Using Hertzian contact theory (Eq. 3.3 and 3.4), we find the elastic modulus E of the particles.

to 0.33 MPa, and the average value is 0.31 MPa. For gelatin, the range is from 0.28 MPa to 0.36 MPa, and the average is very similar to that of PAAm: 0.32 MPa. The particles thus differ only in their chemical composition, which may result in differences in their surface structure or other physico-chemical properties, such as adhesion.

3.3 Results

3.3.1 Flow profiles

We image the flow of the hydrogel particle suspension in our Couette cell, and plot the results of our image analysis in Figure 3.5. In Figure 3.5a, we plot the velocity profiles of the PAAm suspension, showing that the shear band widens as we increase the driving rate of the inner cylinder Ω_i , as expected and similar to the findings in References [13, 14]. For the gelatin suspension (Figure 3.5b), the shear is much more localized at the same Ω_i . Particles in the outer half of the gap show very little movement, even at the highest rates applied. This finding shows that hydrogel material properties affect flow properties in this dense limit. We can find another difference between the PAAm and gelatin flow profiles in Figure 3.5b+d, where we have normalized the angular velocity Ω with the applied driving rate Ω_i . For the PAAm suspension (Fig. 3.5c), the width of the shear band does not depend much on rate, only a small widening of the shear band can be seen to

Figure 3.5: (a,c) Flow profiles for the PAAm particles. (a) Radial velocity Ω as a function of the radius r , for seven driving rates Ω_i . (c) Normalized velocity Ω/Ω_i as a function of r . (b,d) Flow profiles for the gelatin particles. Legend in (b) applies to all panels. Insets of (c) and (d) show the width of the shear band r_w as a function of Ω_i , for PAAm and gelatin particles respectively.

occur. However for the gelatin suspension (Fig. 3.5d), the shear bands appear to widen with rate. To quantify this observation, we determine the width of the shear band r_w . We define r_w as the radius at which the radial velocity has dropped to 10% of the driving rate, i.e. where $\Omega/\Omega_i = 0.1$. We plot r_w as a function of Ω_i in the insets of Figure 3.5c+d. This shows that for the PAAm suspension, there is no clear trend in r_w and it can be considered roughly constant. However, for the gelatin suspension, r_w indeed increases with Ω_i .

Figure 3.6: Normal force F_n as a function of time t of four individual particles in compression for PAAm particles (a), and gelatin particles (b). Note that the applied amount of strain on each particle is not constant. For PAAm particles (a), from top to bottom the strains ϵ are 0.29, 0.29, 0.20 and 0.18. For gelatin particles (b), the strains are 0.25, 0.25, 0.23 and 0.22, respectively.

3.3.2 Relaxation after shear

In emulsions, the fluidity field, which governs the width of the shear band, is intrinsically linked to shear rate fluctuations [15]. The ability of particles to have such fluctuations, should also influence the mechanical response when shear is suddenly stopped. We perform relaxation experiments, in which we suddenly stop the inner cylinder of the Couette cell by setting its rotation rate to zero. This halts the imposed deformation instantaneously, but not the flow, as we shall see shortly. Note that a granular system of particles does not typically show stress relaxation after driving has ceased. This is in contrast to dense colloidal systems [16], where thermal fluctuations are always able to drive relaxation processes. However, stress relaxation in dry granular materials can be induced by vibration [17]. Here we investigate if a suspension of *soft* particles can show stress relaxation, and if there is a relation between the relaxation process and the flow profiles that we observe.

We use two different metrics to look at the relaxation process. First, we look at relaxation of the shear stress, which we measure over 145 seconds after stopping the rotation of the inner cylinder, keeping the angle of the inner cylinder fixed. Our second metric is measured simultaneously and is based on imaging; we will look at the difference between images to find out how the suspension comes to rest. To be able to interpret the relaxation process of the suspensions, let us first consider the relaxation processes that occur in individual particles. We compress

Figure 3.7: Remaining stress τ_r , divided by the driving stress τ right before stopping rotation of the inner cylinder, as a function of time t for PAAm (a) and gelatin (b). Legend in (a) applies to both panels and shows the driving rates before stopping.

a single particle between two parallel plates, as in our measurement of the elastic modulus. After compressing the particle to a finite strain $\epsilon = \frac{R-z}{R}$ of about 0.2-0.3, we measure the resulting normal force F_n as a function of time t , plotted in Figure 3.6 for four PAAm particles as well as four gelatin particles. At time scales up to about 10 seconds, no relaxation can be seen to occur. However, there is a slow relaxation process in both the PAAm and the gelatin, which is likely to be poroelastic relaxation [18, 19], a process in which the water inside the gel is slowly transported through and out of the network, thereby relaxing the gel. It appears that this phenomena plays a bigger role in the gelatin, because the normal force relaxes by about $\frac{2}{5}$ of its original value, as compared to $\frac{1}{5}$ for the PAAm gels.

Now that we know how individual particles relax, we can try to understand the relaxation of the suspensions. We plot the remaining shear stress τ_r divided by the driving stress before stopping τ as a function of time t in Figure 3.7, after driving at the four lowest driving rates. At higher rates, inertia of the rotating tool becomes so large that the negative torque required to slow it down dominates the signal. Comparing the PAAm suspension (Fig. 3.7a) to the gelatin (Fig. 3.7b), we can observe a clear difference. For both suspensions, the remaining shear stress τ_r relaxes at time scales much shorter than those observed for individual particles (Fig. 3.6), suggesting not only poroelasticity plays a role, but also some form of structural relaxation occurs. However, this is particularly evident for the PAAm suspension, where a larger fraction of τ_r has relaxed after our maximum waiting time ($t = 145$ s).

As structural relaxation in the form of particle shape changes or rearrangements should be visually detectable, we image the suspension during the relaxation process. For simplicity, we use raw images obtained without polarizers, in their original polar coordinate system (example shown in Fig. 3.2b). To quantify the relaxation process, we use the difference between an image A at some time t and an image B taken at time $t = 145$ s. We define S as the root of the sum of squared differences of images A and B with $m \times n$ pixels:

$$S = \sqrt{\sum_{i=1}^m \sum_{j=1}^n (A_{ij} - B_{ij})^2} \quad (3.5)$$

Thus, S is small for an image that resembles the final frame of the video, and as such should decay for a suspension that exhibits structural changes during the relaxation process. We plot $S(t)$ in Figure 3.6 for both suspensions and the four driving rates previously considered. Again, there are clear differences between the PAAm and gelatin suspensions. S starts at much larger values for PAAm, which suggests structural changes take place in the suspension during the relaxation process. What's more, in the gelatin suspension hardly any relaxation can be seen to occur after approximately 10 seconds, consistent with the picture of poroelastic relaxation where the stress τ decreases (Fig. 3.7) while the particles keep their position. For PAAm, the decay of S also continues at long time scales, suggesting particle rearrangements take place long after the flow has stopped. Note that S does not become zero due to pixel noise. S tends to reach a final value of about 0.8×10^3 , the sum of squared differences (S^2) is approximately 6×10^5 , which resembles the number of pixels that we use (5×10^5), so that the noise is about 1 intensity unit per pixel. In both the gelatin and PAAm case, there are a few sharp peaks in the $S(t)$ -plot. From our videos, we do not observe any events occurring at these t . We thus attribute these peaks to minor mechanical disturbances of the setup. Note that in principle, the displacements of particles can be detected using PIV. However, because the time scales are relatively short and the displacements small (S is only a few times the pixel noise), we do not obtain a clear average shift in the pixel intensity profiles.

3.4 Discussion

In both the flow profiles and the relaxation process, we have seen clear differences between suspensions of PAAm and gelatin particles. Since the particles have similar size, stiffness and polydispersity, we believe these differences to be related to either the frictional or adhesive properties of the materials. It is known that hydro-

Figure 3.8: (a,c) S , the root of the sum of squared differences, as a function of time for a suspension of PAAm particles, with logarithmic (a) and linear (c) t -axis. (b,d) Idem for gelatin particles. Legend applies to all panels.

gels may have very complex frictional behavior [20], where the friction coefficient may depend on the load as well as the sliding velocity. Gel friction depends on the chemical structure of the gel [21]. It is likely that the two types of gel examined here have different frictional behavior, resulting in different rheological behavior. The results obtained here could be well explained by the PAAm having a lower friction coefficient than gelatin. A lower friction coefficient would allow particles to move with respect to each other more easily, which may explain the wider shear bands, as less energy is dissipated in every “layer” of particles. If PAAm particles

are indeed more mobile, this also provides a mechanism to relax the shear stress, by means of structural rearrangements. This simple scenario provides a qualitative description of the origin of the observed relaxation behavior. Note that PAAm having a lower friction coefficient is in agreement with our experimental observation that we can not achieve $P^p > 0.3$ kPa by filling the particles through the hole in the lid, as they easily slip away during the manual filling process, whereas we can readily achieve pressures above 1 kPa with gelatin particles.

3.5 Conclusion

We developed an experimental system to probe the role of stress and velocity fluctuations in a model suspension, with the aim to find the origin of granular fluidity. We show that we can resolve stress fields in the bulk of suspensions using gelatin particles, and demonstrate that we can successfully perform PIV on suspensions in transmission mode, using a custom Couette cell. We compare the flow profiles of suspensions of gelatin particles with those of PAAm, to assess robustness of phenomenology. We find that, although composed of very similar particles (cross-linked hydrogels), gelatin and PAAm suspensions have very different mechanical features. The shear bands for PAAm are wider than those for gelatin, and less rate-dependent. We also use an optical technique to obtain information about how the shear stress relaxes after the flow is suddenly stopped. The shear stress relaxes more rapidly for PAAm, and image analysis suggests this may be due to increased structural rearrangements. We speculate on the origin of the observed differences by considering the frictional properties of materials. In the next chapter, we will investigate the role of friction in the suspension rheology in more detail.

References

- [1] R. Hartley and R. Behringer, “Logarithmic rate dependence of force networks in sheared granular materials,” *Nature*, vol. 421, no. 6926, pp. 928–932, 2003.
- [2] P. Schall and M. van Hecke, “Shear bands in matter with granularity,” *Annual Review of Fluid Mechanics*, vol. 42, no. 1, p. 67, 2009.
- [3] P. Coussot, J. Raynaud, F. Bertrand, P. Moucheron, J. Guilhaud, H. Huynh, S. Jarny, and D. Lesueur, “Coexistence of liquid and solid phases in flowing soft-glassy materials,” *Physical Review Letters*, vol. 88, no. 21, p. 218301, 2002.
- [4] G. Ovarlez, S. Rodts, A. Ragouilliaux, P. Coussot, J. Goyon, and A. Colin, “Wide-gap couette flows of dense emulsions: local concentration measurements, and comparison between macroscopic and local constitutive law measurements through magnetic resonance imaging,” *Physical Review E*, vol. 78, no. 3, p. 036307, 2008.
- [5] H. De Cagny, A. Fall, M. M. Denn, and D. Bonn, “Local rheology of suspensions and dry granular materials,” *Journal of Rheology (1978-present)*, vol. 59, no. 4, pp. 957–969, 2015.
- [6] J. Goyon, A. Colin, G. Ovarlez, A. Ajdari, and L. Bocquet, “Spatial cooperativity in soft glassy flows,” *Nature*, vol. 454, no. 7200, pp. 84–87, 2008.
- [7] L. Bocquet, A. Colin, and A. Ajdari, “Kinetic theory of plastic flow in soft glassy materials,” *Physical Review Letters*, vol. 103, no. 3, p. 036001, 2009.
- [8] K. Kamrin and G. Koval, “Nonlocal constitutive relation for steady granular flow,” *Physical Review Letters*, vol. 108, no. 17, p. 178301, 2012.
- [9] D. L. Henann and K. Kamrin, “A predictive, size-dependent continuum model for dense granular flows,” *Proceedings of the National Academy of Sciences*, vol. 110, no. 17, pp. 6730–6735, 2013.
- [10] K. Kamrin and G. Koval, “Effect of particle surface friction on nonlocal constitutive behavior of flowing granular media,” *Computational Particle Mechanics*, vol. 1, no. 2, pp. 169–176, 2014.
- [11] A. Kuske and G. S. Robertson, *Photoelastic stress analysis*. Wiley-Interscience, 1974.
- [12] V. Popov, *Contact mechanics and friction: physical principles and applications*. Springer Science & Business Media, 2010.
- [13] N. Huang and D. Bonn, “Viscosity of a dense suspension in couette flow,” *Journal of Fluid Mechanics*, vol. 590, pp. 497–507, 2007.
- [14] G. Koval, J.-N. Roux, A. Corfdir, and F. Chevoir, “Annular shear of cohesionless granular materials: from the inertial to quasistatic regime,” *Physical Review E*, vol. 79, no. 2, p. 021306, 2009.
- [15] P. Jop, V. Mansard, P. Chaudhuri, L. Bocquet, and A. Colin, “Microscale rheology of a soft glassy material close to yielding,” *Physical Review Letters*, vol. 108, no. 14, p. 148301, 2012.
- [16] M. Ballauff, J. M. Brader, S. U. Egelhaaf, M. Fuchs, J. Horbach, N. Koumakis, M. Krüger, M. Laurati, K. J. Mutch, G. Petekidis, *et al.*, “Residual stresses in glasses,” *Physical Review Letters*, vol. 110, no. 21, p. 215701, 2013.
- [17] G. H. Wortel and M. van Hecke, “Anisotropy of weakly vibrated granular flows,” *Physical Review E*, vol. 92, no. 4, p. 040201, 2015.
- [18] Y. Hu, X. Zhao, J. J. Vlassak, and Z. Suo, “Using indentation to characterize the poroelasticity of gels,” *Applied Physics Letters*, vol. 96, no. 12, p. 121904, 2010.
- [19] Y. Hu, E. P. Chan, J. J. Vlassak, and Z. Suo, “Poroelastic relaxation indentation of thin layers of gels,” *Journal of Applied Physics*, vol. 110, no. 8, p. 086103, 2011.
- [20] J. P. Gong, “Friction and lubrication of hydrogelsits richness and complexity,” *Soft Matter*, vol. 2, no. 7, pp. 544–552, 2006.
- [21] J. P. Gong and Y. Osada, “Soft and wet materials: from hydrogels to biotissues,” in *High Solid Dispersions*, pp. 203–246, Springer, 2010.

Chapter 4

Friction & flow of soft sphere suspensions

In Chapter 3, we conjectured that differences in the frictional properties of the particles are responsible for the difference in the flow profiles and stress relaxation of suspensions composed of gelatin and polyacrylamide (PAAm) particles. In this chapter, we investigate the role of friction in our soft sphere suspensions in more detail. We combine tribological and rheological measurements. We use hydrogels made of cross-linked gelatin as well as PAAm, and measure the friction coefficient of the materials using a custom tribometer. We find that cross-linked gelatin has a high friction coefficient which depends on the polymer concentration, while that of PAAm is much lower. Using the Couette cell from Chapter 3, we characterize the rheology of the soft hydrogel suspensions. We show that the shear stress ratio μ depends on the friction coefficient of the material μ_m at low shear rates, provided μ_m exceeds a critical value. At higher shear rates, μ decreases to the critical value, resulting in a flow instability for the gelatin particles. These findings suggest at least two mechanisms dominate slow dense suspension flows, one of which is directly determined by friction.

This chapter is based on:

M. Workamp and J.A. Dijksman, *Macroscopic friction and flow instabilities in granular emulsions (working title)*, Submitted (2017). arXiv:1709.10311.

4.1 Introduction

Suspensions of discrete athermal particles in a Newtonian fluid are abundant in industry and nature and belong to the broad class of structured fluids to which also foams, emulsions and colloidal suspensions belong. The importance of these materials is highlighted in particular by the flurry of work that has been devoted to the understanding of their flow behavior. Continuum models such as inertial number and fluidity based models [1–4] are very well able to capture much of the flow behavior while relying on very few fitting parameters. The connection between the discrete reality of these structured fluids and their continuum modeling is however still a subject of intense debate.

It is evident from historical references [5, 6] and recent innovative work [7–10] that particle interactions and in particular interparticle friction play a huge role in the macroscopic flow behavior of particulate suspensions. It is becoming evident that above a certain critical stress, suspended particles and even colloids can indeed form *enduring frictional contacts* that inhibit rearrangements and increase viscosity (sometimes by orders of magnitude), despite the lubrication force that was long believed to prevent suspended particles from getting in contact [10]. It is noteworthy that particulate flows in real world applications are in fact mostly encountered in confined flow environments in which some body force (gravity, electric or magnetic fields) or external driving provides particles with enduring contacts. Frictional contacts are generally modeled with simple Coulomb like interactions in which the frictional force F_f is proportional with the normal force F_n through the friction coefficient $F_f = \mu_m F_n$. Although numerical data on the effect of μ_m on the local [11, 12] and nonlocal rheology [13] of granular materials exists, some works report contradicting results. Measuring the effect of μ_m through experiments can then provide clarification. However, measuring the effect of μ_m on granular rheology is far from trivial, mainly because it is hard to measure (let alone control) the friction coefficient of particulate matter.

Here, we resolve this experimental issue by synthesizing our own particles, using materials of which we can measure the frictional behavior in independent experiments. We show that in a granular suspension with enduring contacts, the microscopic friction coefficient μ_m directly sets the shear resistance at low driving rates, provided it exceeds a critical value. At intermediate rates, we find that the ratio of shear stress and pressure tends to a universal value, independent of material characteristics. For particles with μ_m above the critical value, this leads to the emergence of a flow instability. To isolate the role of friction in the rheology, our model system has to satisfy a number of constraints: we require a granular material of which we can tune the friction coefficient with great accuracy. We need

Figure 4.1: Schematic side and top view of a gel head. The head has teeth to secure it in a holder, initially proposed to us and designed by Jonathan Barés.

to be able to measure both shear and normal stress during suspension flow at a range of driving rates. Additionally, to be able to compare the sliding velocities used in the friction experiments to the relative particle velocities in a suspension flow, we need to know the velocity profiles in the bulk, hence require material transparency. These constraints are satisfied by hydrogels, of which we can indeed make spherical particles in large volumes using the methods described in Chapter 2. In particular, we use cross-linked gelatin and polyacrylamide (PAAm). We also need to be able to quantify the frictional behavior of these hydrogels; we achieve this with a custom built pin-on-disk tribometer. As some hydrogels are known to have rate-dependent friction coefficients [14–16], we measure μ_m as a function of sliding velocity v . We then measure in a custom Couette cell the shear stress τ for suspensions of spheres made of equivalent materials as used in the tribology experiments. We perform the experiments at high volume fractions (above random close packing), at varying shear rate $\dot{\gamma}$. For the low friction PAAm particles, we observe standard yield stress behavior. However, for the gelatin particles, we observe a flow instability at intermediate shear rates and strong shear banding in the velocity profiles (see Chapter 3). By combining our tribology measurements with the rheological data, we link microscopic contact friction to collective flow behavior.

4.2 Tribology

4.2.1 Materials

To measure the frictional behavior of the hydrogels, we use a modified version of the “pin-on-disk” method. In this method, a pin (usually hemispherically shaped), is slid over a flat sheet or slab of the same material, on a circular track. Typically, the

Figure 4.2: Image of the tribometer components. The gel head is secured in its holder, which attaches to the rheometer axis. The gel slab is securely held to the bottom of a cylinder, to ensure it stays stationary during measurements. Image courtesy of Pieter de Visser.

pin is held stationary while the disk rotates, see e.g. Reference [17]. Instead, we drive the pin using custom 3D-printed geometries suited for a rheometer (Anton-Paar MCR501). In Figure 4.1, we show schematically the shape of the hydrogel head. The gel head has teeth, to ensure a tight connection with the holder that is attached to the rheometer arm. The gel head is created in three steps. First, we 3D-print a base with teeth, that has a cavity in which we insert a 12 mm smooth steel ball (for use in bearings). This creates a solid “positive” of the gel head. The steel ball ensures a perfectly smooth surface of the mold. After inserting the steel ball in the 3D-printed base, we mold this entire structure using a silicone rubber (Smooth-On OOMOO® 30). This creates a “negative” mold of rubber. Lastly, the hydrogels are cast using the “negative” rubber mold.

