From Tribology to Rheology
Impact of interparticle friction in the shear thickening of non-Brownian suspensions

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Aux Petits Débrouillards,
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Abstract

Recently, new cement pastes with low carbon footprint, low water content and outstanding mechanical properties after hardening have been developed. However, these cement pastes cannot be commercialized because they shear thicken at high shear rates, causing severe processing problems. The shear thickening of non-Brownian suspensions such as these cement slurries is to date poorly understood.

In this thesis, a theoretical framework has therefore been developed to predict and understand the shear thickening of dense non-Brownian suspensions. It links the macroscopic transition from Newtonian to shear-thickening regimes to the microscopic transition in lubrication regimes between the particles from hydrodynamic to boundary lubrication. It also shows that the suspension volume fraction and the boundary-lubrication friction coefficient control the nature (continuous or discontinuous) of the shear-thickening regime.

This model is first validated by computer simulations based on a tailored contact dynamics algorithm. The simulated flow curves not only exhibit the three different flow regimes described in the literature, but also display the transitions between the regimes in a realistic way.

The relevance of the framework is then experimentally confirmed on suspensions of quartz particles coated with different polymer brushes that modify the boundary-lubrication friction coefficient between the particles. These experiments validate the link between the nature of shear thickening, the suspension volume fraction and the boundary friction coefficient. Moreover, based on extensive tests, the influence of different polymer architectural parameters on the shear thickening of different filler suspensions is evaluated.

Finally, emphasizing the key role of the friction between particles in the rheology of dense suspensions, a precise and robust technique to measure the friction between two microspheres based on lateral force microscopy (LFM) has been developed and successfully applied.
Résumé

De nouvelles pâtes de ciment contenant très peu d’eau ont récemment été développées pour leurs excellentes propriétés mécaniques à l’état durci et leur faible empreinte carbone. Néanmoins, ces pâtes rhéoépaississent à haut taux de cisaillement. Or le rhéoépaississement est un phénomène mal compris, en particulier en ce qu’il concerne les suspensions non-Browniennes comme les pâtes de ciment.

Cette thèse expose, en premier lieu, un nouveau cadre théorique pour décrire et comprendre le rhéoépaississement des suspensions non-Browniennes. Il montre que la transition entre le régime Newtonien et le régime rhéoépaississant s’accompagne d’un changement du régime de lubrification dominant dans les contacts entre grains, d’une lubrification hydrodynamique vers une lubrification limite. Il souligne aussi que la fraction volumique et le coefficient de friction en régime limite des grains détermine la nature, continue ou discontinue, de ce rhéoépaississement.

Ce modèle est d’abord validé par le biais de simulations informatiques basée sur un algorithme de Contact Dynamics modifié. Ces simulations reproduisent, de manière réaliste, à la fois les trois différents régimes d’écoulement des suspensions denses décrits dans la littérature mais aussi les transitions de l’un à l’autre.

La pertinence de ce modèle est ensuite validée expérimentalement sur des suspensions de grains de quartz dont le coefficient de frottement en régime limite a été modifié par adsorption de brosses de polymère à leur surface. Ces expériences confirment le lien étroit entre la nature du rhéoépaississement d’une part et la fraction volumique et le coefficient de frottement en régime limite d’autre part. Des tests sur de nombreux polymères ont, par ailleurs, permis d’analyser les paramètres de leur architecture qui influencent leur capacité à réduire le rhéoépaississement de différentes pâtes de fillers.

Enfin, prenant acte du rôle-clé du frottement entre grains dans la rhéologie des suspensions concentrées, une nouvelle technique, simple et robuste pour mesurer le frottement entre deux microphères, dérivée de la Lateral Force Microscopy, a été développée.
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Chapter 1

Industrial and Scientific Background

The problem of climate change obliges the concrete industry to design new products that have a lower carbon footprint. This chapter describes the origin of concrete’s carbon footprint and shows that one major way of reducing CO₂ emissions involves the use of cement pastes with less water content. Nevertheless, this approach brings with it new issues in terms of the flow of these slurries (i.e. of their rheology) and in terms of the friction between cement grains (i.e. of tribology). This has prompted us to examine the state of art in these two fields.
1.1 Dense cement pastes: an emerging need

1.1.1 Environmental impact of concrete

Concrete is an artificial composite stone produced by a mixture of water, some finely ground (0.1 to 100 \( \mu \text{m} \)) hydraulic binders and some inert powders (referred to, depending on their size, as filler: \( d < 100 \mu \text{m} \), sand: \( 100 \mu \text{m} < d < 5 \text{mm} \), gravel: \( 5 \text{mm} < d < 5 \text{cm} \) and crushed stones: \( d > 5 \text{cm} \)). The mix of hydraulic binders and fillers is called "cement". In the presence of water, the hydraulic binders hydrate and form a plastic paste that sets (first rigidity within a few hours) and then hardens (over some weeks), creating a matrix that traps and glues together the sand grains and gravel [81].