To create gelatin gels we dissolve 5, 10, or 15 wt% of gelatin powder (from porcine skin, type A, Bloom 300) in deionized water by heating it to 60°C while stirring with a stirring bar. We then pour the solution in the rubber mold to make the gel head, as well as in a Petri dish to make a flat gel slab. After at least 12 hours of gelation in a refrigerator, the gels are removed from their molds or Petri

Figure 4.3: Measured normal force F_n (o) and torque M ($\square$) in one measurement run, with velocity $v = 1.9 \times 10^{-3} \text{ m s}^{-1}$ for 15% cross-linked gelatin.

dishes and submersed in a 5 wt% glutaraldehyde solution [18], where they are left to cross-link overnight. After this, traces of glutaraldehyde are removed from the gels by leaving them in a large container with deionized water for a week, while replacing the deionized water on a daily basis.

To produce polyacrylamide (PAAm) gels we start by dissolving 20 wt% acrylamide, 1 wt% N,N'-methylenebis(acrylamide) and 1 wt% ammonium persulfate in deionized water. For the gel heads, we fill the rubber molds with the solution, and leave it for 25 minutes in an oven at 60°C . Because the PAAm gel still swells when submersed in water, we fix the gel head in its holder before submersing it in a container with deionized water. We leave the gel head in the water overnight to ensure the gel swells to its equilibrium size and any unreacted materials are removed. To create PAAm gel slabs, we dissolve 20 wt% acrylamide, 1 wt% N,N'-methylenebis(acrylamide) and 0.05 wt% ammonium persulfate. After complete dissolution, we add 0.05 wt% tetramethylethylenediamine (TEMED) to catalyze the reaction at room temperature. After mixing briefly, we cover a Petri dish with an acrylic glass lid that has a hole in the center, through which we fill the Petri dish entirely with the solution, making sure no air remains trapped under the lid. The solution then gels within a few hours. Leaving the acrylic glass off results in a gel with a wrinkly surface. After removing the gel from the Petri dish, we keep it in water overnight to swell it and to remove the unreacted materials. As in the gelatin case, we use the top side of the gel slab to do the friction measurements.

Figure 4.4: Frictional force F_f as a function of normal force F_n , for the same data as used in Figure 4.3. Inset shows the normal force regime that we fit to obtain μ_m . The solid line represents this fit.

4.2.2 Methods

The gel head is securely held on a 3D-printed arm connected to the rheometer axis, and rubs over a flat gel slab of the same material. The arm has length $l = 30$ mm, which is precisely known because this dimension is embedded in the 3D drawing of the arm. The gel slab is secured to the bottom of a container using a ring and four nylon threaded rods. Figure 4.2 shows a picture of the geometry. Note that we submerge the gels and the 3D-printed arm in deionized water. We drive the arm at rotation rates ranging from 10^{-3} to 10^{-1} rps, corresponding to sliding velocities v from 1.9×10^{-4} to 1.9×10^{-2} m s $^{-1}$, while measuring the torque M and the normal force F_n for two full rotations (see Fig. 4.3 for an example). Because the hydrogels are usually not completely flat, we get a range of F_n at any fixed height of the rotating arm. If necessary, we can expand this range by measuring at different heights.

As the hydrogel surfaces as well as the arm are submersed in water, we correct F_n for buoyancy. Similarly, we correct M for the viscous contribution of the water, by subtracting the torque required to rotate the arm in the water without the gel surfaces touching. We calculate the frictional force as $F_f = M/l$. In Figure 4.4 we plot $F_f(F_n)$ for the same data as in Figure 4.3. We use only the data where $2 \text{ mN} < F_n < 20 \text{ mN}$; in this regime $F_f(F_n)$ is linear for all materials and regression yields μ_m , see inset Figure 4.4. Note that the resolution of the normal force measurement of our rheometer is specified to be 2 mN, while it's accuracy should be 30 mN. However, we have found our rheometer to be accurate below these thresholds. We

Figure 4.5: Material friction coefficient μ as a function of sliding velocity v for 5, 10 and 15 wt% cross-linked gelatin (XG) as well as polyacrylamide (PAAm). The PAAm has a very low μ_m , which does not depend much on rate. Gelatin has a much higher μ_m , which, for 5 and 10 wt% gelatin, depends on v .

justify the choice for the narrow normal force range (2-20 mN) by considering the load on each particle in our suspensions, which can be estimated as $P^p d^2$, with P^p the confining pressure of the suspension and d the mean particle diameter. As we use P^p around 1 kPa, normal forces on the particles are in the mN range.

Note that there is an error associated to measuring a friction coefficient on a circular sliding path rather than in a straight line. This inaccuracy decreases when increasing the ratio of the radius of the sliding path (here $l = 30$ mm) and the radius of the contact area a [19]. Using Hertzian contact mechanics, the modulus of our softest material (see Section 4.3), and our maximum normal force of 20 mN, we obtain the maximum radius of our contact area, $a_{max} \approx 1$ mm. The ratio l/a_{max} is thus approximately 30, for which the error is negligible [19].

4.2.3 Results

In Figure 4.5, we plot μ_m as a function of the sliding velocity v , for the different materials. The error bars denote the 95% confidence interval for μ_m based on linear regression of $F_f(F_n)$ (see inset of Fig. 4.4). For the polyacrylamide surfaces, the friction coefficient is on the order of 10^{-2} and only a small role for v is observed, in agreement with Reference [20]. Only at the highest rate a small decrease can be

Figure 4.6: Typical results of uni-axial compression tests of hydrogel particles made of 5, 10 and 15 wt% cross-linked gelatin (XG) as well as polyacrylamide (PAAm). Normal force F_n as a function of overlap δ . Using Hertzian contact theory (Eq. 3.2 and 3.3), we find the elastic modulus E of the particles.

seen. However, the error bar on this data point is relatively large as the frictional force is small while viscous contributions from the fluid in which the arm is rotating are significant at this rate. Although their results only concern PAAm hydrogels, Reference [20] also helps interpret the polymer concentration dependence of μ_m for the cross-linked gelatin (XG). The authors show that decreasing the mesh size (i.e. increasing the polymer concentration) of the gel increases its friction coefficient, in agreement with our findings here. Although for 15% gelatin μ_m is rather constant, for 5 and 10% gelatin μ_m decreases roughly logarithmically with v . In section 4.4 we test how the rheology of a suspension of particles composed of these materials is influenced by μ_m .

4.3 Particle characterization

We make particles of 5, 10 and 15 wt% cross-linked gelatin (XG) as well as PAAm using the methods described in Chapter 2. This means our particles have the same chemistry as the gels we use in the friction measurements. We make the particles in two sizes (around 1.9 and 2.3 mm), creating a bidisperse mixture that avoids crystallization. Apart from the frictional properties of the particles, their stiffness may also play a role in the rheology of their suspensions. We measure the elastic modulus of the particles by uni-axial compression, as in Chapter 3. In Figure 4.6 we plot the normal force F_n as a function of overlap δ for one particle of each material.

We measure the elastic moduli of 5 particles per material and find the mean E to be approximately 0.081 MPa (5% gelatin), 0.32 MPa (10% gelatin), 0.89 MPa (15% gelatin) and 0.31 MPa (PAAm). Note that since the modulus and all other particle parameters are the same for PAAm and 10 wt% gelatin, the main difference between them is their frictional behavior. Differences in adhesive properties may also exist, although we do not observe any aggregation in either gelatin or PAAm particles.

4.4 Rheology

As in Chapter 3, we use our custom, 3D-printed Couette cell to perform the flow experiments. We use water as the solvent. The maximum hydrostatic pressure generated by the density difference between the particles and the fluid can be estimated as $P_g = \Delta\rho gh \approx 20$ Pa, with $\Delta\rho$ the density difference. As the confining pressure P^p exerted is always much larger than P_g , we expect no influence of P_g . We measure the confining pressure P^p on a part of the lid with a simple analog load cell. Note that in contrast to Reference [2], we use the second normal stress. Note that our particles are more dense than the solvent (water) and we measure a finite P^p even at zero shear rate, suggesting the volume fraction exceeds random close packing, which means the particles are somewhat compressed.

We can connect the pressure to our rheological measurements by using the analog output of the rheometer to simultaneously record the torque and rotational velocity using the I/O device described in Chapter 3. We perform measurements at different volume fractions ϕ , characterized by the pressure P_0^p at the lowest shear rate $\dot{\gamma}_0 = 1.2 \times 10^{-2} \text{ s}^{-1}$. Before measuring the flow curve, we pre-shear the sample at our maximum shear rate ($1.2 \times 10^2 \text{ s}^{-1}$) for 10 seconds. After this, we decrease the rate, measuring the required stress for one full rotation of the tool for 41 logarithmically spaced shear rates.

We plot flow curves for all four materials in Figure 4.7 for at least three values of ϕ per material. For the PAAm particle suspension (Fig. 4.7d) the rheology is what one may expect for a dense suspension: there is a yield stress and τ increases due to viscous effects at higher flow rates. Although the gelatin particle suspensions behave similarly in the high rate regime, at low rates the flow curves look very different. Because of their high friction coefficient, τ starts at a high level, but we observe a negative slope at intermediate $\dot{\gamma}$. Their flow curves thus display a “dip”. The depth of the dip increases with increasing polymer concentration, while the location of the dip seems to change little with ϕ . In agreement with available literature [21, 22], we find no continuous shear thickening at any of the measured

Figure 4.7: Flow curves of suspensions in the shear cell described in Chapter 3. We plot the shear stress τ as a function of shear rate $\dot{\gamma}$ for 15% (a), 10% (b) and 5% (c) cross-linked gelatin, as well as for PAAm (d). The volume fraction in the shear cell is characterized by the pressure exerted on the lid at the lowest shear rate, P_0^p , as indicated in the legends.

shear rates, owing to the deformability of the particles.

We further investigate the rheology by measuring P^p for all points in the flow curve and calculating the effective friction coefficient $\mu = \tau/P^p$. We plot $\mu(\dot{\gamma})$ in Figure 4.8, again for the four different materials. At sufficiently high $\dot{\gamma}$, the data of all suspensions are similar, in agreement with Reference [11] but in contrast to Reference [12]. Importantly, for gelatin particles at low shear rates, μ increases with polymer concentration, in agreement with our measurement of μ_m . Note that the dip persists in the $\mu(\dot{\gamma})$ -curve. For the PAAm suspension, μ has a plateau-value

Figure 4.8: Macroscopic friction coefficient $\mu = \tau/P^p$ as a function of shear rate $\dot{\gamma}$ for 15% (a), 10% (b) and 5% (c) cross-linked gelatin, as well as for PAAM (d). Same symbols as in Figure 4.7.

of about 0.16-0.17. The gelatin suspensions also reach this value in the minima of their flow curves, which suggests that under certain circumstances there is a universal value of μ that is independent of the material characteristics.

4.5 Linking tribology to rheology

We can now look back at the data presented in Figure 3.5 from Chapter 3, where we showed the flow profiles of suspensions of both 10% gelatin and PAAM, at $P^p \approx$

Figure 4.9: Material friction coefficient μ_m as a function of the effective friction coefficient of the suspension μ for all materials, sliding velocities and volume fractions. The dashed line represents $\mu_m = \frac{3}{2}\mu$, dash-dotted line denotes the critical value μ_0 . Same symbols as in Figure 4.5. Arrow indicates the shift of μ for PAAm particles from $\mu = \frac{2}{3}\mu_m$ to $\mu = \mu_0$.

0.2 kPa. As μ_m is small and constant for PAAm, the shear bands of the PAAm suspension are relatively wide and change little with rate, especially in the regime where $\mu(\dot{\gamma})$ is relatively flat. Because μ_m is much higher for gelatin, the shear bands are more narrow at low driving rates. The observed widening of the shear bands for the 10% gelatin suspension could possibly be explained by the decrease of μ_m with v for this material.

We can use the suspension flow profiles to obtain an estimate of the relative velocities in the suspension, to establish how $\mu_m(v)$ and $\mu(\dot{\gamma})$ are connected. For both materials, Ω decays to less than 10% of Ω_i within a few particle diameters $d = 2$ mm. We therefore estimate the relative velocities (sliding velocities) as $\Omega_i r_i$. This means that $v \simeq 0.013\dot{\gamma}$, and we get sliding velocities similar to the ones probed in our friction measurements at shear rates $\dot{\gamma} \leq 1.5 \text{ s}^{-1}$. Note that these values of $\dot{\gamma}$ are below the observed minima in $\mu(\dot{\gamma})$.

We compare $\mu_m(v)$ and $\mu(\dot{\gamma})$ by plotting $\mu_m(v)$ for each $\mu(\dot{\gamma})$ with a similar sliding velocity. We plot μ_m as a function of μ in Figure 4.9, for all materials and ϕ . The dashed line represents $\mu_m = \frac{3}{2}\mu$. For the cross-linked gelatin, all data points lie close to this line, suggesting $\mu \propto \mu_m$ in this slow flow limit. However, for the PAAm, at much lower μ_m , μ differs distinctly from μ_m and is given by a critical value μ_0 . This suggests that at least two mechanisms determine the shear stress in slow dense suspension flows, one of these is directly controlled by friction. If μ_m exceeds $\frac{3}{2}\mu_0$, the shear stress is determined by μ_m , i.e. $\tau = \frac{2}{3}\mu_m P^p$. However, for

Figure 4.10: Schematic of the contributions to the shear stress. If $\mu_m > \frac{3}{2}\mu_0$, at low rates the shear stress is given by $\tau = \frac{2}{3}\mu_m P^p$ and decreases with rate until it reaches a universal value μ_0 (solid line). For $\mu_m < \frac{3}{2}\mu_0$, $\tau = \mu_0 P^p$ (dashed line). At higher rates $\tau \propto \dot{\gamma}^n$ (dash-dotted line), as in the Herschel-Bulkley model.

$\mu_m < \frac{3}{2}\mu_0$, τ is given by $\tau = \mu_0 P^p$. We find $\mu_0 \approx 0.16$. In simulations of slow flows of frictionless suspensions [12] and frictionless dry granular materials [23], values of approximately 0.1 are typically found, suggesting a bigger contribution of fabric and force anisotropy [23, 24] in our experiments. To the best of our knowledge, this is the first experimental evidence of the existence of μ_0 in granular suspensions.

As the shear rate increases, the number of frictional contacts may decrease (perhaps due to lubrication), which provides a qualitative explanation for the decrease of μ for the gelatin suspensions. Another possible reason for the dip is the rate-dependence of the friction coefficient μ_m . For 5 and 10% gelatin, μ_m decreases significantly, but it appears rather constant for 15% gelatin. Because the sliding velocities we can obtain in our friction experiments relate to shear rates below the minima, our data is inconclusive on the role of the rate-dependence of μ_m . We summarize our findings in Figure 4.10, where we schematically plot the flow curve for a dense suspension.

4.6 Discussion

To interpret our results, we find the picture from References [25–27] particularly illuminating: in these numerical simulations of dry granular materials, also with

enduring contacts, μ is estimated to be half the sum of three anisotropy parameters, i.e. $\mu = \frac{1}{2}(a_c + a_n + a_t)$, in which a_c represents the contact orientation anisotropy, a_n the average normal force anisotropy, and a_t the average tangential force anisotropy [25–27]. The anisotropy parameters were empirically observed in a pioneering numerical study [25] yet have been repeatedly observed in later work [26, 27]. In fact, Reference [26] showed that there is an excellent agreement between this estimation and the global stress ratio $\mu = \tau/P^p$ for hard particles with $\mu_m = 0.4$, across many decades of the rescaled shear rate $I = \frac{\dot{\gamma}d}{\sqrt{P^p/\rho}}$, where ρ is the particle density [1]. For our experiment, the PAAM suspension will have $a_t \simeq 0$ since μ_m is almost zero [27]. Knowing that even in the absence of tangential contact force components a finite μ_0 is observed makes it all the more surprising that $\mu = \frac{2}{3}\mu_m$ for the gelatin suspensions: the contributions of friction and geometric effects to the shear stress do not seem to be simply additive. Consider the case of $0 < \mu_m < \frac{3}{2}\mu_0$: for such a material μ should either be $\frac{2}{3}\mu_m$ or μ_0 . As a_t is finite in this case, a_c and a_n must be balanced to achieve either $\frac{2}{3}\mu_m$ or μ_0 . In either case, these anisotropy parameters must therefore depend explicitly on μ_m . Knowing exactly how the three anisotropy parameters a_c , a_n and a_t emerge from grain-scale friction, shear rate and perhaps also other microscopic contact and force correlations is hence a crucial next step to understanding suspension rheology, that we leave as an outlook for future experimental or numerical work.

4.7 Conclusion

To summarize, for a dense suspension of soft particles, we show that frictional interactions at the grain-scale influence the macroscopic rheology. The high friction coefficient of the cross-linked gelatin translates into the emergence of a flow instability, which suggests that flow instabilities in suspension flows may be intrinsically linked to the frictional behavior of their microscopic ingredients. The measured values of $\mu_m(v)$ also provide a qualitative explanation for the differences in flow profiles and relaxation observed in Chapter 3. Importantly, we show that the friction coefficient of the material μ_m and the effective friction coefficient of the suspension μ are directly related, if μ_m exceeds a critical value. In slow suspension flows with enduring contacts, at least two microscopic anisotropy inducing mechanisms contribute to the shear resistance and one of these is directly related to friction.

References

- [1] GDR-MiDi, “On dense granular flows.,” *European Physical Journal E*, vol. 14, no. 4, 2004.
- [2] F. Boyer, É. Guazzelli, and O. Pouliquen, “Unifying suspension and granular rheology,” *Physical Review Letters*, vol. 107, no. 18, p. 188301, 2011.
- [3] J. Goyon, A. Colin, G. Ovarlez, A. Ajdari, and L. Bocquet, “Spatial cooperativity in soft glassy flows,” *Nature*, vol. 454, no. 7200, pp. 84–87, 2008.
- [4] K. Kamrin and G. Koval, “Nonlocal constitutive relation for steady granular flow,” *Physical Review Letters*, vol. 108, no. 17, p. 178301, 2012.
- [5] S. B. Johnson, G. V. Franks, P. J. Scales, D. V. Boger, and T. W. Healy, “Surface chemistry–rheology relationships in concentrated mineral suspensions,” *International Journal of Mineral Processing*, vol. 58, no. 1, pp. 267–304, 2000.
- [6] Z. Zhou, P. J. Scales, and D. V. Boger, “Chemical and physical control of the rheology of concentrated metal oxide suspensions,” *Chemical Engineering Science*, vol. 56, no. 9, pp. 2901–2920, 2001.
- [7] R. Seto, R. Mari, J. F. Morris, and M. M. Denn, “Discontinuous shear thickening of frictional hard-sphere suspensions,” *Physical Review Letters*, vol. 111, no. 21, p. 218301, 2013.
- [8] M. Wyart and M. Cates, “Discontinuous shear thickening without inertia in dense non-brownian suspensions,” *Physical Review Letters*, vol. 112, no. 9, p. 098302, 2014.
- [9] C. Clavaud, A. Bérut, B. Metzger, and Y. Forterre, “Revealing the frictional transition in shear-thickening suspensions,” *Proceedings of the National Academy of Sciences*, p. 201703926, 2017.
- [10] J. Comtet, G. Chatté, A. Niguès, L. Bocquet, A. Siria, and A. Colin, “Pairwise frictional profile between particles determines discontinuous shear thickening transition in non-colloidal suspensions,” *Nature Communications*, vol. 8, p. 15633, 2017.
- [11] S. Gallier, E. Lemaire, F. Peters, and L. Lobry, “Rheology of sheared suspensions of rough frictional particles,” *Journal of Fluid Mechanics*, vol. 757, pp. 514–549, 2014.
- [12] M. Trulsson, E. DeGiuli, and M. Wyart, “Effect of friction on dense suspension flows of hard particles,” *Physical Review E*, vol. 95, no. 1, p. 012605, 2017.
- [13] K. Kamrin and G. Koval, “Effect of particle surface friction on nonlocal constitutive behavior of flowing granular media,” *Computational Particle Mechanics*, vol. 1, no. 2, pp. 169–176, 2014.
- [14] J. Gong and Y. Osada, “Gel friction: a model based on surface repulsion and adsorption,” *The Journal of Chemical Physics*, vol. 109, no. 18, pp. 8062–8068, 1998.
- [15] J. P. Gong, “Friction and lubrication of hydrogelsits richness and complexity,” *Soft Matter*, vol. 2, no. 7, pp. 544–552, 2006.
- [16] T. Baumberger and C. Caroli, “Solid friction from stick–slip down to pinning and aging,” *Advances in Physics*, vol. 55, no. 3–4, pp. 279–348, 2006.
- [17] A. Pitenis, J. Uruena, K. Schulze, R. Nixon, A. Dunn, B. Krick, W. Sawyer, and T. Angelini, “Polymer fluctuation lubrication in hydrogel gemini interfaces,” *Soft Matter*, vol. 10, no. 44, pp. 8955–8962, 2014.
- [18] L. O. Damink, P. Dijkstra, M. Van Luyn, P. Van Wachem, P. Nieuwenhuis, and J. Feijen, “Glutaraldehyde as a crosslinking agent for collagen-based biomaterials,” *Journal of Materials Science: Materials in Medicine*, vol. 6, no. 8, pp. 460–472, 1995.
- [19] B. A. Krick and W. G. Sawyer, “A little analysis of errors in friction for small wear tracks,” *Tribology Letters*, vol. 39, no. 2, pp. 221–222, 2010.
- [20] J. M. Urueña, A. A. Pitenis, R. M. Nixon, K. D. Schulze, T. E. Angelini, and W. G. Sawyer, “Mesh size control of polymer fluctuation lubrication in gemini hydrogels,” *Biotribology*, vol. 1, pp. 24–29, 2015.
- [21] E. Brown and H. M. Jaeger, “Shear thickening in concentrated suspensions: phenomenology, mechanisms and relations to jamming,” *Reports on Progress in Physics*, vol. 77, no. 4, p. 046602, 2014.
- [22] H. Barnes, “Shear-thickening (dilatancy) in suspensions of nonaggregating solid particles dispersed in newtonian liquids,” *Journal of Rheology*, vol. 33, no. 2, pp. 329–366, 1989.
- [23] P.-E. Peyneau and J.-N. Roux, “Frictionless bead packs have macroscopic friction, but no dilatancy,” *Physical Review E*, vol. 78, no. 1, p. 011307, 2008.

- [24] P.-E. Peyneau and J.-N. Roux, "Solidlike behavior and anisotropy in rigid frictionless bead assemblies," *Physical Review E*, vol. 78, no. 4, p. 041307, 2008.
- [25] L. Rothenburg and R. Bathurst, "Analytical study of induced anisotropy in idealized granular materials," *Geotechnique*, vol. 39, no. 4, pp. 601–614, 1989.
- [26] E. Azéma and F. Radjai, "Internal structure of inertial granular flows," *Physical Review Letters*, vol. 112, no. 7, p. 078001, 2014.
- [27] É. Azéma, F. Radjaï, and J.-N. Roux, "Internal friction and absence of dilatancy of packings of frictionless polygons," *Physical Review E*, vol. 91, no. 1, p. 010202, 2015.

Part II

Driven Granular Systems

Chapter 5

Collective behavior of an active granular material

What happens if sand grains come to life? In nature, particles often have some form of internal driving, leading to complex collective behavior. This can be observed in microtubule assemblies, schools of fish, and bird flocks. In the previous Chapters we showed that interparticle friction plays a crucial role in the rheology of *passive* particles. In this Chapter we study the mechanics of a granular material composed of *active* particles. In particular, we use particles that experience a finite torque, within a circular arena. The particles are equipped with “bumps” to provide them with geometric friction, of which we vary the size. Although all particles rotate counterclockwise, the ensemble of particles shows a transition from clockwise to counterclockwise motion with respect to the center of the arena when increasing the volume fraction. Surprisingly, the translational energy of the system is a rather universal function of volume fraction. However, the partition of energy depends strongly on the bump size. Finally, we provide a perspective on the origin of the observed collective behavior. Our findings highlight the role of geometric friction, which governs the coupling of rotational and translational degrees of freedom, in the emergent collective phenomena of active granular materials.

This chapter is based on:

M. Workamp, G. Ramirez, K.E. Daniels and J.A. Dijksman, *Symmetry-reversals in chiral active matter*, Submitted (2018).

5.1 Introduction

In nature, many “materials” consist of “particles” that are not passive, but individually driven to move. Such materials exist at different length scales: microtubule assemblies, schools of fish and bird flocks are examples, which display complex collective phenomena. How do the microscopic interactions play a role in this collective behavior? Just like for passive granular materials, answering this question has been one of the main reasons to study active materials, with an aim to develop new materials with functionalities absent in passive matter. In recent years, active matter has developed into a trend in the physics community, highlighted by a plethora of high-impact papers (e.g. Refs. [1–5]), and a number of reviews [6–8]. Although most of the literature concerns particles with self-propulsion, some recent numerical works deal with the case of actively rotating particles without self-propulsion. Such particles are continuously driven to rotate, and acquire translational momentum through collisions or hydrodynamic interactions. Arguably, such particles can be considered more thermal-like than their self-propelled analogues, as the translational degrees of freedom are not actively driven. Actively rotating particles may display interesting collective phenomena, such as reversal of the forces between active particles in a passive medium [9], as well as complex phase behavior [10–12].

Active rotation may also be achieved in vibrated granular materials [13–15], using asymmetric particles in a quasi-two-dimensional container. Strongly driven granular systems are often called “granular gases” [16, 17]. Arguably, all granular gases can be considered active matter systems, as energy is injected to the system, although the particles are driven by motion of the boundaries, rather than at the individual particle level. Indeed, granular gases may display collective phenomena, such as clustering [17–19] and giant number fluctuations [20]. Despite differences between a real gas, and a non-equilibrium granular gas that dissipates energy in every collision, granular gases sometimes display features of molecular gases, such as Brownian motion [21] and equipartition of kinetic energy among the available degrees of freedom [22]. However, in contrast to molecular gases, the velocity distribution in granular gases is typically not simply Gaussian. High energy tails are usually observed and considered to be exponential, and the probability of the high velocities v is often found to scale as $p(v) \sim \exp(-v^{\frac{3}{2}})$ [23–26], in agreement with kinetic theory of granular gases [27]. Because the particles in a typical granular gas obtain their momentum from the boundaries, one may expect the structure of these boundaries to influence the distribution. Indeed, when rough boundaries are used, the transfer and randomization of linear momentum is more effective than for smooth boundaries, and the velocity distributions may approach a Gaussian [28]. Apparently, the source of linear momentum has profound consequences

for the obtained velocity distribution. In a system of actively rotating particles, the particles will obtain linear momentum in collisions, drawing energy from the rotation. How does this coupling of rotational and linear momentum affect the velocity distributions of a granular gas composed of these rotating particles?

In this Chapter, we experimentally investigate the mechanics of such a granular gas. In contrast to the granular gases with asymmetric particles described in References [13–15], our particles are driven at the individual level: each particle experiences a continuous, finite torque. However, the type of interactions that occur are still typical for granular materials, with frictional contacts and inelastic collisions. Inspired by numerical work [10], we use disks to which peripheral disks (“bumps”) are added to provide the particles with geometric friction. We study systems composed of particles that rotate counterclockwise, varying the number of particles within a circular arena, as well as the length l that the bumps protrude from the main disk. The particles are levitated on an air table to eliminate friction with the base, and obtain a finite torque through a pinwheel-like design, drawing power from the same air flow that levitates them. The particles have a hole in the bottom, through which air from the table enters. The air exits the particles through three channels which redirect the air, such that it exits at a finite angle compared to the radial direction of the particle. This provides the particle with a finite, constant torque.

We find that the system displays collective behavior: at low particle density, the average translational motion of the particles is in the clockwise direction with respect to the center of the arena, switching to counterclockwise at higher density. Where does this symmetry breaking come from? In the first part of this chapter, we investigate the *velocity distributions* of particles for fixed l and varying volume fraction ϕ , and find that the velocity distributions are Gaussian for a range of ϕ , where they can be fitted using the Maxwell-Boltzmann distribution of speeds. We obtain the effective thermal energy from the fits, which, surprisingly, is a rather universal function of ϕ for finite l and matches the translational energy per particle well. This indicates that the mechanics of our system of active particles can be captured well with the tools of statistical physics for a large range of ϕ . In the second part, we will consider the *partition of energy*, for systems with varying l and ϕ . We show that the ratio of the rotational energy and the energy stored in the cooperative motion depends strongly on l . Finally, we provide a qualitative description of the origin of the observed collective behavior, highlighting the role of the bump size l , which governs the coupling of rotational and translational degrees of freedom. Our findings demonstrate the importance of the type of driving to the mechanics of granular gases, and highlights the role of geometric friction in the emergent collective behavior.

Figure 5.1: Top view of the particles. The main disk diameter is 15.5 mm, the diameter of the hole in the bottom is 5.6 mm, and the diameter of the disks that make up the “bumps” is 4 mm. From (a) to (d), the amount the bumps protrude from the main disk is 0, 1, 2, and 3.25 mm respectively.

5.2 Materials & methods

5.2.1 Particle design

To make rotating disk-shaped particles, we use a 3D-printer (Stratasys Objet 30 Scholar). We achieve active rotation by using a pinwheel-like design. Air flows in the particle through a hole in the bottom, and exits through three exit channels. The air exits the channels at a finite angle compared to the radial direction of the particle. This provides the particles with a finite torque, making the particles spin counterclockwise. The main disk diameter is 15.5 mm, and the hole in the bottom is 5.6 mm. We vary the interaction between particles by adding five “bumps” to the particles. The bumps are created by placing smaller disks onto the main disk perimeter. The diameter of the bumps is 4 mm, and they are placed such that the bumps protrude from the main disk 0, 1, 2 or 3.25 mm. We call this the bump size l . See Figure 5.1 for top view drawings of the four different particles used. A picture of a particle with $l = 2$ mm is shown in Figure 5.2a.

Figure 5.2: (a) Particle with $l = 2$ mm. Black and red labels are used to facilitate tracking of position and angle of the particle. (b) Picture of the experimental setup. (c) Video still from an experimental video, showing the hole pattern in the air table surface.

5.2.2 Air table setup

We place the particles on an air table, which levitates them to eliminate friction with the base, and powers the rotation of the particles. The table is similar in spirit to an “air hockey” table. The main surface of the air table is 3D-printed like the particles themselves. The circular arena in which the particles reside has a diameter of 150 mm, and has holes of approximately 1 mm in diameter, in a square pattern (see Fig. 5.2c). The air is supplied to the air table surface as follows. Two 6 bar wall outlets for compressed air are connected to a single manifold with four outlets using 8 mm pneumatic tubing. The four outlets are connected to a 3D-printed plate sealed to a 125 mm tube. Directly behind this plate, on the inside of the tube, a stainless steel wire sponge is placed to homogenize the air flow. The tube has a 90 degree bend, which aims the air flow vertically, and a subsequent adapter widens the tube from 125 to 150 mm. The tube is held in position by clamping it between three rubber fixtures connected to a frame of optical rails, which is itself placed on a breadboard. The air table surface is placed on top of the tube and the connection is sealed using Parafilm. The table is leveled using four adjustable feet. Leveling of the table is crucial, because the particles will experience a gravitational field if the leveling is not correct. After initial leveling with a high resolution bubble level, we check that the table is level by recording a video with approximately 10 particles from which we obtain the particle positions (see Section 5.2.3), and compute a 2D histogram of these positions. We level the table using the adjustable feet until this 2D histogram is symmetric around the center of the arena. See Figure 5.2b for an image of the experimental setup.

5.2.3 Imaging and particle tracking

To measure the behavior of our particles, we need to track them. We image the particles from above using a Canon EOS 70D DSLR camera in video mode. The frame rate is set to 50 frames/second. We illuminate the experiment using a high power LED lamp. As the finish of the 3D-printed materials is rather glossy, we place polarizers in front of the lamp as well as the camera lens, to block any reflection of the particles or air table. In every experiment, we image the particles for a total of 10^4 frames, corresponding to 3 minutes and 20 seconds. We label the particles to obtain contrast with the table surface. We mark the center of the particle with a black marker, and one of the 3 air outlets with a red marker; see Figure 5.2a+c. We locate the particles by finding the “center of mass” of the black dots, and obtain their angle using the four-quadrant inverse tangent of the relative position of the center of mass of the red air outlet.

In contrast to typical particle tracking applications (e.g. microscopy on colloidal systems), we know the number of particles N in our videos. Therefore, our particle locating scripts are designed to locate exactly N particles in each frame. To find the trajectories of the particles we use tracking algorithms initially developed by D. Grier, J. Crocker and E. Weeks, adapted to MATLAB and made available online by D. Blair and E. Dufresne [29]. When the maximum distance traveled per frame is set to a sufficiently small number, this always yields N trajectories, implying that we never miss a particle. The angle of each particle is between $-\pi$ and π rad, and is as such a discontinuous function of time, even for a freely rotating particle. We resolve this issue by adding (subtracting) 2π rad when the sign of the angle changes from positive to negative (negative to positive) values.

5.2.4 Particle characterization

We characterize the particles by determining their weight, moment of inertia, and torque. As the torque depends on the air flow of the air table and thus on the air pressure from the wall outlets, we perform all experiments in quick succession not to depend on possible fluctuations in pressure. We measure the torque M of the particles by measuring the angular acceleration $\ddot{\theta}$ of a particle after a collision. In Figure 5.3, we plot the angle θ of a particle with $l = 2$ mm, as a function of time. We fit this with a simple quadratic function to obtain $\ddot{\theta}$. We calculate the torque as $M = I_{zz}\ddot{\theta}$, with I_{zz} the moment of inertia about the z -axis (the symmetry axis of the particle). As measuring the moment of inertia is challenging, we obtain an estimate from our 3D drawing software, SOLIDWORKS, which we have used to design the particles as described in Section 5.2.1. The software also provides us

Figure 5.3: Angle θ of a particle with $l = 2$ mm after a collision with the wall. Solid line represents a quadratic fit, from which we obtain the torque.

with an estimate of the particle mass m_s . As 3D-printing is not perfect, we find that the real mass m differs from this estimate by approximately 10%. To correct I_{zz} for this difference, we multiply the value of I_{zz} given by SOLIDWORKS with the ratio of m and m_s . This neglects that the main reason for the difference between m and m_s is likely that the thickness of the bottom layer (with the bumps) is slightly larger than in the drawing. An overview of the physical properties of the particles is given in Table 5.1. Note that the torques are measured for a single particle. As the design element that generates the torque M is the same for all particle types, and our measured values of M are very similar, we assume that M is constant in all our experiments.

Table 5.1: Physical properties of the particles.

l (mm)	m (g)	I_{zz} (g mm ⁻²)	M (N m)
0	0.344	10.4	4.87×10^{-8}
1	0.366	11.8	6.00×10^{-8}
2	0.374	12.6	5.83×10^{-8}
3.25	0.393	14.4	5.43×10^{-8}

Figure 5.4: Vector plots of the average translational velocity of 2 (a), 7 (b), 27 (c), and 45 (d) particles with $l = 2$ mm. Corresponding volume fraction ϕ are 0.025, 0.088, 0.339 and 0.564, respectively. At low particle densities, the average direction is clockwise, while at higher densities the average direction is counterclockwise.

5.3 Results & discussion

5.3.1 Phenomenology

We perform experiments by varying the number of particles N , characterized by the volume fraction $\phi = NA_p/A_a$, with A_p the area underneath the particle (including the bumps), and A_a the area of the arena. We increase N in steps of single particles from $N = 2$ up to $N = 5$, and steps of two or more particles from $N = 5$

until the collection of particles starts to display (intermittent) dynamic arrest. As we track the particles and their rotation, we have access to their translational velocity as well as rotational velocity. We define the translational velocity v of a particle as the difference in the position between two consecutive frames multiplied with the frame rate. We obtain the rotational velocity ω of a particle in the same way, from the difference in the angle of the particles. We have verified that our main results do not depend significantly on the time step we choose; changing the time step from 1 to 8 frames yields similar results, for the entire range of velocities that occur in the experiments. In dilute systems, the rotational velocity of the particles can become very large, such that the rotation can not be adequately tracked using a time step of 8 frames. Because the probability of these high rotational velocities is small, this only marginally affects measures such as the mean rotational energy of the system.

In Figure 5.4 we plot the average translational velocity vector of the particles in the circular arena. At very low particle densities, although the particles' own rotation is counterclockwise, the average motion is in the clockwise direction with respect to the center of the arena (Fig. 5.4a). However, at high particle densities, the average motion is in the counterclockwise direction (Fig. 5.4c+d). At intermediate density, the motion of the particles is random; there is no net motion of the ensemble of particles (Fig. 5.4b). Although we only depict this collective effect here for particles with $l = 2$ mm, we find it occurs with all the particles used. However, we will show that the critical volume fraction at which the transition occurs depends on l .

For particles without bumps, at $\phi < 0.16$ ($N < 15$), a collection of particles initially placed in “random” positions on the air table, quickly find a steady state in which all particles “walk” along the boundary of the arena, so that their trajectories are perfectly parallel with the boundary. In this state, the particles move at a constant velocity, and have no interactions or collisions with each other. We have excluded these data sets from our analysis. When $\phi \geq 0.16$, such a state does not appear, likely because the collision frequency is then sufficiently high to prevent it.

5.3.2 Distribution of speeds

We first consider the velocity distribution of the rotational velocity ω , for particles with $l = 2$ mm. Since the particles are actively driven to rotate, we expect the probability density function (PDF) of the rotational velocity ω to be asymmetric. This is indeed the case, as can be seen in Figure 5.5, where we plot the PDF for six different ϕ . The mean rotational velocity is indicated with a filled symbol and depends strongly on ϕ , but remains positive due to the finite torque the particles

Figure 5.5: Probability density function (PDF) of the rotational velocity ω for particles with $l = 2$ mm, for six different volume fractions. Filled symbols represent the mean ω . For better visibility, the curves are shifted vertically by one or more orders of magnitude.

experience. Qualitatively, the reason for the ϕ -dependence is obvious; at low ϕ , the time between collisions (with the wall or another particle) is large, which leaves for sufficient time for the particles to accelerate to high ω . As ϕ is increased, collisions become more frequent, so that the particles do not get a chance to obtain high ω before colliding with another particle. Thus, increasing ϕ narrows the PDF. The probability of finding particles with negative ω is non-zero for all ϕ due to collisions, and decays roughly exponentially. The ϕ -dependence of the probability of finding a particle at negative ω can be qualitatively explained by considering two particles in a head-on collision. Because the particles rotate in the same direction, at the point of contact, the linear velocities of their outer edges (or bumps) are

Figure 5.6: Probability density function (PDF) of the speeds V_x ($\circ$) and V_y ($\square$) for particles with $l = 2$ mm, for six different volume fractions. Solid lines represent Gaussian fits. For better visibility, the curves are shifted vertically by one or more orders of magnitude.

opposite in sign. If the rotation rate of particle i is larger than that of particle j , the result of the collision may be a negative rotation rate for particle j . Since at low ϕ , much higher ω can be achieved, the difference between the rotation rates of the two colliding particles may be larger, leading to increased probability of large negative ω . Note that at low ϕ , ω may take on values as high as 50 rad s^{-1} , which suggests our frame rate of 50 frames per second may be only marginally sufficient. However, as stated before, the probability of finding these high ω is low so that measures such as the mean rotational energy of the system do not depend much on the frame rate.

As the particles collide, angular momentum is converted to translational momentum and the particles obtain finite velocities. We consider the PDF of the

Figure 5.7: Probability density function (PDF) of the speed V for particles with $l = 2$ mm, for six different volume fractions. Solid lines represent fits using Equation 5.1. For better visibility, the curves are shifted vertically by one or more orders of magnitude.

velocity components V_x and V_y , the velocities in the x and y direction of our images. We plot the PDF of V_x and V_y for particles with $l = 2$ mm in Figure 5.6. Also plotted in Figure 5.6 are Gaussian fits to the data. At high ϕ , these fits deviate from the data strongly, while at low to intermediate ϕ the fits are good and the PDFs can be considered Gaussian, in contrast to PDFs from granular gases driven from the boundaries [15, 22–28]. Thus, for a range of ϕ , the ensemble displays translation similar to that of an idealized gas. In a granular gas, the linear momentum is driven from the boundaries. Here, we are driving the rotational degrees of freedom and leave the coupling to linear momentum for the system to decide. Apparently, this leads to a more randomized linear momentum, resulting in Gaussian velocity distributions. Note that, as all distributions are centered around zero, the PDFs

demonstrate that our air table surface is correctly leveled.