Concrete is by far the most consumed material in the world, with a rate of 2 m\(^3\) per year, per person [193]. Indeed, it combines an exceptional set of advantages. A concrete block can take virtually any shape and, after hardening, is able to sustain high compressive loads for a long time and is relatively resistant to fire, water and most other stressors. It only requires resources that are readily available in vast amounts all around the world (clay, limestone and heat) and thus can be produced in virtually every country. Moreover, it is non-toxic and chemically fairly inert. Nowadays, in many applications, concrete cannot be replaced.

However, as with most other industrial products, concrete production is also associated with environmental impact. In the case of concrete, the main impact is the huge release of CO\(_2\), which represents 5% [209] of the total human production of CO\(_2\) in the world.

It should be emphasised at this point that the carbon footprint of concrete, as well as that of most other building materials, is a minuscule part of the life-time carbon footprint of a building (usually less than 5% [154]), the dominating contribution arising from the heating and cooling systems. From a long-term point of view, the quality of the insulation of the concrete building is, for example, far more important than the footprint of the concrete itself.

Nevertheless, because of its huge production volume, reducing the carbon footprint of concrete is a potentially powerful lever to influence climate change.
1.1.2 Why does concrete production release CO$_2$?

In terms of CO$_2$, around 90% of the footprint of concrete is due to its hydraulic binder content (around 250 kg/m$^3$) [89]. The production of the other components such as the filler, sand and gravel quarrying and grinding are negligible in this respect. Transportation of these materials could represent an important source of CO$_2$ but for economic reasons, the raw material mines, the cement plant, the concrete factory and the building site are usually close to each other.

The majority of today’s hydraulic binder mixes are mainly composed of Portland cement [189]. It is produced by calcination of calcium carbonate, CaCO$_3$, at 900°C into quicklime (CaO) and CO$_2$. Quicklime is then sintered with clay (silicon oxides with various amounts of aluminium and iron oxides) at 1400°C to create calcium silicates, calcium aluminate, and calcium alumino-ferrite. All these compounds have hydraulic binding properties [81]. At this stage, the product is called clinker nodules (5 to 25 mm) and becomes Portland cement after grinding and addition of small amounts (less than 5%) of mineral additives (mainly gypsum and limestone that control the cement setting). On average, the decarbonation of calcium carbonate directly generates 550kg of CO$_2$ per ton of Portland cement [209] and the energy that is required to heat up the materials and produce the chemical reactions generates around 400 kg of CO$_2$ per ton.

1.1.3 Towards greener concrete constructions

Several ways have been investigated to reduce the carbon footprint of concrete. Since the core of the problem is the Portland cement production, many routes have been tried to improve the production process, e.g. mixing the Portland cement with other compounds, substituting the Portland cement by other hydraulic binders, reducing the binder content in concrete and the volume of concrete in each building.

Improving cement plants

Since the 1970s the energy performance of cement plants has been radically improved in developed countries by the spread of new production processes that use dry raw materials (for review Ref.[209] and references
within). This infrastructure modernization is still underway in developing countries, especially in China. The substitution of combustible materials from fossil hydrocarbons to renewable materials (waste wood, farming wastes, ...) and industrial wastes (solvents, oils, landfill gas, tires, dried sewage sludges, ...) is also leading to the reduction of net emissions. For example, in 2009, 18% of the fuels used in European cement plants were from non-fossil sources [38].