In an idealized gas, in thermodynamic equilibrium and where the particles interact through non-dissipative collisions, the probability to find a particle at a speed V is given by the Maxwell-Boltzmann PDF, which for the 2D case writes [30]:

$$p(V) = \frac{mV}{kT} e^{\frac{-mV^2}{2kT}} \quad (5.1)$$

where k is Boltzmann's constant and T the temperature. Our system differs from an idealized gas in many ways: collisions are dissipative, the system is not in equilibrium, and collective motion occurs. Surprisingly, the Maxwell-Boltzmann distribution does a reasonable job in capturing the velocity PDFs of our active materials, as can be seen in Figure 5.7, where we plot the PDFs of the speed $V = \sqrt{V_x^2 + V_y^2}$ for particles with $l = 2$ mm, at six different ϕ , along with fits of Equation 5.1. At low and high ϕ , the velocity distribution is clearly not Maxwellian. At intermediate ϕ the fits are reasonable, although the high V regime is not captured perfectly.

For the data sets where the fit matches the experimental data reasonably, we obtain an effective thermal energy kT_{eff} . In particular, we check that the peak in the PDF is well-captured by the fit. This means that, from the six data sets shown in Figure 5.7, we use only the four middle data sets. We plot the obtained thermal energy for this selection of ϕ in Figure 5.8a, for the four different particle types. The function $kT_{eff}(\phi)$ is a rather universal function, except for at low ϕ where it increases with bump size. Furthermore, at $\phi \approx 0.42$ for particles with no bumps, there is a jump to lower kT_{eff} , which becomes roughly constant at higher ϕ .

The effective thermal energy kT_{eff} should match the translational energy of the particles. We obtain the translational energy in the system as $E_{tr} = \sum_i^N \frac{1}{2} m V_i^2$, with V_i the magnitude of the velocity of the i -th particle. We average E_{tr} over time to obtain the mean translational energy $\bar{E}_{tr}$, and plot this energy *per particle*, in the inset of Figure 5.8a for all ϕ , which shows that $\bar{E}_{tr}/N$ is indeed very similar to kT_{eff} . In Figure 5.8b, we plot the ratio of the thermal energy and the translational energy per particle. This ratio is slightly smaller than one at volume fractions up to about 0.3, because the Maxwell-Boltzmann fits underestimate the probability of high speeds. At higher ϕ , the fits *overestimate* the probability of high speeds (see $\phi = 0.464$ in Fig. 5.7), which causes the ratio to go up. Importantly, since the ratio is very close to unity, our results indicate that the mechanics of our system composed of actively rotating disks can be captured well with the tools of statistical physics for a large range of ϕ .

Figure 5.8: (a) Effective thermal energy kT_{eff} obtained from the Maxwell-Boltzmann fits, as a function of volume fraction ϕ . We plot kT_{eff} only for volume fractions where the Maxwell-Boltzmann fit is good, see main text for details. Inset shows the mean translational energy per particle $\bar{E}_{tr}/N$ as a function of ϕ . (b) Ratio of kT_{eff} and $\bar{E}_{tr}/N$, as a function of ϕ . Legend in (b) applies to all panels.

5.3.3 Partition of energy

We have shown that the mean translational energy $\bar{E}_{tr}$ is a universal function of ϕ . We can also obtain the rotational kinetic energy, as $E_{rot} = \sum_i^N \frac{1}{2} I_{zz} \omega_i^2$, with ω_i the angular velocity of the i -th particle. We define the mean total kinetic energy as $\bar{E}_{tot} = \bar{E}_{tr} + \bar{E}_{rot}$. Since it may be easier for particles with small bumps to rotate steadily in an ensemble of particles, we expect $\bar{E}_{rot}$ and hence $\bar{E}_{tot}$ to depend on the bump size l .

In Figure 5.9, we plot $\bar{E}_{tr}$, $\bar{E}_{rot}$ and $\bar{E}_{tot}$ per particle as a function of ϕ , for all particle types. This shows that no matter the bump size l , the rotational energy decreases roughly exponentially with ϕ . This decrease in $\bar{E}_{rot}/N$ is because the time between collisions decreases with ϕ , which prevents particles from accelerating to high ω , as is also clear from the PDFs in Figure 5.5. As shown before, for particles without bumps (Fig. 5.9a), the translational energy is roughly constant, with a small jump to lower energy at $\phi \approx 0.42$. For all ϕ , the translational energy is considerably smaller than the rotational energy, hence the total energy per particle also decreases roughly exponentially with ϕ . This means the total energy of the system decreases with ϕ .

This is very different for particles with bumps (Fig. 5.9b-d), where $\bar{E}_{tr}$ starts to exceed $\bar{E}_{rot}$ at intermediate ϕ . For these systems, the total energy per parti-

Figure 5.9: Mean translational energy $\bar{E}_{tr}$, rotational energy $\bar{E}_{rot}$ and total energy $\bar{E}_{tot} = \bar{E}_{tr} + \bar{E}_{rot}$ per particle as a function of the volume fraction ϕ for $l = 0$ mm (a), $l = 1$ mm (b), $l = 2$ mm (c), $l = 3.25$ mm (d). Legend in (a) applies to all panels.

cle becomes rather constant at intermediate ϕ , and for larger bump sizes at high ϕ a small increase can even be observed (Fig. 5.9c+d). This represents a strong collective effect: adding one particle to the system gives all individual particles a higher energy level, despite an increase in probability of dissipative collisions. In this regime, the total energy of the system $\bar{E}_{tot}$ thus increases strongly with ϕ for particles with finite bump size.

To study the collective behavior in more detail, we start by computing the velocity component in the azimuthal direction of the arena, V_{coll} . We do this by converting the positions of the particles from cartesian (x, y) to polar (r, θ) coor-

Figure 5.10: (a) Mean velocity component of the particles in the azimuthal direction $\bar{V}_{coll}$ as a function of volume fraction ϕ for the four different particles used. Legend also applies to (c) and (d). (b) Critical volume fraction ϕ_c at which $\bar{V}_{coll} \approx 0$ as a function of the bump size l . Error bars denote ± 1 particle. (c) Mean energy stored in azimuthal motion $\bar{E}_{coll}$ as a function of ϕ . (d) Ratio of the mean energy stored in azimuthal motion $\bar{E}_{coll}$ and the mean rotational energy $\bar{E}_{rot}$ as a function of volume fraction ϕ .

ordinates, using the center of the arena as the origin, and subsequently obtain the velocity in the θ -direction. We plot the mean velocity $\bar{V}_{coll}$ for the four different values of l in Figure 5.10a. This shows that the transition depicted in Figure 5.4 occurs for all of the four different particle types. At low ϕ , V_{coll} is negative, but switches to positive values when ϕ is increased, corresponding to the transition from clockwise to counterclockwise motion of the particles with respect to the center of the arena. Although this effect is universal, the critical volume fraction at

which the transition occurs depends on the bump size l , as shown in Figure 5.10b. This highlights the importance of the coupling between rotational and translational degrees of freedom in the collective motion of these materials, which is governed by the geometric friction of the particles. Note that the particles without bumps, although lacking geometric friction, still have frictional interactions, because the material they are composed of is not frictionless. Hence, even for these systems, the rotational and translational degrees of freedom are coupled.

We also compute the energy stored in the collective motion. This energy $\bar{E}_{coll}$, is plotted as a function of ϕ in Figure 5.10c, for the four different particles used. As $E_{coll} \propto V_{coll}^2$, E_{coll} is positive for both clockwise and counterclockwise motion. Note that we compute E_{coll} as $\sum_i^N \frac{1}{2} m V_{coll,i}^2$, which means that $\bar{E}_{coll} \neq \frac{1}{2} m \bar{V}_{coll}^2$. At intermediate volume fraction, the particle properties seem to matter very little and $\bar{E}_{coll}$ is similar for the different particles. At large ϕ , $\bar{E}_{coll}$ is lower for the particles without bumps ($l = 0$ mm).

In a system where individual particles do not rotate, but the collective of particles rotates around a common axis, $\bar{E}_{rot}$ is zero while $\bar{E}_{coll}$ is maximized. The ratio of $\bar{E}_{coll}$ and $\bar{E}_{rot}$ can thus be considered a measure of the collective behavior in the system, and is plotted in Figure 5.10d. For all particle types, $\bar{E}_{rot}$ dominates at low to intermediate ϕ . For particles with bumps, the ratio $\bar{E}_{coll}/\bar{E}_{rot}$ rapidly increases to well above unity, indicating that the collective motion dominates individual rotation. For particles with larger bumps, the increase is more pronounced. However, for particles without bumps, $\bar{E}_{coll}/\bar{E}_{rot} < 1$ at all ϕ . Thus, in the absence of sufficient geometric friction, the individual contributes little to the collective.

5.3.4 Understanding the transition

So far, although we showed that friction plays an important role in the collective behavior of actively rotating particles, the mechanism behind the change of direction, depicted in Figure 5.4, remains elusive. Since the number of particles is limited, boundaries are likely to play a crucial role in the observed behavior. At low values of ϕ , most collisions are with the outer wall, and as the particles rotate counterclockwise around their own axis, this tends to give the particles momentum in the clockwise direction of the arena (negative $\bar{V}_{coll}$). We speculate that the transition occurs because particles close to the center of the arena, act like an inner boundary for the particles on the outside to grip onto.

We test this hypothesis by placing an additional boundary on the inside of the arena. We use two different inner boundaries, both are circular shapes with diameter 80 mm, and one of them has bumps that have the same size and spacing as particles with $l = 2$ mm. To compare the cases with and without an inner bound-

Figure 5.11: (a) Drawing of the experiments with an inner boundary. The outside diameter of the inner boundary is 80 mm while the bumps have the same size and spacing as particles with $l = 2$ mm. (b) Average velocity in the azimuthal direction $\bar{V}_{coll}$ for two particles in an arena without inner boundary ('None'), with an inner boundary that has no bumps ('Smooth'), with the inner boundary depicted in (a) ('Rough'). Error bars denote the values of each individual particle. Addition of a rough boundary reverses the general direction of the particles.

ary, we use two particles with $l = 2$ mm. When the inner boundary is present, the particles reside in the annulus between the inner and outer boundary. For a drawing of the experiments with inner boundaries, see Figure 5.11a.

In Figure 5.11b, we plot the mean velocity component in the azimuthal direction $\bar{V}_{coll}$ for the three different cases. Error bars denote the values of each individual particle. For the case without inner boundary, the particles have only the outer boundary to collide with and we observe clockwise motion (negative $\bar{V}_{coll}$), as also shown in Figure 5.4a. For the case with a smooth inner boundary, the probability of collision with the inner and outer boundary are approximately equal. This results in $\bar{V}_{coll}$ being very close to zero here. When we add bumps to the inner boundary, although the probabilities of collision are still the same, the transfer of rotational energy to translational energy is more effective at the inner boundary, as the particles can “grab” onto the bumps, thereby breaking the symmetry of the system. This results in an overall counterclockwise motion. Note that the air table was not perfectly leveled in this additional experiment, which is why $\bar{V}_{coll}$ for the case without inner boundary deviates slightly from the result shown in Figure 5.10a.

The simple experiment described above provides a basic understanding of the

principles involved in the transition from clockwise to counterclockwise collective motion. As ϕ increases, the particles start acting like an inner boundary for other particles to grab onto, changing the direction of the collective motion. How effective this mechanism is, should depend on the bump size l , which qualitatively explains the results plotted in Figure 5.10.

5.4 Conclusion

We experimentally study a granular gas composed of actively rotating disks, made rough using bumps. We find interesting collective behavior, characterized by a transition of clockwise to counterclockwise translational motion of the particles with respect to the center of the arena. We show that the distribution of the rotational velocity ω is highly asymmetric due to the finite torque. However, in contrast to vibrated granular gases, the PDFs of the translational velocity components V_x and V_y are Gaussian for a large range of ϕ . The PDF of the speed $V = \sqrt{V_x^2 + V_y^2}$ can be fitted with the Maxwell-Boltzmann distribution, from which we obtain the effective thermal energy, which is a rather universal function of ϕ for particles with bumps, and matches the mean translational energy of the particles. We also look at the partition of energy in the system, and show that the ratio $\bar{E}_{coll}/\bar{E}_{rot}$ depends strongly on bump size l as well as ϕ , signifying the role of friction in the collective behavior. The critical volume fraction, at which the transition of clockwise to counterclockwise motion occurs, depends strongly on l as well. By adding an inner boundary to the system, we provide a qualitative description of the origin of the collective behavior, in which geometric friction plays a key role. Our findings demonstrate that the type of driving matters for the statistical mechanics of granular gases, and establishes the role of geometric friction in emergent collective phenomena.

References

- [1] R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. Bastiaansen, D. J. Broer, and B. L. Feringa, “Molecular machines: nanomotor rotates microscale objects,” *Nature*, vol. 440, no. 7081, pp. 163–163, 2006.
- [2] T. Sanchez, D. T. Chen, S. J. DeCamp, M. Heymann, and Z. Dogic, “Spontaneous motion in hierarchically assembled active matter,” *Nature*, vol. 491, no. 7424, pp. 431–434, 2012.
- [3] W. Bialek, A. Cavagna, I. Giardinà, T. Mora, E. Silvestri, M. Viale, and A. M. Walczak, “Statistical mechanics for natural flocks of birds,” *Proceedings of the National Academy of Sciences*, vol. 109, no. 13, pp. 4786–4791, 2012.
- [4] L. Berthier and J. Kurchan, “Non-equilibrium glass transitions in driven and active matter,” *Nature Physics*, vol. 9, no. 5, pp. 310–314, 2013.
- [5] S. C. Takatori, W. Yan, and J. F. Brady, “Swim pressure: stress generation in active matter,” *Physical Review Letters*, vol. 113, no. 2, p. 028103, 2014.
- [6] S. Ramaswamy, “The mechanics and statistics of active matter,” *Annual Review of Condensed Matter Physics*, vol. 1, pp. 323–345, 2010.
- [7] M. C. Marchetti, J.-F. Joanny, S. Ramaswamy, T. B. Liverpool, J. Prost, M. Rao, and R. A. Simha, “Hydrodynamics of soft active matter,” *Reviews of Modern Physics*, vol. 85, no. 3, p. 1143, 2013.
- [8] A. M. Menzel, “Tuned, driven, and active soft matter,” *Physics Reports*, vol. 554, pp. 1–45, 2015.
- [9] J. Aragones, J. Steimel, and A. Alexander-Katz, “Elasticity-induced force reversal between active spinning particles in dense passive media,” *Nature Communications*, vol. 7, 2016.
- [10] N. H. Nguyen, D. Klotsa, M. Engel, and S. C. Glotzer, “Emergent collective phenomena in a mixture of hard shapes through active rotation,” *Physical Review Letters*, vol. 112, no. 7, p. 075701, 2014.
- [11] S. Sabrina, M. Spellings, S. C. Glotzer, and K. J. Bishop, “Coarsening dynamics of binary liquids with active rotation,” *Soft Matter*, vol. 11, no. 43, pp. 8409–8416, 2015.
- [12] B. C. van Zuiden, J. Paulose, W. T. Irvine, D. Bartolo, and V. Vitelli, “Spatiotemporal order and emergent edge currents in active spinner materials,” *Proceedings of the National Academy of Sciences*, p. 201609572, 2016.
- [13] J.-C. Tsai, F. Ye, J. Rodriguez, J. P. Gollub, and T. Lubensky, “A chiral granular gas,” *Physical Review Letters*, vol. 94, no. 21, p. 214301, 2005.
- [14] C. Scholz and T. Pöschel, “Actively rotating granular particles manufactured by rapid prototyping,” *Revista Cubana de Física*, vol. 33, no. 1, pp. 37–38, 2016.
- [15] C. Scholz and T. Pöschel, “Velocity distribution of a homogeneously driven two-dimensional granular gas,” *Physical Review Letters*, vol. 118, no. 19, p. 198003, 2017.
- [16] C. S. Campbell, “Rapid granular flows,” *Annual Review of Fluid Mechanics*, vol. 22, no. 1, pp. 57–90, 1990.
- [17] H. M. Jaeger, S. R. Nagel, and R. P. Behringer, “Granular solids, liquids, and gases,” *Reviews of Modern Physics*, vol. 68, no. 4, p. 1259, 1996.
- [18] I. Goldhirsch and G. Zanetti, “Clustering instability in dissipative gases,” *Physical Review Letters*, vol. 70, no. 11, p. 1619, 1993.
- [19] J. Eggers, “Sand as maxwell’s demon,” *Physical Review Letters*, vol. 83, no. 25, p. 5322, 1999.
- [20] V. Narayan, S. Ramaswamy, and N. Menon, “Long-lived giant number fluctuations in a swarming granular nematic,” *Science*, vol. 317, no. 5834, pp. 105–108, 2007.
- [21] G. D’Anna, P. Mayor, A. Barrat, V. Loreto, and F. Nori, “Observing brownian motion in vibration-fluidized granular matter,” *Nature*, vol. 424, no. 6951, pp. 909–912, 2003.
- [22] K. Nichol and K. E. Daniels, “Equipartition of rotational and translational energy in a dense granular gas,” *Physical Review Letters*, vol. 108, no. 1, p. 018001, 2012.
- [23] W. Losert, D. Cooper, J. Delour, A. Kudrolli, and J. Gollub, “Velocity statistics in excited granular media,” *Chaos: An Interdisciplinary Journal of Nonlinear Science*, vol. 9, no. 3, pp. 682–690, 1999.
- [24] F. Rouyer and N. Menon, “Velocity fluctuations in a homogeneous 2d granular gas in steady state,” *Physical Review Letters*, vol. 85, no. 17, p. 3676, 2000.
- [25] I. Aranson and J. Olafsen, “Velocity fluctuations in electrostatically driven granular media,” *Physical Review E*, vol. 66, no. 6, p. 061302, 2002.

- [26] A. Prevost, D. A. Egolf, and J. S. Urbach, "Forcing and velocity correlations in a vibrated granular monolayer," *Physical Review Letters*, vol. 89, no. 8, p. 084301, 2002.
- [27] T. Van Noije and M. Ernst, "Velocity distributions in homogeneous granular fluids: the free and the heated case," *Granular Matter*, vol. 1, no. 2, pp. 57–64, 1998.
- [28] P. M. Reis, R. A. Ingale, and M. D. Shattuck, "Forcing independent velocity distributions in an experimental granular fluid," *Physical Review E*, vol. 75, no. 5, p. 051311, 2007.
- [29] D. Blair and E. Dufresne, "The matlab particle tracking code repository," *Particle-tracking code available at <http://physics.georgetown.edu/matlab>*, 2013.
- [30] W. J. Moore, *Physical Chemistry*. Longman Group Limited, 1972.

Chapter 6

A simple low pressure drop microfluidic mixer based on suspensions

Particles moving in slowly flowing granular suspensions have recently been shown to exhibit diffusion, thus breaking the time reversibility of the flow. In this chapter we apply this knowledge to accomplish efficient mixing in a microfluidic chip. We present a novel microfluidic mixer that is easy to fabricate and simple to use. The mixer features a single mixing chamber in which particles are driven by a moving magnet. We show that the mixing efficiency is markedly increased by addition of particles to the chip, as a result of the diffusive motion of the sheared particles. The mixer is efficient for a range of driving rates and due to its simple design features a low pressure drop, making the mixer design compatible with soft chip material. It is therefore ideal to incorporate in lab-on-a-chip devices.

This chapter is based on:

M. Workamp, V. Saggiomo and J.A. Dijkman, *A simple low pressure drop suspension-based microfluidic mixer*, Journal of Micromechanics and Microengineering 25(9) (2015), 094003.

6.1 Introduction

Microfluidics is a recent field of research that studies fluid manipulation and control in highly constrained channels, chambers and chips. Since their emergence, microfluidic chips have been used in a wide range of applications, spanning from molecular biology [1] to continuous chemical synthesis [2] to mimicking multiple organs for in-vitro drugs analysis [3] and more. The small volume of fluids required, coupled with the great portability and the relatively low price of microfluidic chips makes them of great interest and broad application. However, confining liquids to the small volumes typical in microfluidic chips has some undesirable consequences. A main disadvantage is that mixing fluids inside the microfluidic chip is notoriously difficult [4, 5], due to the small flow rates and small dimensions of the chip. We show here that we can design and fabricate an efficient microfluidic mixer based on driven advective mixing.

An easy way to see that mixing in microfluidics chips is challenging, is by calculating the Reynolds number of the fluid flow inside a typical chip. The Reynolds number Re [6], indicates whether the flow is laminar (small Re) or turbulent (large Re); roughly speaking, turbulent flows mix easily, but laminar flows do not. In microfluidic devices, the Reynolds number can be quantified by $Re \propto \rho Q / r \eta = \rho u r / \eta$, with ρ the fluid density, Q the volume flow rate through the chip, η the dynamic viscosity of the fluid, r the channel radius (or typical length scale) and u the flow speed. Because of the microscopic dimensions and relatively small flow rates, Re is inherently small (< 100) in microfluidic devices, especially for fluids of high viscosity. At such low Re , mixing can happen through diffusion and chaotic advective flow [7]. In most microfluidic chips, flow channels are geometrically simple, so flow is predominantly laminar, limiting the chaotic advective flow. This leaves only diffusion as a mixing mechanism. Quantitatively, one can look at the importance of diffusion with the Péclet number, which compares the diffusive transport rate to the mass flow rate as $Pe \propto u r / D$, with D a diffusion coefficient; in microfluidics context typically the Einstein result is used, in which $D \propto kT / \eta d$, with k the Boltzmann constant, T the temperature and d the hydrodynamic radius of the molecules that need to mix. If Pe is small, diffusion alone is sufficient for efficient mixing. The small volumes and flow speeds of microfluidics chips help diffusive mixing, but most mixers still feature $Pe \sim 10^4$. Reducing this number is challenging; to make diffusion more efficient by for example reducing the flow rate would result in prohibitively low processing speeds.

So far, commercially available microfluidic mixer chips are based on geometrically nontrivial channels that break the laminar flow, and introduce chaotic advective mixing [8, 9]. Current approaches that use such a mechanism have two

disadvantages. First, to achieve the goal of complete mixing at the chip outlet, the channel with passive mixing elements needs to be sufficiently long, which increases the required *pressure drop* over the channel. A large pressure drop puts stringent demands on chip material and tubing coupling; this complicates design, fabrication and use. For example, it limits the use of the easy to manipulate, but rather soft polydimethylsiloxane (PDMS) as chip material. The pressure drop ΔP for a channel, assuming laminar (Poiseuille) flow, is given by the proportionality $\Delta P \propto \eta QL/r^4$, with L the length of the channel [10]. The small r of microfluidic chips already gives rise to huge pressure drops, hence any reduction in L through smart chip design is advantageous. A second drawback of commercially available mixers is that they are passive, meaning the mixing quality and quantity cannot be controlled externally; once the design is made, its mixing efficiency is set. To compensate for these effects, many other mixer chips have been proposed; for a review see [11]. These mixers range from the use of micro-magnetic stirrers [12, 13] to even more complex channel geometries [14]. The drawback of the proposed mixers is that they are often complex to make and/or use. The challenge is thus to come up with a microfluidic mixer that is both simple in design and in production and features a small pressure drop.

Here we present a simple microfluidic mixer chip in which *passive particulate matter* is used to improve the mixing of flowing liquids at low Reynolds number. The mixing mechanism is based on the observation made in Reference [15] on the irreversible motion of particles in a cyclically sheared suspension. The authors described that even in low Re oscillatory suspension flow, in which the fluid flow *should* be entirely reversible, the particles exhibit diffusive motion, breaking the time reversibility of the flow. This suggests that irreversible fluid motion must also exist in the suspending fluid, meaning that chaotic advective mixing takes place under those conditions. Indeed, the enhanced mixing in the suspending phase was shown to exist in recent elegant work [16]. The particles were shown to induce fluctuations causing over 200% enhancement of the (thermal) transport properties. Reference [16] also showed that the mixing efficiency in the suspending fluid has a maximum as a function of the volume fraction ϕ of solid particulate matter. The mechanism behind this optimum is simple: with more particulate matter, there are more moving and thus mixing elements in the fluid; however, ϕ should not be so high that particle displacement and rotation becomes too restricted, since that reduces mixing capacity. The maximum mixing efficiency was found to occur at $\phi \approx 40\%$ [16].

We show here that we can design and fabricate a microfluidic mixer using the physical principles described above. The mixer is cheap and simple to make in PDMS, features a low pressure drop, and the mixing rate can be externally con-

Figure 6.1: (a) Schematic of the microfluidic mixer chip. The mixing chamber is filled with 30-40 vol% of glass microspheres and a small magnet. (b) 3D rendering of the microfluidic chip and (c) actual microfluidic mixer chip. We use a dye to visualize the flow and mixing efficiency.

trolled if desired. The chip features a single cylindrical mixing chamber, in which passive particulate matter is driven by a single moving magnet. We compare the mixing efficiency of a viscous fluid in mixers with and without particles and show that indeed the presence of particulate matter significantly enhances the mixing. We quantify the mixing efficiency with literature standards [17, 18] and measure it as a function of the driving rate to show that we achieve complete mixing already at very low driving rates. We conclude that the presence of particulate matter enhances the mixing sufficiently to allow for increased flow rates through the microfluidic chip.

6.2 Materials & methods

As proof of concept we designed and constructed a simple microfluidic chip (Fig. 6.1) with a mixing chamber filled with 30-40% volume of glass microspheres with diameter 200-500 μm (Retsch, Prod. Nr.: 22.222.0002). A small magnet (cylindrical,

Figure 6.2: Microfluidic mixers shown here after pumping Rhodamine B-dyed (inlet 1) and undyed (inlet 2) tetraethylene glycol at flow rate of $20 \mu\text{L}/\text{min}$ for 45 seconds. (a) shows the mixing chamber in which only a magnet was stirring the flow; (b) shows a mixing chamber in which glass particles were used to enhance the mixing capacity of the same magnetic stirrer. Red line indicates the pixels used for Figure 6.3.

$1 \times 1 \text{ mm}$, www.magnetshop.net, Prod. Nr.: SM-01x01-N) was added to the chamber to drive the glass particles. We choose for a small magnet to reduce drag on the magnet, which makes external driving easier. A larger magnet may be able to achieve a higher mixing rate at the same driving rate, but we did not test this hypothesis. The mixing chamber (cylindrical, diameter = 6 mm, height = 2 mm) is connected to two inlets and one outlet, all of $500 \mu\text{m}$ width and $100 \mu\text{m}$ height, to ensure the particles remain confined to the mixing chamber, yet do not block inlet or outlet channels.

The master is printed with a 3D-printer (Stratasys Objet 30 Scholar) and cast with PDMS (Dow Corning SYLGARD 184). The PDMS is subsequently cured for 5 hours at 70°C . The PDMS is peeled from the master, the particles and the magnet inserted in the mixing chamber, and the PDMS is sealed to a microscope slide after plasma treatment. We pump two tetraethylene glycol solutions (viscosity $\eta = 58 \text{ mPas}$, density $\rho = 1125 \text{ kg}/\text{m}^3$) at equal rates ($20 \mu\text{L}/\text{min}$), through both inlet channels; in one inlet channel, the tetraethylene glycol has added dye (Rhodamine B or Methylene Blue) to visualize the mixing of the two fluids. We drive the small magnet inside the mixing chamber using an external magnet attached to an inverted overhead stirrer motor; a standard stirring plate is also able to drive the internal magnet. We image the flow inside the device from above with a Canon 70D DSLR camera in video-mode at 50 frames/s (Fig. 6.2). We convert the RGB-videos to gray-scale image sequences for ease of analysis. The largest value of Re , calcu-

Figure 6.3: (a,b) Pixel intensity as a function of time for 16 seconds, in the outlet channel of the microfluidic mixer chip. The red line in Figure 6.2b indicates the pixels used to produce this figure. A periodicity in the signal can be clearly seen in the mixer without particles (a), while a more homogeneous signal is observed in the mixer with particles (b).

lated by choosing the diameter of the mixing chamber as the length scale r and u the largest speed found in our system (the speed of the magnet), does not exceed order 10 throughout our experiments, far below the threshold for turbulence [6]. The smallest value of Pe is also found in the mixing chamber, again taking its diameter as the length scale r , but defining u as the flow velocity of the fluid through the area A spanned by the height and width of the chamber ($u = Q/A$). This is the largest surface area present in the system. By estimating the diffusion coefficient D of Rhodamine B in tetraethylene glycol as 5.5×10^{-12} [19], we find the minimum value of Pe to be of order 10^5 , which means that diffusion does not play a significant role in our chip.

6.3 Results & discussion

6.3.1 Mixing Efficiency

We use two different metrics to compare the mixers with and without particulate matter. First, we monitor fluctuations in intensity at the outlet channel. The rate at which the stirring magnet performs circular motion inside the chamber is

Figure 6.4: Fourier transform of the intensity at 5 pixels in the center of the outlet channel, for the case with ($\square$) and without particles ($\circ$). The significant reduction of the periodicity in intensity in the mixer with particles suggests the fluid is homogeneously mixed.

fixed at 0.5 Hz throughout the experiment. In the case of complete mixing, we expect no periodicity in concentration at the output channel. To test this, the intensity of a column of 8 pixels perpendicular to the outlet channel (see Fig. 6.2, red line) as a function of time is plotted in Figure 6.3. In the mixer without particles (Fig. 6.3a) a clear periodicity is visible, suggesting that variations in dye concentration are mainly due to rotation of the magnet, indicative of poor mixing inside the mixing chamber. On the contrary, with particles present in the mixing chamber, the concentration of dye in the outlet channel is fluctuating much less (Fig. 6.3b) suggesting the mixing is at least significantly improved. To quantify this mixing efficiency, we select a column of 5 pixels at the center of the outlet channel, and follow its average intensity for a total of 400 seconds. The Fourier transform of the intensity signal is shown in Figure 6.4. Indeed, for the case without particles, we find a large peak at a frequency of 0.5 Hz, corresponding to the rotation frequency of the magnetic stirrer. Although still visible, the intensity of this peak, and its overtones, are strongly reduced after the addition of particles to the mixing device, showing that the intensity variations are limited and the fluid in the outlet is thus more homogeneous, and that mixing seems more complete.

From Figure 6.2a it is obvious that the dye is not equally distributed in the mixing chamber without particles. This provides our second method to compare mixing efficiency; this second method allows us to estimate the mixing enhancement due to the presence of the particles in the mixing chamber. In our chip geometry, the chamber sets the minimal time to complete mixing; this “dwell” time

Figure 6.5: Averaged pixel intensity I_r as a function of radial position r in the mixing chamber; high intensity means low dye concentration. Legend applies to both panels. For the case without particles (a), the dye is concentrated near the edge of the chamber and migrates slowly to the center. In the mixing chamber with particles (b), the dye is evenly distributed shortly after the start of the experiment.

is set by the chamber volume ($57 \mu\text{L}$) divided by the flow rate ($Q = 40 \mu\text{L}/\text{min}$) and is about 1.5 minutes. Using azimuthal averaging, we compute the radial intensity profile of the mixing chamber, plotted in Figure 6.5 for different times after the start of the experiment. As expected, for the mixer without particles, the dye is concentrated near the edge of the mixing chamber. Even after 400 seconds of operation, well beyond the chamber dwell time, the dye remains heterogeneously distributed (Fig. 6.5a). For the mixer with particles, the situation is different. Figure 6.5b shows that the dye is more homogeneously distributed at all times, even shortly after starting the experiment. Indeed, mixing occurs within the dwell time of the chamber. Only an overall drop in pixel value, corresponding to a darkening of the chamber and thus to an increase of the dye concentration, can be seen to occur; this is due to a slow equilibration of the dye concentration by pushing out the initially clear fluid from the chamber. We can thus conclude that the particulate material inside the chamber allows for the fluid mixing to occur with at most the chamber dwell time.

At a driving rate of 0.5 Hz, the magnet makes about 50 revolutions inside the chamber during the dwell time. To test whether this number is sufficient for complete mixing, we measure the mixing efficiency for a range of driving rates of the magnet. To indicate complete mixing, we need to show that the mixing signal in the outlet channel is independent of the magnet driving rate ω . We use a measure similar to the one introduced by Reference [17]. After the mixer has obtained a

Figure 6.6: Image of the mixing chip with stationary magnet showing parallel flow (no mixing occurs). Fluid flows from left to right. The area within the rectangle spans the width of the outlet-channel and is used for mixing efficiency analysis.

steady state, we calculate the average intensity value μ_k for every frame k from a 9×5 pixel area in the outlet channel with intensity values I_{ij} , as indicated by the rectangle in Figure 6.6:

$$\mu_k = \frac{\sum_{i=1}^m \sum_{j=1}^n I_{ij}}{mn} \quad (6.1)$$

We subsequently compute the standard deviation of the signal:

$$\sigma_k = \sqrt{\frac{\sum_{i=1}^m \sum_{j=1}^n [(I_{ij} - \mu_k)^2]}{(mn) - 1}} \quad (6.2)$$

After averaging σ_k over 4000 frames (80 seconds) to find σ , we calculate the mixing efficiency α :

$$\alpha = 1 - \frac{\sigma}{\sigma_{max}} \quad (6.3)$$

where σ_{max} is the standard deviation in a mixer without driving, where the particles are stationary. In that case the flow is parallel (Fig. 6.6), no mixing occurs, and the standard deviation is large. We plot α as a function of the driving rate ω in Figure 6.7. The mixing efficiency here appears constant for almost a decade of driving rates. The driving of particles inside the chamber creates the flow disturbance necessary to enhance mixing by random displacements of the particles normal to the shear direction, as was measured in a study of thermal diffusion in suspensions of PMMA particles [16]. The authors found this enhanced mixing to be linear with the shear rate (see Fig. 9a in Ref. [16]); since increasing the driving rate does not improve mixing, we conclude that even for the lowest nonzero driving rate we could achieve with our magnetic stirrer, the mixing efficiency is

Figure 6.7: Mixing efficiency α as a function of driving frequency ω . Mixing is complete already at very low driving rates.

maximized and hence the fluid at the outlet is homogeneously mixed. The already complete mixing observed at the lowest driving rate indicates that the maximum pump rate for our chip is much higher than the one used here.

6.3.2 Pressure Drop

Microfluidic devices often require large pressure drops to operate, and such pressures induce leaking at connectors and seams, especially with soft materials such as PDMS. Our microfluidic mixer does not require large ΔP for mixing, as the essential mixing element is a large mixing chamber, which has a low flow resistance and intrinsic small footprint, set only by the inlet/outlet channels, and the particle size. At low Re , the pressure drop can be estimated by [10]:

$$\Delta P = \frac{8\eta QL}{\pi r^4} \quad (6.4)$$

Using this equation with our experimental fluid parameters ($Q = 40 \mu\text{L}/\text{min}$, $\eta = 58 \text{ mPas}$) for a commercially available glass micromixer [9] we find $\Delta P \approx 250 \text{ kPa}$. This clearly illustrates the need for a low pressure drop mixer: incorporating the design of this mixer in a PDMS microfluidic chip would inevitably lead to leakage, as ΔP approaches the elastic modulus E of the material ($E \approx 1 \text{ MPa}$ [20]). To use Equation 6.4 for channels with rectangular cross sections, an estimate of r should be used. It is instructive to use the smallest dimension (in microfluidics context usually the height), as the highest shear rates, leading to head loss by viscous

Figure 6.8: Pressure distribution in a chip with 5 mm (a) and 1 mm (b) in- and outlet channels.

dissipation, will occur in that dimension. Using this approach for our micromixer, using an inlet/outlet channel length of 5 mm and neglecting the contribution of the mixing chamber, we find $\Delta P \approx 10$ kPa. For comparison, again using Equation 6.4, the same flow rate and viscosity for the chips proposed in [12] and [18] result in pressure drops of roughly 2.5 MPa and 120 kPa, respectively.

To verify the assumptions behind the calculated ΔP for our mixer, the flow is simulated using a commercially available software package (SOLIDWORKS Flow Simulation). We design the three-dimensional chip in SOLIDWORKS and perform a pressure drop calculation with the built in solver. This results in a pressure drop of about 8 kPa (Fig. 6.8a), in agreement with the simple analysis made above. In Figure 6.8a it is evident that indeed ΔP over the mixing chamber is negligible: the pressure drop can thus be tuned by adjusting the dimensions of the in- and outlet channels. Removing them entirely reduces the pressure drop to less than a tenth of the original device (Fig. 6.8b). Thus, compared to commercially available microfluidic chips, ΔP is reduced by two orders of magnitude, making our mixer ideal for incorporation in PDMS-based microfluidic devices.

6.4 Conclusion

We present a simple microfluidic mixing device, in which optimal mixing is achieved by forcing fluid through externally driven particulate matter. We show, both qualitatively and quantitatively, that particulate matter significantly enhances mixing efficiency in this microfluidics context. The mixing efficiency is constant for a range of driving rates. Due to the universal character of mixing with the aid of particulate matter, the mixing principle used here can easily be adapted to other situations. For example, the exact nature of the driving force is irrelevant, so other

driving forces including thermal or density gradients and electric fields, could also be employed. Furthermore, if driving is controlled externally, the mixing strength can be easily controlled. The device we presented can also be easily scaled down to soft-lithography length scales, as particles of smaller size are also commercially available at low cost. In contrast to commercially available chips, the functionality of this mixer does not depend on the length of the chip, giving it a small footprint. The mixer can be fabricated easily with a simple 3D-printer and by introducing particulate matter in the microfluidic PDMS or glass chip before sealing. The composition of the particulate matter used to enhance mixing is not important for the operation of the mixer, thus materials with high melting temperature can be used in glass microfluidic chips, without interfering with the glass sealing procedure. The length of the mixer chip is only dependent on the size of the mixing chamber and can hence be greatly reduced with respect to existing designs. The mixer presented here is thus a versatile tool; we expect it to significantly extend the toolbox of the microfluidics expert.

References

- [1] A. M. Streets and Y. Huang, "Microfluidics for biological measurements with single-molecule resolution," *Current Opinion in Biotechnology*, vol. 25, pp. 69–77, 2014.
- [2] P. M. Valencia, O. C. Farokhzad, R. Karnik, and R. Langer, "Microfluidic technologies for accelerating the clinical translation of nanoparticles," *Nature Nanotechnology*, vol. 7, no. 10, pp. 623–629, 2012.
- [3] A. D. van der Meer and A. van den Berg, "Organs-on-chips: breaking the in vitro impasse," *Integrative Biology*, vol. 4, no. 5, pp. 461–470, 2012.
- [4] J. P. Brody, P. Yager, R. E. Goldstein, and R. H. Austin, "Biotechnology at low reynolds numbers," *Biophysical Journal*, vol. 71, no. 6, pp. 3430–3441, 1996.
- [5] H. E. Meijer, M. K. Singh, T. G. Kang, J. M. den Toonder, and P. D. Anderson, "Passive and active mixing in microfluidic devices," *Macromolecular Symposia*, vol. 279, no. 1, pp. 201–209, 2009.
- [6] O. Reynolds, "An experimental investigation of the circumstances which determine whether the motion of water shall be direct or sinuous, and of the law of resistance in parallel channels," *Proceedings of the Royal Society of London*, vol. 35, no. 224–226, pp. 84–99, 1883.
- [7] J. M. Ottino, *The kinematics of mixing: stretching, chaos, and transport*, vol. 3. Cambridge university press, 1989.
- [8] Micronit Microtechnologies B.V. <http://www.micronit.com/products/micromixers/>.
- [9] The Dolomite Centre LTD. http://www.dolomite-microfluidics.com/webshop/microfluidic-chips-mixer-chips-c-17_26.
- [10] T. E. Faber, *Fluid dynamics for physicists*. Cambridge University Press, 1995.
- [11] V. Hessel, H. Löwe, and F. Schönfeld, "Micromixers: a review on passive and active mixing principles," *Chemical Engineering Science*, vol. 60, no. 8, pp. 2479–2501, 2005.
- [12] K. S. Ryu, K. Shaikh, E. Goluch, Z. Fan, and C. Liu, "Micro magnetic stir-bar mixer integrated with parylene microfluidic channels," *Lab on a Chip*, vol. 4, no. 6, pp. 608–613, 2004.
- [13] S. H. Lee, D. van Noort, J. Y. Lee, B.-T. Zhang, and T. H. Park, "Effective mixing in a microfluidic chip using magnetic particles," *Lab on a Chip*, vol. 9, no. 3, pp. 479–482, 2009.
- [14] T. Egawa, J. L. Durand, E. Y. Hayden, D. L. Rousseau, and S.-R. Yeh, "Design and evaluation of a passive alcove-based microfluidic mixer," *Analytical Chemistry*, vol. 81, no. 4, pp. 1622–1627, 2009.
- [15] D. Pine, J. P. Gollub, J. Brady, and A. Leshansky, "Chaos and threshold for irreversibility in sheared suspensions," *Nature*, vol. 438, no. 7070, pp. 997–1000, 2005.
- [16] B. Metzger, O. Rahli, and X. Yin, "Heat transfer across sheared suspensions: role of the shear-induced diffusion," *Journal of Fluid Mechanics*, vol. 724, pp. 527–552, 2013.
- [17] R. Goovaerts, T. Van Assche, M. Sonck, J. Denayer, and G. Desmet, "A micromixer with consistent mixing performance for a wide range of flow rates," *ELECTROPHORESIS*, vol. 36, no. 3, pp. 405–412, 2015.
- [18] A. D. Stroock, S. K. Dertinger, A. Ajdari, I. Mezić, H. A. Stone, and G. M. Whitesides, "Chaotic mixer for microchannels," *Science*, vol. 295, no. 5555, pp. 647–651, 2002.
- [19] P.-O. Gendron, F. Avaltroni, and K. Wilkinson, "Diffusion coefficients of several rhodamine derivatives as determined by pulsed field gradient–nuclear magnetic resonance and fluorescence correlation spectroscopy," *Journal of Fluorescence*, vol. 18, no. 6, pp. 1093–1101, 2008.
- [20] I. Johnston, D. McCluskey, C. Tan, and M. Tracey, "Mechanical characterization of bulk sylgard 184 for microfluidics and microengineering," *Journal of Micromechanics and Microengineering*, vol. 24, no. 3, p. 035017, 2014.