**Blending Portland cement**

Cement producers have created new cement mixes that not only contain Portland cement, but also up to 40% of other reactive materials [189]. These mineral additions are mainly metal oxide wastes from other high-temperature industrial processes, such as silica from coal combustion fly ash and slags from the metallurgy industry or natural pozzolanic materials from volcanic areas. This blending of Portland cement with industrial wastes drastically reduces the net emissions of the cement production. Moreover, apart from the transportation cost, these materials are usually cheaper than Portland cement. Nevertheless, these additions are not reactive by themselves and most of them require the presence of an alkaline pH to react as binders. Moreover, their hydration is slower than Portland cement, and time is a restricted resource on building sites and their availability is quantitatively and geographically constrained. For these reasons, they can only replace a fraction of the Portland cement.

**Replacing Portland cement**

Some less polluting binders, which can react without any Portland cement, have also been proposed, such as sulfoaluminate-bellite cement (e.g. Aether by Lafarge, France), magnesium-silicate-based cement (e.g. Novecem, US) or even alkali-activated alumino-silicates (e.g. Zeobond, Australia) [73, 180]. Nevertheless, the long approval process, the conservative attitude of the building industry, and the poor availability of the reagents, as well as some technical issues, have delayed their widespread use.
Using less cement

It is also possible to reduce the quantity of binder in each cubic meter of concrete: in other words, using less “glue”. Cement paste does not harden by drying (as plaster does) but by a chemical reaction between the binder and the water (so called hydration). So, it is not possible to reduce only the proportion of hydraulic binder for a given volume of concrete. Indeed, in that case, an excess of unreacted water inside the concrete block would lead to porosity and structural weakness. Thus, the quantity of water needs to be reduced in proportion of the reduction of binder. Nevertheless, the volume to be filled (i.e. the volume of voids between the sand and gravel grains) remains constant. In order to keep the same volume of gluing paste, the volume of the paste is increased by the addition of inert fillers (see Fig. 1.1). Thus, the cement paste contains more and more solid grains (Portland cement and filler) separated by less and less water.

Using less but stronger concrete

It is also possible to reduce the quantity of concrete in a given building. For the optimisation of structures, it is a civil engineering or architecture problem, and some progress has been made. There is also a production-management issue on the building site if the optimisation implies the simultaneous use of different concrete types. But these two fascinating problems lie beyond the scope of this thesis. More
related to materials science, there is the option of using less of a stronger concrete for making thinner walls and columns. This implies increasing the compressive strength of the materials. An effective way to achieve this is to reduce the quantity of water, to get closer or even below the stoichiometric ratio with respect to the binder.

Two major ways to reduce concrete’s carbon footprint involve the use of denser cement pastes. Nevertheless, such dense suspensions do not flow easily, cannot be easily pumped and may not properly fill the formwork. Using concrete of this type would certainly reduce CO$_2$ emissions but would require new approaches to make the pastes flow. This thesis addresses this last issue by taking a new look at the rheology of dense cement pastes.
1.2 Rheology of dense non-Brownian suspensions

1.2.1 Scope of the study

This part of the introductory chapter describes the state of the art in the rheology of dense suspensions. In the first sections about low and intermediate shear, we focus only on dense-suspension rheology directly related to cement pastes—phenomena that are quite well understood. In the last section concerning higher shear, we include a wider scope of experiments, since cement rheological behaviour under high shear is still a controversial issue.

For the sake of clarity, we need to specify which elements are considered and which ones are disregarded. In this thesis, cement slurry rheology has been examined within the following limits:

- The particles are between 1 and 100 μm in diameter, because the phenomena we are interested in take place at the cement scale.
- The particles represent at least 50 % of the total volume of the suspension, because only the densest cement pastes are being studied.
- The suspending solution is alkaline (pH>11) and salty (ionic strength above 0.3 mol/L) and in particular contains a high concentration of calcium ions. This is representative of a typical cement solution composition.
- Any chemical reaction is disregarded.
- Only rheology in simple shear, homogeneous and steady states is addressed.

1.2.2 Generalities concerning the rheology of cement suspensions

Rheology nomenclature

A suspension is a mixture of solid particles with a liquid In the rest of the chapter, we will only focus on simple shear, i.e. the fluid is sheared
between two parallel solid planes that move relative to each other along one of their directions [175]. For the sake of clarity, in this nomenclature section, the shear direction is called \( \vec{e}_x \), the other plane direction, \( \vec{e}_z \) and \( \vec{e}_y \) completes the orthonormal basis. Some rheological parameters can then be defined. The shear stress, \( \tau \), is the ratio of the force applied on the moving plates divided by their area. The deformation or strain, \( \gamma \), is the ratio of the relative displacement of the plates by the distance between them and the shear rate, \( \dot{\gamma} \), is its first time derivative. The apparent viscosity, \( \eta \), is then defined by \( \eta = \tau / \dot{\gamma} \).