Chapter 7

General discussion

In the previous chapters, we have made an effort to answer questions about the mechanics of granular materials, with a particular interest in the role of friction. Although we answered some questions, during our studies many new questions were raised. These questions could form the basis for future research. In this Chapter, we focus on these new questions, discuss their relevance, propose methods to answer them, and provide preliminary data where possible.

7.1 Anisotropic rheology in suspensions

7.1.1 Imaging anisotropic force networks

Unlike in traditional solids composed of molecular entities, in granular packings, stresses are not evenly distributed over the system, but rather organized in networks of particles that carry a bigger than average load [1–3]. In 2D systems, these force networks can be visualized using photoelastic particles [4, 5]. Photoelastic materials become birefringent when a stress is applied, which means that their refractive index will depend on the polarization and propagation direction of light. The photoelastic effect can be used to visualize stresses using simple optics. In 3D systems, soft particles combined with innovative imaging techniques may be used to visualize force networks in granular materials [6–8]. In the majority of the literature on these force networks, strain is applied very slowly, in small strain steps. However, as evident from phenomena like discontinuous shear thickening, or the flow instability shown in Chapter 4, performing experiments at finite shear rate may be crucial to the understanding of the flow behavior of granular materials and suspensions. For example, it is unclear what happens to the force network when entering the viscous regime of the flow curve. Will the force chains disappear? How does the structure of the force network depend on driving rate? To answer these questions, obtaining quantitative data on the evolution of force networks at finite shear rates is necessary. Obtaining such data is however not trivial. In Chapter 3, we showed that we can visualize forces in gelatin particle suspensions. Gelatin has a surprisingly large stress-optical coefficient, meaning that a small amount of stress yields a large optical response [9]. We have cross-linked the gelatin particles with glutaraldehyde, which apparently keeps the photoelastic properties of the gel. By imaging the three dimensional flow from below, we obtain a 2D representation of the force network. An example of the photoelastic response is shown in Figure 7.1. Note that the forces are visible only in a small part of the gap. We used simple linear polarizers here. If circular polarizers are used, the forces will likely be visible in the entire image. It would be interesting to measure if the stresses indeed show

Figure 7.1: Example of an image made using linear polarizers, showing the photoelastic response of the gelatin particles. Stresses are anisotropic and point against the direction of shear (inner cylinder rotating clockwise).

the expected $1/r^2$ dependence in a Couette cell. This could possibly be verified by using the so-called “gradient-squared” method [10], which can be used to extract forces on relatively low-resolution images. In Figure 7.1, we can observe that the force “chains” are anisotropic, and are pointing *against* the direction of shear. Note that, because friction is expected to influence the amount of anisotropy that can be built up in the system (see Discussion of Chapter 4), it is unclear if results obtained with gelatin particles would be transferable to other systems, as the friction coefficient of gelatin depends on sliding velocity.

7.1.2 Refractive index matching of gelatin particles

We have used our gelatin particles in water to obtain the image in Figure 7.1. Because the particles have a higher refractive index than water, scattering of light may occur, which potentially distorts the photoelastic signal. To avoid such issues, the refractive index of the solvent could be matched with that of the gelatin particles. However, as gelatin is a hydrogel, changing the solvent may lead to de-swelling of the particles. Because hydrogels are porous, changing the solvent to index match the particles usually has a temporary effect, as solvent leaks into the particle slowly, and the refractive index mismatch between the solvent and the gelatin polymer backbone remains. The only way to resolve this issue is by using a solvent that has the same refractive index as the gelatin polymer backbone itself (rather than the gelatin hydrogel). We have done this by using an 80% tetrakis hydroxymethyl phosphonium chloride (THPC) solution, which has a similar refractive index to gelatin itself, and also acts as the cross-linker [11]. However, the chemistry for this cross-linker is different from glutaraldehyde, and affects the photoelastic response:

Figure 7.2: Torque M as a function of inner cylinder displacement x for driving a gelatin particle suspension (at finite P^P) after briefly stopping. When the flow is continued in the same direction, the torque immediately returns to the steady state value, while for driving in the opposition direction, it takes a few particle diameters d to obtain the steady state torque.

we did not obtain any photoelastic signal using particles cross-linked and index matched using THPC. To still be able to index match a gelatin particle suspension while retaining photoelasticity, one could use a solution of high molecular weight polymers, with the same refractive index as the gelatin particles. If the polymers are sufficiently large, they will not be able to enter the hydrogel matrix, so that the particles remain index matched. This method has been used to index match hydrogel particles, using high molecular weight polyvinylpyrrolidone [6]. Another option to obtain a good index match could be to find a solvent with the same refractive index as the gelatin polymer backbone. However, even for a perfectly index matched suspension some scattering will occur due to the photoelastic effect itself, as the photoelastic response is based on small changes of refractive index.

7.1.3 Rheological evidence of anisotropy

Anisotropy buildup in the particle packing can not only be seen in the force network, but can also be measured in the rheological response. This can be done with shear reversal experiments [12, 13], or by first shearing a granular material and relaxing the anisotropy through vibration [14]. We have used the first approach to show that a gelatin suspension indeed has an anisotropic rheological response. We first shear the suspension at low driving rate until a steady state is reached, after which we briefly stop the flow. Subsequently, we continue shearing at the same

driving rate as before, either in the same direction, or in the opposite direction. In Figure 7.2, we plot the results of this experiment. When we continue shearing in the same direction, the torque M immediately returns to the steady state value. However, when driving in the opposite direction, the material first has to build up an anisotropic network: it takes a finite amount of strain to reach the steady state torque. As we discussed before, the ability to build an anisotropic network should depend on interparticle friction. It remains an open question whether suspensions of polyacrylamide (PAAm) particles also display this behavior, since they have a very low friction coefficient. Answering this question could help in understanding the dissipation mechanism in PAAm suspensions, which, as we show in Chapter 4, does not appear to be dominated by friction.

7.2 Soft sphere suspensions

7.2.1 Role of adhesion

In Chapter 3 and 4 we investigated the rheology of suspensions consisting of gelatin and PAAm particles. In Chapter 3, we demonstrated that flow profiles and stress relaxation of these two types of suspensions are different, even though the particle stiffness is the same. We speculated on the difference to be due to differences in physico-chemical properties, such as adhesion or friction. Although in Chapter 4 we show that the frictional properties differ greatly between gelatin and PAAm, adhesion may still play some role in the rheology, even though we did not observe any aggregation of particles. We have measured the adhesion of PAAm and gelatin surfaces, using the hemispherical gel head and flat gel slab also used for the friction measurements (Chapter 4). Using a well-controlled vertical stage, we lowered the gel head from a few millimeter above the slab, until they were touching, after which we move the head up again. We measured the resulting forces using a load cell, and found a small adhesive force, for both gelatin and PAAm samples. However, the results proved to be highly irreproducible. When repeating the measurement with a new gel head and slab, made in exactly the same way, adhesive forces often changed by an order of magnitude. In fact, we also measured adhesive forces between solid-solid interfaces, for example between stainless steel and glass. These findings suggest that our measurement system needed improvement, and therefore we do not know if adhesive forces exist in gelatin and PAAm suspensions. Gelatin is composed of proteins; long polymers of amino acids. Depending on pH, some of these amino acids may be charged, and these charges could play a critical role in the adhesive properties. This means that if gelatin does have adhe-

Figure 7.3: Confining pressure P^p as a function of shear rate $\dot{\gamma}$, measured on the outer wall of the shear cell as well as on the lid, for a suspension of 10% gelatin particles.

sive properties, they may be tuned by varying the pH or by addition of salt, which shields the charged moieties. The rheological response of a suspension of gelatin particles is thus potentially tunable with the environmental conditions. It is noteworthy that the chemistry used to make PAAm gels is very versatile, so that charged groups could be obtained by polymerizing acidic monomers. In this way, the adhesive behavior (and possibly the frictional behavior) of these materials could also be tuned.

7.2.2 Measurement of P^p and μ

We have used the pressure P^p on the lid of the Couette cell to normalize the shear stress, to compute the macroscopic friction coefficient of the suspension μ . If we consider our Couette geometry in cylindrical coordinates (r, ϕ, z) , the pressure is the second normal stress τ_{zz} . However, typically, the first normal stress is used to compute μ (e.g. [15]), which corresponds to τ_{rr} . We have done an experiment using an additional pressure sensor in the *wall* of the outer cylinder of our Couette cell, to measure τ_{rr} . In Figure 7.3, we plot the pressure P^p obtained both from the lid (P_{lid}^p) as well as from the wall (P_{wall}^p), using a suspension of 10% gelatin particles. We observe that P_{lid}^p and P_{wall}^p are very similar. However, this is not necessarily expected, because of what's known as the Janssen effect [16]. Janssen measured the pressure of a granular packing on the bottom of a cylinder, and found that, contrary to what one expects from simple hydrostatics, the pressure does not scale linearly with the height of the bead pack. This is because in a granular mate-

rial, the gravitational forces are redirected to the walls of the cylinder, which thus carry part of the weight. In our system, the shear stresses are also expected to be redirected to the walls, which would cause the outer wall to be somewhat shielded from shear stress, suggesting P_{wall}^p should be lower than P_{lid}^p . However, it should be noted that normal forces originating from the shear flow are not the only contributions to the pressures P_{wall}^p and P_{lid}^p . The elastic pressure originating from the compression of the particles, as well as the hydrostatic pressure originating from the density differences between the particles and the fluid, also add to the pressure P^p , although we expect the latter to be of little importance because the density difference is small.

The pressure enters the rheology of the suspensions through the macroscopic friction coefficient $\mu = \tau/P^p$. However, the friction law $\mu = \tau/P^p$ is a local law, meaning that one *should* compute μ using locally obtained shear stress τ and pressure P^p . This can be done in computer simulations, but is much harder (if not impossible) in experimental systems. In Chapter 4, we have calculated μ by dividing the average shear stress (as defined in Eq. 1.3) with the pressure on the lid, which is the force on the lid F_{lid} divided by the area of the pressure sensor. However, a more exact measurement of μ can also be obtained, which does not require averaging of the shear stress. In case of an isotropic fluid, such as a Newtonian liquid, we know that $\tau_{zz} = \tau_{rr} = \tau_{\phi\phi}$. In this isotropic case, we can write the following for frictional flow behavior, in which normal and shear forces acting on the particles are connected through a friction coefficient μ . The shear stress $\tau_{r\phi}$ acting on the inner rotating wall of the Couette cell and measured by the rheometer is coupled to the component τ_{rr} through $\tau_{r\phi} = \mu\tau_{rr}$. Isotropy then tells us that $\tau_{r\phi} = \mu\tau_{zz}$: measuring the force on (a piece of) the top plate tells us something about the friction coefficient μ , once we know the driving stress $\tau_{r\phi}$.

We measure the driving stress as a torque M , which is the integral over the stress acting on the inner Couette cylinder:

$$M = \int_0^{2\pi} \int_0^L \tau_{r\phi} r_i d\phi dz \quad (7.1)$$

In which r_i denotes the (effective) radius of the inner Couette cylinder, and L its height. Similarly, the normal force F_t acting on the pressure sensor in the top plate is:

$$F_t = \int_{R_i}^{R_o} \int_0^\theta \tau_{zz} r dr d\phi \quad (7.2)$$

where R_i and R_o are the inner and outer radius of the pressure sensor, and θ its opening angle. To achieve shear stress balance at all r in a Couette setup, the shear stress profile in the gap must decay with the radius:

$$\tau(r) = \tau_{r\phi}(r) = \frac{M}{2\pi L r^2} \quad (7.3)$$

For an isotropic frictional fluid, the normal force acting on the confining plate is then given by:

$$F_t = \int_{R_i}^{R_o} \int_0^\theta \frac{M}{2\pi L \mu r^2} r dr d\phi = \frac{\theta M}{2\pi L \mu} \int_{R_i}^{R_o} \frac{1}{r} dr = \frac{\theta M}{2\pi L \mu} \log \frac{R_o}{R_i} \quad (7.4)$$

which can be rewritten as:

$$\mu = \frac{\theta M}{2\pi L F_t} \log \frac{R_o}{R_i} \quad (7.5)$$

Thus, μ can be calculated directly from the driving torque M and the force on the pressure sensor F_t . We have found that the values of μ calculated using Equation 7.5 are about 10% lower than those obtained using $\mu = \langle \tau \rangle / P^p$. As we also showed that $P_{wall}^p \approx P_{lid}^p$, values of μ depend very little on the choice of the boundary at which the pressure is measured, or on the choice of using $\langle \tau \rangle / P^p$ or Equation 7.5. The values of μ we report in Chapter 4 are thus very robust.

7.2.3 Soft sphere suspensions as granular emulsions

One unique feature of our experimental system is that we can tune the pressure on the particles. Because of this finite pressure P^p , and because we use soft particles, the particles are deformed, although only very slightly. The volume fraction of particles in our suspensions is thus higher than the random close packing density of 0.64, and the particles experience enduring contacts. We can thus consider our soft particles suspensions as “granular emulsions”: the soft nature of the particles allows them to be suspended at high volume fraction, yet their interactions are frictional, as in a granular material. In this perspective, the PAAm suspension is of particular interest, because the particles are nearly frictionless, resembling the frictionless droplets of an emulsion. In emulsions, it is challenging to control the pressure in a rheological experiment, because it is hard to confine the fluid/droplet mixture, in particular because the droplets are extremely deformable. Due to the macroscopic size of our particles and the fact that they are solids, we can tune the pressure in our suspensions. The PAAm suspension combined with our Couette cell is thus unique by its combination of (nearly) frictionless particles and pressure control. That our soft sphere suspensions are much like an emulsion is also clear from the rheology. Fitting the PAAm suspension flow curves depicted in Figure 4.7d with the Herschel-Bulkley model yields exponents n of roughly 0.5-0.6, similar to what is found in emulsions [17] and in agreement with available literature on soft particle rheology [18, 19].

Figure 7.4: (a) Normalized standard deviation (NSD) of the pixel intensity time series as a function of radius r for a suspension of PAAm particles at $P^p \approx 0.2$ kPa, showing that intensity fluctuations are present throughout the gap at all driving rates. (b) Idem for a suspension of gelatin particles, where fluctuations are localized to a narrow band, slightly wider than the shear band (compare to Fig. 3.5). Legend in (b) applies to both panels.

7.2.4 Fluctuations and the fluidity model

In Chapter 3, we showed that PAAm and gelatin suspension have very different mechanical behavior. In Chapter 4, we demonstrate that the frictional properties of the two materials are very different. We have shown that this greatly affects the macroscopic rheology (e.g. $\mu(\dot{\gamma})$), but the precise mechanism behind the differences in flow profiles and stress relaxation is still not completely clear. As, in emulsions, shear rate fluctuations are intrinsically linked to the fluidity field [20] that governs the local flow behavior, one thing that may be of importance is the ability of the particles to fluctuate in speed (and hence position). Such fluctuations can be observed (by eye), in videos of our suspension flows. We can make particle position fluctuations more quantitative using image analysis. For our transformed images (Fig. 3.2c), we calculated for each pixel the standard deviation of the pixel intensity time series, and average this standard deviation over the azimuthal direction. By normalizing with the mean pixel intensity, we obtain the normalized standard deviation (NSD). The NSD signifies both the correlated and uncorrelated particle motion. We plot the NSD, as a function of the radius r in Figure 7.4. This shows that, even at very low driving rates, in PAAm suspensions, fluctuations are present throughout the gap of our shear cell, even though the flow (i.e. correlated particle motion) is localized to a shear band of only a few particle diameters (compare to Fig. 3.5, mean particle diameter $d \approx 2$ mm). By contrast, in the case of

gelatin particles, the NSD decays to zero within 1 or 2 particle diameters from the shear band. These findings show that mechanical noise is much more easily transferred within PAAm suspensions (with low friction coefficient), then in the case of gelatin (with high friction coefficient), which may explain why the shear bands are wider in the PAAm suspension, and stress relaxation more efficient.

Fluctuations of particle positions also mean that the local shear rate will fluctuate. Shear rate fluctuations have been linked to the fluidity field in emulsions [20], where the fluidity was shown to scale linearly with the fluctuations. The fluidity field has been used extensively to predict the flow profiles of structured fluids. Can we predict the flow profiles of our suspensions using this approach? To do this, we need to solve the fluidity equation (Eq. 1.13), where we will use the emulsion variant of the fluidity model because we have seen earlier that the rheology of the PAAm particle suspension closely resembles emulsion rheology, at least at the macro-scale. We are interested in the flow field $\dot{\gamma}(r)$, which we can obtain by solving the equation

$$\tau(r) = \frac{1}{f(r)} \dot{\gamma}(r) \quad (7.6)$$

where f is equivalent to the rate of plastic rearrangements divided by an elastic modulus [21]. In a Couette cell, in which we have azimuthal symmetry, Equation 1.13 can be written as:

$$f(r) = f_{loc}(r) + \frac{\xi^2}{r} \frac{\partial}{\partial r} \left(r \frac{\partial f}{\partial r} \right) \quad (7.7)$$

where we assume that $f_{loc}(r)$ is set by the local rheology of the material in a homogeneous environment:

$$f_{loc}(r) = \frac{\dot{\gamma}(\tau)}{\tau(r)} \quad (7.8)$$

where $\dot{\gamma}(\tau)$ is then simply an “inverted” form of the usual constitutive equation of a material $\tau(\dot{\gamma})$. For a Herschel-Bulkley fluid, we know that:

$$\tau(r) = \tau_0 + k \dot{\gamma}(r)^n \quad (7.9)$$

so that

$$\dot{\gamma}(\tau) = ((\tau(r) - \tau_0)/k)^{1/n} \quad (7.10)$$

Using Equation 7.10 as input for Equation 7.8, while satisfying the condition that for $\tau < \tau_0$, $f_{loc} = 0$, we obtain:

$$f_{loc}(r) = \frac{((\tau(r) - \tau_0)/k)^{1/n}}{\tau(r)} H\left(\frac{\tau(r)}{\tau_0} - 1\right) \quad (7.11)$$

where $H(x)$ denotes the Heaviside function, which equals one for $x > 0$, and zero for $x < 0$. This yields our final expression for $f(r)$:

$$f(r) = \frac{\xi^2}{r} \frac{\partial}{\partial r} \left(r \frac{\partial f}{\partial r} \right) + \frac{((\tau(r) - \tau_0)/k)^{1/n}}{\tau(r)} H\left(\frac{\tau(r)}{\tau_0} - 1\right) \quad (7.12)$$

Figure 7.5: Effect of the nonlocal amplitude A and the torque M on the predicted flow profiles using the fluidity model. (a) Reduced velocity v/v_i as a function of radius r at $M = 5$ mN m and varying A . (b) v/v_i as a function of r at $A = 0.5$ and varying M .

where we will use that in a Couette geometry the shear stress decays as $\tau(r) = M/2\pi Lr^2$, with M the applied torque and L the height of the cylinders. The length scale ξ is a correlation length, and can be understood as the distance that the fluctuations caused by a local plastic event may travel (see Fig. 1.4). ξ is typically not taken to be constant, but considered stress dependent, diverging at the yield stress [22]:

$$\xi(\tau) = \frac{dA}{|\tau(r) - \tau_0|^\alpha} \quad (7.13)$$

where A is a numerical pre-factor commonly referred to as the nonlocal amplitude, and d is the particle scale. For α , a value of 0.5 was derived for emulsions [22], while for granular materials values of 0.6 and 0.5 have been used [23, 24]. Here, we choose $\alpha = 0.5$. To solve Equation 7.12, we need two boundary conditions, which we find at the walls where the fluidity equals the local law, i.e. $f(\text{wall}) = f_{\text{loc}}$. The flow profile can then be obtained by combining Equations 7.6 and 7.12. This requires fitting of the nonlocal amplitude A . We solve Equation 7.12 numerically using Maple 2016. By integrating $\dot{\gamma}(r)$ we obtain the velocity field $v(r)$, and we can show the effects of varying the torque M and nonlocal amplitude A on the flow profile, which allows us to explore the meaning of these parameters for the flow profiles of a suspension. We need an expression for the local law, which we obtain by fitting the Herschel-Bulkley equation to the torques obtained in the experiments shown in Chapter 3, for a PAAM suspension. This fit serves to obtain values for k and τ_0 , we have assumed $n = 0.5$.

In Figure 7.5, we plot the reduced velocity v/v_i as a function of radius r , for

two distinct cases. In Figure 7.5a, we set the torque M to 5 mN m and vary the nonlocal amplitude A from 0.1 to 10. The effect of nonlocal amplitude is evident, it broadens and smooths the transition from finite to zero rate. In Figure 7.5b, we set the nonlocal amplitude A to 0.5, varying the torque M from 4 to 20 mN m. Not surprisingly, the shear band widens when increasing the torque. This simple result however already indicates the complexity of the gelatin suspension, where we observe a widening shear band while the torque *decreases* (see Fig. 3.5). This means that the local law must have a non-monotonic aspect. Finding out if such a local law could yield a solution to Equation 7.7, and how it affects the flow profiles, could lead to a more thorough understanding of the gelatin suspension rheology.

7.3 Active granular matter

7.3.1 Microscopics of collective behavior

In Chapter 5 we studied the mechanics of actively rotating particles, and showed that they display collective behavior in which geometric friction between the particles plays a crucial role. By doing experiments with an additional boundary in the system, we provide a qualitative explanation for the observed phenomena. However, an understanding of the system based on the microscopics of the interaction is still lacking. More insight could be obtained by studying the collision dynamics. When two particles collide, rotational energy can be converted to translational energy (and vice versa). Measuring the effectiveness of this conversion, which is likely to depend on the bump size, could provide a more quantitative viewpoint on the collective behavior.

As the density of particles increases, the probability of dissipative collisions increases, which could lead to the formation of clusters. Because all particles rotate in the same direction, when they are touching, their surfaces move in opposite direction. This means that for particles with bumps, the rotation of particles within a cluster could be completely blocked. Because in our system, translation of particles is driven by their rotation, this blocking of rotation could lead to a complete stop of the dynamics of the particles in the cluster. However, the particles in a cluster may use their individual torque to drive the rotation of the cluster. Hence, cluster formation may be another mechanism behind the observed collective motion. Note that, when the cluster starts rotating, the particles will experience an increasing centrifugal force, which may lead to the break up of the cluster. Thus, finding a way to detect these clusters and monitoring their evolution may prove essential to a full understanding of our active granular material.

Figure 7.6: Driving torque M normalized with its steady state value M_∞ as a function of deflection angle θ , for different driving rates of the vane Ω_i . This transient behavior depends little on driving rate, and M/M_∞ may be approximated with a power law with a slope of roughly $1/2$.

7.3.2 Active matter as an idealized gas

We have studied active materials in a system with fixed boundaries, and showed that part of the dynamics resembles that of an idealized gas. Could these particles also adhere to the ideal gas law? One way to investigate this question, is by using a more rectangular geometry, with one of the boundaries being able to move, acting like a piston. This piston could be used to apply a small but finite pressure on the system, which the active particles would have to withstand. By measuring the position of the piston, one could monitor the volume of the particles as a function of pressure. It would be particularly interesting to be able to vary the activity of the material itself, which may require particles with varying torque levels. This can be achieved by tuning the amount of air flow that levitates and rotates the particles, or through smart particle design.

7.3.3 Rheology of active materials

How do active materials flow? It is becoming increasingly clear that active materials may have interesting rheological properties. In simulations of dry granular materials with self-propulsion, the value of μ_c (see Eq. 1.10) decreases linearly with a dimensionless activity parameter $A = F/Pd$ (with F the propulsion force),

and becomes zero for $A > 0.6$ [25]. Similarly, semi-dilute suspensions of highly active bacteria can achieve zero viscosity, by compensating viscous dissipation with swimming activity [26].

Inspired by this use of living organisms as active materials, we have performed rheological experiments with fly larvae (maggots) in a large jar, driven by a vane. Since these maggots may fracture easily, it is essential to keep driving rates and stresses low. Surprisingly, we find that, when starting the shear from rest at a finite driving rate, the torque M displays transient behavior which depends little on driving rate, see Figure 7.6. Here, θ is the deflection angle of the vane, and M/M_∞ is the torque normalized with its steady state value. The function $M/M_\infty(\theta)$ is approximately a power law with a slope of roughly $1/2$. These materials of living organisms also display other fascinating features, for example, when lowering the vane in a jar filled with larvae, we observe a sudden increase in the volume of the larval mass. This volume change, triggered by an external stress, may be caused by shape changes of the particles. By combining flow measurements with volumetric imaging techniques (e.g. x-ray tomography), a more quantitative understanding of this finding could be obtained. The shape changes of the larvae, triggered by an external stress, are likely to last a finite amount of time, before the larvae relax and start crawling around once more. This relaxation time could potentially be measured, by moving the vane up and down at different frequencies. Alternatively, one could test the effect of this relaxation time on the viscosity of the “larval liquid”, by doing continuous shear experiments, where the balance of the time of shear (inverse shear rate) and the relaxation time may govern the stress response. All these observations strongly suggest that active matter rheology contains a wealth of unexplored and surprising phenomena. Understanding these phenomena in active matter systems composed of biological or artificial particles, could lead to the development of new designer materials, with functionalities absent in passive materials.

References

- [1] D. W. Howell, R. Behringer, and C. Veje, “Fluctuations in granular media,” *Chaos: An Interdisciplinary Journal of Nonlinear Science*, vol. 9, no. 3, pp. 559–572, 1999.
- [2] R. Hartley and R. Behringer, “Logarithmic rate dependence of force networks in sheared granular materials,” *Nature*, vol. 421, no. 6926, pp. 928–932, 2003.
- [3] J. H. Snoeijer, W. G. Ellenbroek, T. J. Vlugt, and M. van Hecke, “Sheared force networks: anisotropies, yielding, and geometry,” *Physical Review Letters*, vol. 96, no. 9, p. 098001, 2006.
- [4] T. S. Majmudar and R. P. Behringer, “Contact force measurements and stress-induced anisotropy in granular materials,” *Nature*, vol. 435, no. 7045, pp. 1079–1082, 2005.
- [5] A. Amon, P. Born, K. Daniels, J. Dijkstra, K. Huang, D. Parker, M. Schröter, R. Stannarius, and A. Wierschem, “Preface: focus on imaging methods in granular physics,” *Review of Scientific Instruments*, vol. 88, no. 5, p. 051701, 2017.
- [6] N. Brodu, J. A. Dijkstra, and R. P. Behringer, “Spanning the scales of granular materials through microscopic force imaging,” *Nature Communications*, vol. 6, 2015.
- [7] D. M. Walker, A. Tordesillas, N. Brodu, J. A. Dijkstra, R. P. Behringer, and G. Froyland, “Self-assembly in a near-frictionless granular material: conformational structures and transitions in uniaxial cyclic compression of hydrogel spheres,” *Soft Matter*, vol. 11, no. 11, pp. 2157–2173, 2015.
- [8] J. A. Dijkstra, N. Brodu, and R. P. Behringer, “Refractive index matched scanning and detection of soft particles,” *Review of Scientific Instruments*, vol. 88, no. 5, p. 051807, 2017.
- [9] A. Kuske and G. S. Robertson, *Photoelastic stress analysis*. Wiley-Interscience, 1974.
- [10] K. E. Daniels, J. E. Kollmer, and J. G. Puckett, “Photoelastic force measurements in granular materials,” *Review of Scientific Instruments*, vol. 88, no. 5, p. 051808, 2017.
- [11] C. Chung, K. J. Lampe, and S. C. Heilshorn, “Tetrakis (hydroxymethyl) phosphonium chloride as a covalent cross-linking agent for cell encapsulation within protein-based hydrogels,” *Biomacromolecules*, vol. 13, no. 12, pp. 3912–3916, 2012.
- [12] F. Gadala-Maria and A. Acrivos, “Shear-induced structure in a concentrated suspension of solid spheres,” *Journal of Rheology*, vol. 24, no. 6, pp. 799–814, 1980.
- [13] M. Toiya, J. Stambaugh, and W. Losert, “Transient and oscillatory granular shear flow,” *Physical Review Letters*, vol. 93, no. 8, p. 088001, 2004.
- [14] G. H. Wortel and M. van Hecke, “Anisotropy of weakly vibrated granular flows,” *Physical Review E*, vol. 92, no. 4, p. 040201, 2015.
- [15] F. Boyer, É. Guazzelli, and O. Pouliquen, “Unifying suspension and granular rheology,” *Physical Review Letters*, vol. 107, no. 18, p. 188301, 2011.
- [16] H. Janssen, “Versuche über getreidedruck in silozellen,” *Z. ver. deut. Ing.*, vol. 39, p. 1045, 1895.
- [17] M. Dinkgreve, J. Paredes, M. Michels, and D. Bonn, “Universal rescaling of flow curves for yield-stress fluids close to jamming,” *Physical Review E*, vol. 92, no. 1, p. 012305, 2015.
- [18] H. Barnes, “Shear-thickening (dilatancy) in suspensions of nonaggregating solid particles dispersed in newtonian liquids,” *Journal of Rheology*, vol. 33, no. 2, pp. 329–366, 1989.
- [19] E. Brown and H. M. Jaeger, “Shear thickening in concentrated suspensions: phenomenology, mechanisms and relations to jamming,” *Reports on Progress in Physics*, vol. 77, no. 4, p. 046602, 2014.
- [20] P. Jop, V. Mansard, P. Chaudhuri, L. Bocquet, and A. Colin, “Microscale rheology of a soft glassy material close to yielding,” *Physical Review Letters*, vol. 108, no. 14, p. 148301, 2012.
- [21] J. Goyon, A. Colin, G. Ovarlez, A. Ajdari, and L. Bocquet, “Spatial cooperativity in soft glassy flows,” *Nature*, vol. 454, no. 7200, pp. 84–87, 2008.
- [22] L. Bocquet, A. Colin, and A. Ajdari, “Kinetic theory of plastic flow in soft glassy materials,” *Physical Review Letters*, vol. 103, no. 3, p. 036001, 2009.
- [23] K. Kamrin and G. Koval, “Nonlocal constitutive relation for steady granular flow,” *Physical Review Letters*, vol. 108, no. 17, p. 178301, 2012.
- [24] K. Kamrin and G. Koval, “Effect of particle surface friction on nonlocal constitutive behavior of flowing granular media,” *Computational Particle Mechanics*, vol. 1, no. 2, pp. 169–176, 2014.
- [25] A. Peshkov, P. Claudin, E. Clément, and B. Andreotti, “Active dry granular flows: rheology and rigidity transitions,” *EPL (Europhysics Letters)*, vol. 116, no. 1, p. 14001, 2016.
- [26] H. M. López, J. Gachelin, C. Douarche, H. Auradou, and E. Clément, “Turning bacteria suspensions into superfluids,” *Physical Review Letters*, vol. 115, no. 2, p. 028301, 2015.

Chapter 8

Summary

Granular materials are ubiquitous in nature and industry, however, their flow behavior remains poorly understood. In particular, it is unclear how specific particle properties, governing the microscopic interactions of the grains, influence the rheology of the bulk. In practice, it is often difficult to vary particle properties, such as stiffness or friction coefficient, in a controlled way. In this thesis, we investigate flows of granular materials with well-defined particle properties, by synthesizing the particles using novel methods.

In **Part I**, we investigate the flow behavior of suspensions of soft spheres. In **Chapter 2**, we first describe how to make particles composed of hydrogels, which are polymer networks solvated by water. Such particles can be made using emulsification, by first making droplets of an aqueous solution in oil and subsequently solidifying these droplets. However, making spherical particles in the millimeter size range is far from trivial, as surface tension is sometimes not strong enough to work against gravitational forces, which deforms the droplets from their spherical shape. The key is to use oils with a high oil-water surface tension, without addition of a stabilizing surfactant. As these surfactants also protect the droplets from merging, we need to make sure the droplets are fully solidified into particles before they touch each other. We achieve this by using a tall column of oil of about 2 meters in length, in which the droplets solidify, while slowly settling. To make gelatin particles, we use a nozzle to drip hot gelatin solution into the column, which is chilled to facilitate the solidification process. To make polyacrylamide (PAAm) particles, the oil contains a catalyst which enables a fast reaction between the acrylamide monomers. For both cases, we can tune the size of the droplets by using an air flow along the nozzle. Using a simple model, in which the drag force generated by the air flow adds to the weight of the droplet hanging on the nozzle, we can predict the size of the resulting droplets (and particles) accurately.

In **Chapter 3**, we investigate some of the flow properties of suspensions composed of these particles, and we present a custom shear cell in which we perform the experiments. This shear cell consists of two concentric cylinders, which is also known as a Couette cell. By using a lid on the cell, we fix the volume. We also measure the pressure that is exerted on the particles using a pressure sensor in this lid. Because the bottom and lid are transparent, we can image the flowing particles and obtain their velocities. We measure the flow profiles of PAAm and gelatin particles at roughly the same pressure, and find that the PAAm particles have wider shear bands. We also measure how the suspension relaxes after shear, where the PAAm shows increased relaxation compared to the gelatin case. Both of the experiments suggest that the PAAm particles can move with respect to each other more easily, which we speculate is caused by differences in the frictional or adhesive properties of the particles.

In **Chapter 4**, we investigate the rheology of PAAm and gelatin suspensions further. We measure the friction coefficient of the materials using a custom-made tribology setup, which uses a rheometer to rub a hemispherical cap of hydrogel over a slab of the same material. We do this for varying sliding velocities, and find that PAAm has a very low friction coefficient, while that of gelatin hydrogels is much higher and depends on the polymer concentration. We also quantify the stiffness of the particles and find that 10% gelatin particles and PAAm particles have the same stiffness, and thus differ only in their frictional properties. We test the effect of this material property on the rheology using the Couette cell of Chapter 3, and find that gelatin particle suspensions display a flow instability: the flow curve displays a “dip”. When rescaling the shear stress with the pressure to obtain the stress ratio (or suspension friction coefficient), the dip persists. We use the flow profiles obtained in Chapter 3 to estimate the relative sliding velocity of the particles in the suspension, to link the material friction coefficient to the stress ratio of the suspension. For gelatin, we find that the stress ratio at low rates is about $\frac{2}{3}$ times the material friction coefficient, while for PAAm the stress ratio is much higher than the friction coefficient. In simulations, a finite stress ratio was also observed for particles without friction. Our measurements are the first experimental evidence for the existence of this minimal stress ratio for particles with very low friction. Importantly, our findings suggest that at least two mechanisms contribute to the shear resistance of a suspension, and one of these is directly proportional to the friction coefficient.

In **Part II** of this thesis, we study granular materials that are driven locally, not via wall stresses, and how this local driving affects the collective dynamics in the granular “fluid”. In **Chapter 5**, we investigate what happens when sand grains come to life. Our 2D experimental system consists of particles (disks) on an air table, which eliminates friction with the base, but also drives the particles to rotate by smart particle design. Besides a driving mechanism, the particles also have “bumps”, which provides them with geometric friction. We show that these systems have collective behavior, characterized by a transition of clockwise to counterclockwise translational motion of the particles with respect to center of the arena, when increasing the volume fraction. We study the statistical mechanics of the system by computing the probability density functions (PDFs) of the velocity components. In contrast to typical granular gases, the PDFs for the velocity in the x and y direction are Gaussian. The PDF of the speed can be captured with the Maxwell-Boltzmann distribution for idealized gases, from which we obtain the effective thermal energy in the system as a function of volume fraction, which is, like the translation energy, a rather universal function for particles with finite bump size. We also investigate the partition of energy in the system, and find that it depends not only on volume

fraction, but also on the bump size. Finally, by performing experiments with an additional boundary in the system, we provide a qualitative description of the origin of the collective behavior, in which geometric friction plays a crucial role.

In **Chapter 6**, we use granular materials to mix two fluids in a microfluidic chip. The mixing chip is made of a glass slide and PDMS, and is easy to fabricate and to use. The chip consists of two inlets for the fluids, a cylindrical mixing chamber which houses glass beads as well as a tiny magnet, and a single outlet. The magnet performs circular motion along the wall of the mixing chamber, driven from below by another magnet that is attached to an overhead stirring device, which is placed upside down. We image the chip from the top to monitor the mixing process of two identical fluids, of which one contains a dye. We first compare the cases with and without particles in the mixing chamber, at a fixed driving rate of the magnet, and show both qualitatively and quantitatively that the addition of particles significantly enhances mixing. We then investigate the role of the driving rate, by comparing with the case of zero driving. At zero driving, the fluids do not mix: we obtain parallel flow of dyed and undyed fluid in the outlet channel, which yields a maximum standard deviation of the outlet pixel intensity. By comparing with this maximum standard deviation, we characterize the mixing efficiency of our chip at different driving rates, but find that even for the lowest driving rate that our motor can achieve, the mixing efficiency is maximized, which suggests that the pump rate of the fluid can be significantly increased. Important for practical purposes, we show that the pressure drop across the chip is low, which prevents leakage of tubing connections and the seal between the PDMS and the glass slide.

Samenvatting

Zowel in de natuur als in de industrie zijn granulaire materialen, zoals zand, koffiebonen en rijst, veelvoorkomend. Desondanks is er beperkt begrip van hun stromingseigenschappen. Het is vooral onduidelijk hoe specifieke eigenschappen van de deeltjes, zoals de hardheid of wrijvingscoëfficiënt, die de interacties op microscopische schaal bepalen, de stromingseigenschappen van het geheel beïnvloeden. In de praktijk is het vaak moeilijk deze eigenschappen op een gecontroleerde manier te variëren. In dit proefschrift bestuderen we stromingen van granulaire materialen bestaande uit deeltjes met goed gedefinieerde eigenschappen door met innovatieve methodes zelf deeltjes te maken.