In the field of suspension rheology, a specific definition problem appears since the material is heterogeneous at the micro-scale. For this reason, the rheology parameters are defined at a meso-scale that is small compared to the volume of the fluid but large compared to the typical size of the heterogeneity, i.e. the particle size. This limit is usually set at ten particle diameters [35].

The viscosity of a fluid can vary with the external parameters such as the pressure, the temperature and the shear. Only this last parameter is pertinent for the rest of the thesis. It leads to a straightforward flow-regime nomenclature. When the viscosity is independent of the shear, the fluid is said to be in a Newtonian regime. When the viscosity decreases with the shear, the fluid is said to be in a shear-thinning regime and in the opposite case, the fluid is said to be in a shear-thickening regime. In both cases, if the variation in the viscosity with the shear rate is infinitely sharp, the flow regime is described as discontinuous; if the evolution is smooth, it is said to be continuous (see Fig 1.2 for graphical representation).

Usually, the force (per unit of surface) that is applied by a volume of fluid on its boundaries in the direction normal to the boundary is called pressure. However, in suspension rheology, this force is not isotropic and depends on the boundary direction. The stress in the \( x \)-direction on a boundary that is perpendicular to \( \vec{e}_x \) is then called \( \tau_{xx} \). The same nomenclature is used for the \( y \) and \( z \)-directions. Two normal stress differences can then be defined:

\[
N_1 = \tau_{xx} - \tau_{yy} \tag{1.1}
\]

\[
N_2 = \tau_{yy} - \tau_{zz} \tag{1.2}
\]
In particular, if $N_2 < 0$ the fluid is called contractant and if $N_2 > 0$ the fluid is called dilatant.

**Particle interactions**

The flow properties of any complex fluid are directly related to the forces between the flowing particles. In dense suspensions, 6 main components are present and have different dependence with the shear rate:

- **Brownian motion** arising from the thermal fluctuations on microscale objects. Given the size range limitations discussed previously, Brownian motion effects play a small role in cement rheology. These forces are shear-rate independent.

- **colloidal interactions** that represent all the interactions between the surface of the particles through the fluid such as van der Waals, electrostatic or steric forces. Most of the time, these forces are also shear-rate independent.

- **gravity** because of the density mismatch between the cement grains and the suspending fluid. This force is shear-rate independent.

- **hydrodynamic forces**, arising from the shear of the bulk of the aqueous solution between two moving grains. A simple examination of the case of a particle pair shows that these forces are linear with shear rate.
• **particle inertia.** It varies proportionally to the square of the shear rate.

• **contact forces** arising from the contact between particle asperities. Here, we will mainly consider elastic and frictional forces. Their dependence on shear is unclear.

Because of this different dependence of the forces with the shear, by going from rest to higher and higher shear rate, the dominating interactions change, affecting the flow behaviour.

### 1.2.3 At low shear: Yield Stress and Shear Thinning

**Brownian Vs. Colloidal Forces**

The ratio between thermal energy and energy of attractive interactions is an important parameter for the smallest particles in a cement suspension, with sizes up to a few microns. To determine the dominant interaction, we consider a dimensionless number introduced by Coussot and Ancy [5]:

\[ N_r = \frac{\Phi_0}{k_B T} \]  

(1.3)

where \( \Phi_0 \) is the typical energy involved in a colloidal interaction, \( k_B \) the Boltzmann constant, \( T \) the temperature and thus \( k_B T \) is the typical energy of thermal agitation. \( N_r \) determines whether two particles that come in close proximity and are then attracted by colloidal forces, can be separated only by thermal agitation. In order to quantify \( \Phi_0 \), we have to describe the relevant non-contact colloidal forces that are in effect. The first and the most important are the van der Waals forces, due to the differences in electromagnetic properties between the particles and the surrounding fluid [69]; here, only the non-retarded forces that are dominant are considered. To a smaller extent, electrostatic repulsion has also been reported [70] but does not play a major role due to the high ionic strength of the surrounding medium. Then \( \Phi_0 \) can be written as:

\[ \Phi_0 = \frac{A_0 a^*}{12h} \]  

(1.4)
where $A_0$ is the Hamaker constant, $h$ is the distance between the particle surface and $a^*$ is the local radius of curvature of the surface at the point of closest proximity. In the case of complex systems, such as cement, these parameters are not easily determined. Nevertheless, the Hamaker constant of tricalcium silicate has been measured to be approximately $10^{-20} \text{J}$ [68]. The distance between particle surfaces, $h$, is of the order of a few nanometres (from 2 to 10nm, depending on the level of flocculation) [71, 116]. Finally $a^*$ is subject to interpretation, and values of around 500nm have been reported [176].