In **Deel I** van het proefschrift bestuderen we het stromingsgedrag van suspensies gemaakt met zachte bollen. In **Hoofdstuk 2** beschrijven we een manier om deeltjes te maken die bestaan uit hydrogel; polymeernetwerken die veel water vasthouden. Zulke deeltjes kunnen worden gemaakt door een waterige oplossing te emulgeren in olie en de gemaakte druppels vervolgens uit te harden. Het is echter lastig om ronde deeltjes te maken op de millimeter-schaal. De oppervlaktespanning, die de druppels rond houdt, wint het op die lengteschaal namelijk soms niet van de zwaartekracht, die de druppels graag plat maakt. Het is daarom belangrijk een olie te gebruiken die een hoge oppervlaktespanning met water heeft, en geen oppervlakteactieve stoffen te gebruiken die de oppervlaktespanning verlagen. Omdat zulke oppervlakteactieve stoffen ook het samengaan van druppels voorkomen, is het noodzakelijk dat de druppels volledig uitgehard zijn voordat ze elkaar raken. Dit bereiken we door een lange kolom van olie van ongeveer 2 meter lang te gebruiken. In deze kolom harden de deeltjes uit, terwijl ze langzaam naar beneden zakken. Om gelatine deeltjes te maken druppelen we een hete gelatineoplossing in de kolom, die gekoeld wordt om het uitharden te bevorderen. Om polyacrylamide (PAAm) deeltjes te maken, voegen we een katalysator toe aan de olie, die een snelle reactie tussen de acrylamide monomeren tot stand brengt. In beide gevallen kunnen we de druppelgrootte controleren door gebruik te maken

van een luchtstroom langs de naald. Met behulp van een eenvoudige krachtbalans, waarin de weerstandskracht die de luchtstroom levert opgeteld wordt bij het gewicht van de druppel die aan de naald hangt, kunnen we de grootte van de resulterende druppels (en deeltjes) nauwkeurig voorspellen.

In **Hoofdstuk 3** bestuderen we de stromingseigenschappen van suspensies die bestaan uit de hydrogel-deeltjes gemaakt met de techniek uit Hoofdstuk 2. Ook presenteren we een op maat gemaakte cel om de stromingseigenschappen te meten. Deze cel bestaat uit twee concentrische cylinders, ook wel bekend als een Couette cel. Door gebruik te maken van een deksel geven we de cel een vast volume. Uniek is dat we ook meten hoe groot de druk is die wordt uitgeoefend op de deeltjes, door middel van een druksensor in de deksel. Doordat zowel de bodem als de deksel transparant zijn kunnen we de stromende deeltjes in beeld brengen en zo hun stromingsprofiel meten. We meten stromingsprofielen van zowel PAAm als gelatine-deeltjes bij ongeveer dezelfde druk en onze bevindingen wijzen uit dat de band waarin de deeltjes stromen breder is bij de PAAm-deeltjes. Ook meten we hoe de suspensie relaxeert nadat de stroming tot halt is gebracht, en laten we zien dat de PAAm-suspensie meer relaxatie vertoont. Beide experimenten suggereren dat de PAAm-deeltjes gemakkelijker ten opzichte van elkaar kunnen bewegen. We speculeren dat dit het resultaat is van verschillen in de wrijvingseigenschappen of adhesieve eigenschappen van de deeltjes.

In **Hoofdstuk 4** bestuderen we deze systemen verder. We meten de wrijvingscoëfficiënt van de materialen met behulp van een op maat gemaakte opstelling, waarin we een reometer gebruiken om een halfronde hydrogel over een plak van hetzelfde materiaal te wrijven. We doen dit met verschillende snelheden, en vinden dat PAAm een zeer lage wrijvingscoëfficiënt heeft, terwijl die van gelatine veel hoger is en van de polymeerconcentratie afhangt. Ook meten we de hardheid van de deeltjes. We tonen aan dat deeltjes van 10% gelatine en PAAm even hard zijn en dus alleen verschillen in hun wrijvingseigenschappen. We testen het effect van deze materiaaleigenschap op het stromingsgedrag door gebruik te maken van de Couette cel uit Hoofdstuk 3. We vinden dat suspensies van gelatine-deeltjes een instabiliteit vertonen: hun stromingscurve vertoont een “dip”. Als we de schuifspanning delen door de druk om zo de “spanningsratio” van de suspensie te bepalen, blijft de dip bestaan. We gebruiken de stromingsprofielen uit Hoofdstuk 3 om de relatieve snelheden van de deeltjes te bepalen, om zo de wrijvingscoëfficiënt van de materialen en de spanningsratio van de suspensie te kunnen vergelijken. Voor gelatine vinden we dat de spanningsratio ongeveer $\frac{2}{3}$ keer de wrijvingscoëfficiënt is, terwijl voor PAAm de spanningsratio veel groter is dan de wrijvingscoëfficiënt. Een eindige spanningsratio was al eerder voorspeld in simulaties van deeltjes zonder wrijving. Onze metingen zijn, naar onze beste kennis, het eerste experimentele

bewijs voor het bestaan van zo'n minimale spanningsratio voor deeltjes met zeer lage wrijvingscoëfficiënt. Van fundamenteel belang is onze bevinding dat er ten minste twee mechanismes zijn die bijdragen aan de schuifspanning in suspensies, waarvan er één proportioneel is aan de wrijvingscoëfficiënt.

In **Deel II** van dit proefschrift, bestuderen we hoe granulaire materialen reageren op aandrijving uit het inwendige van het collectief van deeltjes, in plaats van door de gebruikelijke wandaandrijving. In **Hoofdstuk 5** bekijken we wat er gebeurt als individuele zandkorrels tot leven komen. Het experimentele systeem bestaat uit deeltjes (schijfjes) drijvend op een luchttafel (zoals bij "air hockey"), die ervoor zorgt dat de deeltjes geen wrijving met de ondergrond ondervinden, maar de deeltjes ook tot draaien aanzet door slim ontwerp van de deeltjes. Behalve een aandrijfmechanisme hebben de deeltjes ook "oortjes", die de deeltjes van "geometrische wrijving" voorzien. We laten zien dat deze systemen collectief gedrag vertonen: wanneer we het aantal deeltjes per oppervlak (de pakkingdichtheid) verhogen, ondergaat het systeem een transitie waarin de beweging van de deeltjes ten opzichte van het centrum van de arena waarin ze zich bevinden, van richting verandert. We bestuderen de statistische mechanica van het systeem door de kansdichtheidsfuncties (KDFs) van de verschillende snelheidscomponenten te berekenen. In tegenstelling tot typische granulaire gassen, vinden we dat de KDFs van de snelheidscomponenten in de x - en y -richting Gaussische functies zijn. Totaal onverwacht vinden we dat de KDF van de snelheidsmagnitude kan worden benaderd door de Maxwell-Boltzmann-verdeling voor ideale gassen, waaruit we een effectieve thermische energie halen als functie van de pakkingdichtheid. Deze thermische energie is, net als de translatie-energie, een grofweg universele functie voor deeltjes met oortjes. Ook bestuderen we de verdeling van energie over de verschillende vrijheidsgraden. We vinden dat deze verdeling niet alleen afhangt van de pakkingdichtheid, maar ook van de oorgrootte. Als laatste doen we experimenten met een extra wand in het systeem, waarmee we de oorsprong van het collectieve gedrag kwalitatief beschrijven. Hierin speelt de geometrische wrijving een cruciale rol.

In **Hoofdstuk 6** gebruiken we granulaire materialen om twee vloeistoffen te mengen in een microfluidische chip, waarin het mengen typisch lastig is, omdat door de kleine lengteschaal de stroming meestal laminair van aard is. De chip bestaat uit een objectglas en PDMS en is gemakkelijk te maken en te gebruiken. De chip heeft twee inlaten voor de vloeistoffen, een cilindrische mengkamer met daarin glasdeeltjes en een kleine magneet, en een enkele uitlaat. De magneet kunnen we aandrijven en rondjes laten draaien langs de muur van de mengkamer, met behulp van een andere magneet die aan een ondersteboven geplaatste bovenroerder vastgemaakt is. We brengen de chip van boven in beeld om het mengproces

van twee identieke vloeistoffen te monitoren, waarbij één van de vloeistoffen een kleurstof bevat. We vergelijken eerst een chip met glasdeeltjes met een chip zonder glasdeeltjes in de mengkamer, bij een vaste aandrijfsnelheid van de magneet. We laten zowel kwalitatief als kwantitatief zien dat de toevoeging van glasdeeltjes aan de chip de mengefficiëntie significant bevordert. We bekijken ook de rol van de aandrijfsnelheid, door te vergelijken met het geval waarin de magneet niet aangedreven wordt. Zonder aandrijving mengen de vloeistoffen niet: we krijgen parallelle stroming van vloeistof met en zonder kleurstof in het uitlaatkanaal. Hierdoor is de standaardafwijking van de pixelintensiteit in de uitlaat gemaximaliseerd. Door te vergelijken met deze maximale standaardafwijking, karakteriseren we de mengefficiëntie van de chip bij verschillende aandrijfsnelheden, maar vinden dat zelfs voor de laagste snelheid die onze motor kan bereiken, de mengefficiëntie maximaal is. Dit suggereert dat de stromingssnelheid van de vloeistoffen significant kan worden opgevoerd. Van praktisch belang is onze bevinding dat de drukval over de chip laag is, waardoor de kans op lekkage bij de slangaansluitingen, alsook de afsluiting tussen de PDMS en het objectglas, sterk verkleind wordt.

List of publications

This thesis:

- **M. Workamp**, S. Alaie and J.A. Dijksman, *Coaxial air flow device for the production of millimeter-sized spherical hydrogel particles*, Review of Scientific Instruments 87(12) (2016), 125113. (Chapter 2)
- **M. Workamp**, S. Alaie and J.A. Dijksman, *What is fluidity? Designing an experimental system to probe stress and velocity fluctuations in flowing suspensions*, EPJ Web of Conferences 140 (2017), 03020. (Chapter 3)
- **M. Workamp** and J.A. Dijksman, *Macroscopic friction and flow instabilities in granular emulsions (working title)*, Submitted (2017). arXiv:1709.10311. (Chapter 4)
- **M. Workamp**, G. Ramirez, K.E. Daniels and J.A. Dijksman, *Symmetry-reversals in chiral active matter*, Submitted (2018). (Chapter 5)
- **M. Workamp**, V. Saggiomo and J.A. Dijksman, *A simple low pressure drop suspension-based microfluidic mixer*, Journal of Micromechanics and Micro-engineering 25(9) (2015), 094003. (Chapter 6)

Other work:

- H. Monteillet, **M. Workamp**, J. Appel, J.M. Kleijn, F.A.M. Leermakers and J. Sprakel, *Ultratong anchoring yet barrier-free adsorption of composite microgels at liquid interfaces*, Advanced Materials Interfaces 1(7) (2014).
- H. Monteillet, **M. Workamp**, X. Li, B. Schuur, J.M. Kleijn, F.A.M. Leermakers and J. Sprakel, *Multi-responsive ionic liquid emulsions stabilized by microgels*, Chemical Communications 50(81) (2014), 12197-12200.

Acknowledgements

This thesis wouldn't exist without the efforts of many others. This part of the thesis is dedicated to those people who have helped or supported me in any way in the last four years. Names are bold-faced so you can find yourself easily!

Jasper, thank you for giving me the opportunity to pursue my PhD in your group. I appreciated your comments to my thesis, and the deadline you set for my thesis draft even allowed me to have a proper (and much appreciated) Christmas holiday. Thank you for keeping a great atmosphere in the lab.

Joshua, words cannot express my gratitude to you: you've been an amazing teacher. You have always given me enough freedom to find out how to do things on my own, yet you were always there if I got stuck. You've thought me so much about granular materials, rheology, programming, story-telling and a million other subjects. You've often pushed me to do things I didn't really feel like doing (e.g. a course on presenting), which usually proved very helpful to me. Thank you for four years of constructive criticism, creative ideas, helpful suggestions and ad hoc discussions. For a couple of years you and I were "the Dijksman group" and I like to think we made a great team.

Thank you **Karen**, for giving me the opportunity to spend a month at North Carolina State University, and for your help and guidance with the spinners project. I felt at home quickly in your lab and I really value the experience I got there.

I also want to thank **Frans**, **Renko**, **Marleen**, **Joris**, **Mieke** and **Thomas** for useful discussions during coffee breaks, group meetings, and other social gatherings.

I also owe a lot to my smart students **Sepideh**, **Pieter** and **Hidde**. I enjoyed working with you very much and all of you have contributed to this thesis in some way. I hope you learned as much from me as I did from supervising you.

Vittorio, thanks for your help with the micromixer. I also valued many other, often 3D-printing related, discussions. We should have a Cola some time soon.

Many thanks to **Gustavo** and **Mika** at NCSU for their help with the spinners project, in particular with the particle design and preliminary experiments.

I would like to thank **Hannie**, **Diane**, **Remco**, **Anton K** and **Ronald** for both technical support and fun conversations over coffee. I owe a lot to the always cheerful **Mara**, who was always willing to help with administrative matters and orders of materials. This lab would not function (or be as fun as it is), without you there. Thank you for sending me texts when **Bert** had filled up the candy-box again, who I'd also like to thank for his help with office supplies and binding my thesis. Thank you **Anita** for your help with financial issues and Optare. I also want to thank **Josie** for her help with booking flights and conferences. **Peter** also deserves a spot here, especially for his help with Maple. In memory of **Hans**, founder of our lab and an inspiration to us all.

I would like to thank all of my office mates for keeping a great atmosphere. **Wolf**, thank you for useful discussions on rheology and gelatin cross-linking, and for a number of great bike rides after work. You and your competitive attitude have also been a joy at board game nights and sports days. **Inge**, thank you for many (more or less) serious conversations in our office while Wolf was wearing his head phones. Despite our lack of direction, you guided our lab to a victory at the sports day! Also, I still think you should become a screenwriter. **Lennart**, you were almost never in our office, but I appreciated our talks when you were there. **Natalia**, you are such a cheerful person! Thank you for your encouragements and for being a listening ear. **Raisa**, it's been amazing to have you as an office mate, although I'm sure the level of my jokes has dropped considerably since you arrived. Thank you for useful discussions regarding friction measurements. **Xiufeng**, thank you for great talks about food, science, and "internet music". I still have no clue what that is. **Johan**, thank you for friendly conversations and your plants which provide our office with oxygen. I'd like to thank **Riahna** for being super cheerful and fun, and **Bob** for making me not the only person who wears a hat to work, and of course for fun conversations.

I would like to thank **Ruben** for his help with LaTeX and Photoshop, other useful discussions and in particular lots of useless conversations. Thank you for bringing and explaining great games to board game nights, for volunteering to be my paranymp and for being good company at trips to Gerard's corner. This brings me to my partner in crime for Fries-Friday: **Lione**. Thank you for being there for conversations at coffee breaks, for organizing various social activities, and for keeping me out of the wind during bike rides with Wolf. I also want to thank **Qimeng** for conversations about (asian) food and scientific drama, random discussions, and the occasional hug. Don't worry, you'll make it! Thank you for being my paranymp. A big thank you goes to **Hélène**, who provided the template for this thesis. I really appreciate our discussions about work, life and baby-related issues. I am happy we are still friends.

I'd like to thank **Ties** and **Pieter** for their help with organizing the PhD/Postdoc-weekend. I think it was a great success! I also valued talks with Ties about the last stretch of the PhD.

I was fortunate enough to join the PhD-trip to the UK, thanks to the organizing talent of **Wolf**, **Gosia W**, **Natalia**, **Maarten** and **Hanne**. I had a great time! Thanks to **Jan-Bart** for being a great roommate those days. Sorry to **Maarten** who couldn't sleep due to our chatting.

I enjoyed many coffee/lunch breaks and social events with (former) members and guests of PCC and BIONT: **Stan**, **Julia**, **Anton B**, **Camilla**, **Junyou**, **Rui**, **Maria**, **Aldrik**, **Ilse**, **Joanne**, **Marco**, **Kamuran**, **Gosia B**, **Rene**, **Dirk**, **Huanhuan**, **Tingting**, **Christian**, **Aljosha**, **Anton H**, **Simone**, **Slav**, **Jessica**, **Fabiola**, **Jan Maarten**, **Ram**, **Niek**, **Sven**, **Raoul**, **Justin**, **Jochem**, **Lucile**, **Nicolò**, **Jesse**, **Huy**, **Inge B**, **Dana**, **Junior**, **Esio**, **Mo**, **Merve**, **Hande**, **Jeroen**, **Prachi**, **Duc**, **Kris**, **Marion**, **Martijn** and anyone I forgot to mention here.

I also owe a lot to the people that made my stay at NCSU very enjoyable. **Jonathan**, thank you for your help in the lab and with data analysis, for driving me around town and for friendly conversation during dinner and lunches (also at P&G 2017). Thanks to **Zhu** for picking me up at the airport, and **Zubair** and **Scott** for being great office mates. I also enjoyed conversations with **Arne**, **Shih-Yuan**, **Janina**, **Austin** and **Ted**.

Graag wil ik alle teamleden van MHCB H2 bedanken voor de gezelligheid op woensdagavond en de dramatische wedstrijden op zondag.

Voor mij van groot belang zijn **Ramon** en **Wesley**, die ik al een eeuwigheid ken. Bedankt voor avonden gevuld met Forza, kletspraat over auto's en motoren, en nutteloos herinneringen oproepen. Ik heb deze altijd erg op prijs gesteld.

Graag wil ik mijn schoonfamilie bedanken voor gezellige dagen in het weekend, vooral met de jongste familieleden.

Ik wil ook mijn broer **Casper** bedanken voor zijn steun, nuttige gesprekken en gebietste sigaretten. **Pa** en **Ma**, jullie hebben me de afgelopen jaren, zoals altijd, ontzettend veel steun geboden. Bedankt voor jullie hulp op alle vlakken van het leven, zonder jullie was ik nooit zo ver gekomen.

Kleine **Emma**, wat heb ik een geluk met zo'n lieve dochter! Jij slaapt de hele nacht door zodat ik goed kan nadenken overdag, en vrolijkt me 's avonds op met je brede lach. Ik had nooit gedacht dat papa zijn zo leuk en makkelijk zou zijn!

Lieve **Ana**, bedankt voor al je steun en aanmoediging. Het afronden van dit proefschrift was nooit gelukt zonder jou. Sorry dat ik soms niet luisterde naar wat je zei, mijn gedachten waren vaak gevuld met de zaken die in dit boekje beschreven staan. Ik ben je eeuwig dankbaar voor het op de wereld zetten van onze kleine meid en het geluk wat zij ons brengt.

About the author

Marcel Jan Workamp was born on the 16th of January 1990 in Amersfoort, The Netherlands. He grew up in Barneveld, where he graduated from the Johannes Fontanus College in 2008. He obtained both his Bachelor and Master degree in Molecular Life Sciences at Wageningen University, specializing in Physical Chemistry. During his Master he did a thesis project in the Physical Chemistry & Soft Matter group, and performed an internship at the Van der Waals-Zeeman Institute of the University of Amsterdam. In May 2014, Marcel returned to the Physical Chemistry & Soft Matter group at Wageningen University to pursue a PhD. He worked with Dr Joshua A. Dijksman and Prof. Dr Jasper van der Gucht to investigate the role of particle properties in the rheology of granular materials. The results of this research are presented in this thesis.

Overview of completed training activities

Discipline specific

Modeling Granular Media Across Scales	Montpellier (FR)	2014
Dutch Soft Matter Meeting 16	Amsterdam	2014
Dutch Soft Matter Meeting 17	Leiden	2014
International MicroNanoConference [‡]	Amsterdam	2015
Physics@FOM [‡]	Veldhoven	2015
SoftComp Annual Meeting [†]	Ancona (I)	2015
Dutch Soft Matter Meeting 19*	Utrecht	2015
Electronics for Physicists	Delft	2016
GRC & GRS Granular Matter [‡]	Easton, MA (USA)	2016
Internship North Carolina State University [†]	Raleigh, NC (USA)	2016
Physics@FOM [‡]	Veldhoven	2016
Dutch Soft Matter Meeting 20	Amsterdam	2016
Dutch Soft Matter Meeting 21	Wageningen	2016
Powders & Grains [‡]	Montpellier (FR)	2017
Dutch Soft Matter Meeting 22*	Delft	2017
Dutch Soft Matter Meeting 23 [†]	Enschede	2017
WUR Rheology Workshop [†]	Wageningen	2017

General

Journal Club (PCC)	Wageningen	2014-2018
PhD week (VLAG)	Baarlo	2015
Presenting with impact (WGS)	Wageningen	2016
Teaching & supervising thesis students (ESD)	Wageningen	2016
Career Perspectives (WGS)	Wageningen	2017

Optionals

Proposal	Wageningen	2014
Colloquia (PCC)	Wageningen	2014-2018
Fluid Mechanics (HWM)	Wageningen	2014
PhD trip ^{††††} (PCC)	UK	2015

[†] oral presentation, [‡] poster presentation, * soundbite

Financial support from Physical Chemistry and Soft Matter, Wageningen University & Research, is gratefully acknowledged.

Cover design by Marcel Jan Workamp and Ruben Higler

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