Consequently, at room temperature, $N_r > 10$ and Brownian motion plays a negligible role in the rheology of cement grains. In other words, in the absence of mechanical stress, the particles are trapped in the vicinity of each other and, since the volume fraction of particles is high, they create a stable percolating network throughout the entire system.

**Gravity Vs. Colloidal Forces**

Most cement pastes are designed to remain homogeneous for several hours. This is achieved by achieving a particle percolating network that remains sufficiently strong to counteract gravitational forces and thus prevent bleeding and sedimentation. In other words, gravitational forces are dominated by Van der Waals forces. In the cases where gravity dominates the rheological behaviour, it mainly creates heterogeneity in the system’s particle volume fraction. Such heterogeneous flows are beyond of the scope of this review.

**Yield Stress**

The suspension at rest is thus a percolating hyperstatic network of particles that attract each other, since the volume fraction is high enough to allow this. Consequently, it behaves as an elastic solid. Making it flow implies an initial breaking of bonds, i.e. leaving the elastic regime, and reorganisation of the network. Extensive experimental data show that the rupture of the network starts at a critical deformation, $\gamma_c$. For cement suspensions, $\gamma_c$ has been reported to be around a few percent [158, 178]. Smaller critical displacements have also been reported but seem to be more linked with the chemistry of cement pastes and the rupture of the first hydrate bonding between cement grains. This goes
beyond of the scope of our description. Since the material is elastic, the critical deformation is directly related to a critical shear stress, the yield stress, \( \tau_c = G \gamma_c \) with \( G \) the elastic modulus of the network.

Quantitative predictive models have been based on this concept. One of the most advanced models for cement slurries, the YODEL, proposed by Flatt et al. [71], predicts, for a dense case, that:

\[
\tau_c \approx m_1 \frac{\phi^3}{\phi_{\text{max}}^\text{YODEL} \left( \phi_{\text{max}}^\text{YODEL} - \phi \right)}
\]  

where \( m_1 \) is a pressure parameter that quantifies the impact of the inter-particle binding strength and that scales with \( A_0/r_{50\%} \), \( r_{50\%} \) is the median particle radius, weighted in volume and \( \phi_{\text{max}}^\text{YODEL} \) a maximum packing volume fraction (see [71] for details and quantitative relations). The typical values of yield stress are \( 10^1\text{-}10^3 \) Pa for ordinary cement pastes [67].

**Tuning the yield stress**

In order for the concrete to be as fluid as possible, and, for instance, to flow easily into moulds and around steel bars, it is important to reduce the natural yield stress of the cement paste. The most fluid cement slurries (for Self-Compacting Concretes) have a yield stress, which is just sufficient to prevent sedimentation of the coarsest components [206].

To achieve such a yield-stress reduction, the Van der Waals attraction needs to be reduced. Since these attractions are short-range, a solution is to cover the cement grains with a nanometre-thick layer made of a material with the same refractive index as the surrounding fluid. No refractive-index difference means no further attraction [129].

Several polymers, so called superplasticizers (polynaphtalene sulfonates, polymelanine sulfonates, sugar-free modified lignosulfonates, polymethylmethacrylates and their PEG esters), have been added to cement slurries with this aim. They have two main common characteristics:

- they carry negative ionic groups that can adsorb spontaneously onto the surface of the cement grains (see Section 1.4.3 for details)
- they are highly solvated by the local aqueous media and this solvated
form has electromagnetic properties (e.g. refractive index) very close to those of the surrounding fluid.

This effect is often called "steric repulsion" because these polymers can be imagined as being small entropic springs that hold the particle surfaces apart, this elastic force compensating the Van der Waals attraction of the cement grain surface.

For most charged polymers, certain electrostatic effects also increase the repulsion between grains [70].

These polymers will play a key role in this thesis because they radically change all the properties of the cement-grain interactions. The chemical composition and the physical properties of these polymers are detailed in Section 1.4

**Shear thinning**

When flow is initiated, a competition starts between shear, which breaks the bonds between two neighbouring particles and the attractive forces, which tend to reform these bonds. The typical timescale of the shear-induced bond breaking is $\dot{\gamma}^{-1}$. The timescale of the bond formation is not easy to define. Nevertheless, based on coagulation theory, Roussel et al. proposed a way to quantify the time required for a given particle pair to transition from the (geometrical) average distance between neighbours to the distance $h$ by the action of the attractive force. This yields a typical timescale of a few seconds for dense cement suspensions.

At slightly higher shear rates, the network of interconnected particles no longer percolates, and the suspension can be seen as a collection of
1.2 Rheology of dense non-Brownian suspensions

![Diagram of clusters and forces](image)

**Figure 1.4** – Increasing the shear, the clusters get broken and release the trapped fluid. This leads to a reduction of the effective volume fraction and a reduction of the apparent viscosity.

clusters. The clusters of particles have an apparent volume larger than the sum of the volume of their particles because they include the volume of water present between their particles. Thus the effective volume fraction of the suspension of clusters is higher than the volume fraction of the suspension of the same number of freely moving particles and thus a suspension of clusters has a higher viscosity (see next section) than a suspension of the same number of unbound particles (see Fig.1.4). Due to this phenomenon, the viscosity of the suspension is linked to the size of the particle clusters. Since each cluster, especially the largest, are continuously being destroyed by shear, the faster the shear, the smaller the particle clusters and the lower the viscosity: i.e. the suspension experiences shear-thinning.

In this regime, the apparent viscosity can thus be described as the sum of the network yield stress contribution \( \eta_y = \tau_0 / \dot{\gamma} \) and the shear-dependant contribution also called reduced viscosity \( \eta_r = \eta - \eta_y \) [100].

### 1.2.4 At intermediate shear: Newtonian Flow

As the shear is increased further, the hydrodynamic viscous interactions, which depend linearly on the shear rate, start to dominate over the colloidal interactions. A dimensionless flow number has been proposed to quantify this transition. It compares the stress arising from viscous
and colloidal interactions [176]:

\[ N_F = \frac{\tau_{\text{visc}}}{\tau_{\text{coll}}} = \frac{\eta_f \dot{\gamma} R^2 p h^2 f_{\text{visc}}(\phi)}{A_0 a^* f_{\text{coll}}(\phi)} \]  

(1.6)

where \( \eta_f \) is the viscosity of the suspending fluid, \( \phi \) is the volume fraction, \( R_p \) is the typical radius of the particles, and \( f_i(\phi) \) are the dependences of the viscosity on the volume fraction for each interaction type. The exact formulae for these functions are still under debate, especially at the highest volume fractions. For example, they both diverge at a critical volume fraction, but they may not diverge at the same value. Thus, the use of this number to predict the flow behaviour is still limited.

Since the attraction between particles is no longer important and there is still no inertia, the system has no internal timescale that could be compared to \( \dot{\gamma}^{-1} \), and thus the properties of the system are shear independent. The suspension thus experiences Newtonian behaviour (shear-independent viscosity).

A good prediction of the Newtonian viscosity of dense suspensions, including complex ones, is provided by empirical and macroscopic laws. The most famous is Krieger-Dougherty’s law [119] where:

\[ \eta(\phi) = \eta_f \left(1 - \frac{\phi}{\phi_{\text{div}}}\right)^{-\frac{4}{3}\phi_{\text{div}}} \]  

(1.7)

where \( \phi_{\text{div}} \) is the volume fraction at which the viscosity diverges. The value of the exponent is set to recover the Einstein relation at the lowest volume fraction [58, 59]. Nevertheless this law has almost no microscopic physical basis.

Recently, a theoretical approach have been developed to describe such systems, where the system is fully described by a single dimensionless number, the viscous number [28]:

\[ I_v(\phi) = \frac{\dot{\gamma}\eta_f}{P} \]  

(1.8)

where \( P \) is the confining pressure. The viscosity can then be expressed as a function of \( I_v(\phi) \) alone [28]. In the Newtonian regime, even though hydrodynamic lubrication is the dominant dissipation mechanism,
some frictional contacts are present [28, 163, 211], so the determination of the value of $I_v$ would require a precise knowledge of the frictional properties of the particles, which has so far not been easily measurable experimentally (see Chapter 5). Nevertheless, to date, this theoretical approach has found little application in the prediction of the rheological behaviour of dense suspensions.

### 1.2.5 At high shear: Shear Thickening

At higher shear rates, dense suspensions, such as cement slurries, shear thicken. Their viscosity increases with the shear (see Fig. 1.2).

In contrast with the phenomena that we described previously, the physical origins of shear thickening are still under intense debate [48] and are the main topic of this thesis. For this reason, the focus of this part of the review is wider and includes all experimental results and theories that are relevant to the shear thickening of dense non-Brownian suspensions.
Phenomenology

Shear thickening seems to be a common phenomenon for non-flocculated suspensions [13, 63, 173] although it was not reported before 1938 [79]. It can also appear in many other systems, such as most granular media [76] and some polymer slurries [18]. As defined in Section 1.2.2, two types of shear thickening can be distinguished:

- **Continuous Shear Thickening** (CST) is the gradual increase in viscosity with shear rate, \( \dot{\gamma} \). (i.e., with \( \tau \) the shear stress, \( 0 < \frac{\partial n}{\partial \tau} < 1 \))

- **Discontinuous Shear Thickening** (DST) is a sudden jump of viscosity at a given shear rate (i.e. \( \frac{\partial n}{\partial \tau} = 1 \)).

  - If this sudden jump has a finite size, for example if the DST is followed by a Newtonian plateau, in absence of a standard name, we will call it **step-DST** (sDST).

  - If the viscosity diverges toward infinity, we will call it **divergent-DST** (dDST). In this case, the fluid that experiences dDST appears to take on solid-like properties (e.g. it can sustain loads, it can crack...). A mixture of cornstarch and water is by far the most studied case of dDST.

Rheometrical studies of dense suspensions are experimentally challenging and innumerable artefacts such as wall slip, size effects, breaking, migration or evaporation can influence the measurement [44]. So far only few experiments have managed to avoid all these problems. However, although this field is still under debate [48], some common observations concerning the behaviour of shear-thickening suspensions can be highlighted:

- This viscosity increase is reversible. After stress removal, the fluid will return to its low-shear viscosity after a short relaxation time. A precise measurement of the relaxation time has been reported for example by Bertrand et al. [19].

- As the volume fraction increases, the shear thickening becomes more intense (in terms of \( \frac{\partial n}{\partial \tau} \)) [13, 32, 88] until it becomes discontinuous and divergent (dDST) and appears at lower values of \( \dot{\gamma} \) [42, 63, 98, ...
Several authors have reported that $\dot{\gamma}_c$ tends to zero at the highest concentration [13, 31, 34, 60].

- Shear thickening is less intense for multimodal or polydisperse suspensions [15, 64, 197, 204] and for spherical particles [36, 42]. In fact, suspensions of rough and irregular particles shear thicken more easily [13, 32, 134].

- The critical shear rate decreases with particle size.[111, 197]

- Shear thickening can be obscured if the suspension is too flocculated [31]. This is the reason why shear thickening of cement pastes has only been observed since the invention of effective deflocculating admixtures.

- The boundary conditions play a key role in the intensity [62] and in the shear-rate range [33] of shear thickening. For example, at the highest volume fraction, the dDST stops when the stress is so high that the boundary walls can be deformed by the pressure that the particles exert on them [33].

**Theoretical Background**

The most surprising feature of the shear thickening of dense suspensions is the small number of components that are required to obtain it. Summarising the experimental evidence, it seems that any dense suspension of non-interacting hard spheres in a Newtonian fluid can shear thicken [13, 34].

In a dense suspension, the thickness of the fluid layer between two particles, $h$, is usually small compared to the radius of the particles, $R_p$. As a consequence, all the explanations of shear thickening proposed so far, assume some modifications of the interactions within this small space [13].

**Turbulence Model** Historically, the first explanation was proposed by Andrade [7], based on the idea of a sudden onset of turbulent flow in the suspending fluid. This, however, is in contradiction with the fact that the shear thickening happens at decreasing values of shear rate as the volume fraction increases (i.e. when the channel characteristic size
in which the fluid flows decreases). Moreover, many other occurrences of shear thickening have been observed at low values of Reynolds number [13].

**Order-to-Disorder Transition** The second important theory was proposed by Hoffman [98, 99]. First, he observed that the shear thinning of the suspension at low or moderate shear rate can be linked to the creation of ordered microstructures of particle (layers or strings) within the fluid during the shear. [1, 40, 98, 105, 122, 125, 210]. These preferential flow structures (layers or string) were proved to minimise the viscous dissipation [22, 29] and could explain the shear thinning. At high shear rate, these structures become unstable and the ordered microstructure disappears [40, 98]. This new disordered state was attributed to an hydrodynamic instability within the layers [98], which was thought to create an increase in the collective viscous drag of the particles. So, this order-to-disorder transition was proposed to be sufficient to create shear thickening [23, 57]. Nevertheless, this theory fails to explain several experiments in which no order is observed before the shear thickening and consequently, no order-to-disorder transition can exist [15, 122, 207]. A variation of this theory has been proposed [97], in which the concept of layering is defined only as a mesoscopic and partial order without a microscopic one. Nevertheless, this new version of the order-to-disorder theory still lacks precision and refutability.

Presently, two other main theories are proposed in the literature to explain shear thickening: the hydrocluster theory and the viscous-inertial transition theory. Both of them predict a mild, continuous shear thickening and are relevant for different kinds of suspensions.

**Hydroclusters** The hydrocluster theory was created by Bossis and Brady [30] in a simulation paper, although the core idea can be found in Ref.[16] and the first experimental proof was provided by Boersma [24] (see Ref. [203] for review).

This theory was based on the balance between hydrodynamic forces and a shear-independent repulsive force, such as Brownian, steric or electrostatic interactions. Subsequently, this theory has been mainly developed and used to describe Brownian suspensions. In short, at
Figure 1.6 – Hydrodynamically clustered particles (grey) under shear (blue arrows). Simple shear exhibits a compression in the $\theta = -\pi/4$. Adapted from ref.[30].

low shear, the repulsive force prevents overly strong viscous dissipation in the particle contacts by holding the particles far from each other and preventing the lubrication film from thinning. At high shear, the repulsive force becomes negligible compared to viscous forces and some particles can come closer to their neighbours and consequently experience extremely dissipative viscous interactions.

In detail, any of the above-mentioned repulsive forces are known to maintain the homogeneity of the suspension. When the compressive hydrodynamic forces due to shear become similar to strongest stabilisation force, the rediffusion process is prevented. Because this compressive viscous force is mainly applied along a $-\pi/4$ axis, the pair correlation function is no longer spherically symmetrical. The probability of finding a pair of particles nearly in contact along this axis increases. When this probability becomes large enough, on the mesoscopic scale, some clusters of connected particles, also known as hydroclusters, are created in the fluid along this compressive axis (see Fig.1.6). When the relaxation time of these hydroclusters becomes larger than the characteristic timescale of the flow (inverse of shear rate), the fluid shear thickens continuously [90]. At the same time, this intense compressive hydrodynamic force
leads to a negative first normal stress difference, which scales with the shear stress [17, 77, 183]: i.e. the fluid is contractant.

Even if this theory can be accepted for many colloidal suspensions [203], it does not seem to be relevant for cement suspensions. Firstly, the large surface roughness and the angularity of cement grains prevents any divergence of the hydrodynamic lubrication force in a contact by prevents the closing of the gap between particles [185]. Secondly, shear-thickening cement suspensions are dilatant and not contractant and finally the relative increase of viscosity due to hydroclusters never exceeds a factor of two [34], whereas shear-thickening cement suspension viscosities can increase by several orders of magnitude [197].

**Bagnold Viscous-Inertial Transition** Another theory has been proposed by Bagnold [11] and is based on the competition between the viscous forces and the inertia of the suspended particles. In contrast to the hydrocluster theory, which have been mainly applied to small particles, since the inertial mass scales with $R_p^3$, this theory mainly applies to suspensions of large spheres.

This force competition has been quantified with a dimensionless number (called Bagnold number):

$$Ba = \frac{\tau_{\text{iner}}}{\tau_{\text{visc}}} = \frac{\rho_p \dot{\gamma} R_p^2 f_{\text{iner}}(\phi)}{\eta f_{\text{visc}}(\phi)}$$  (1.9)

where $\rho_p$ is the density of the particles and $f_i(\phi)$ is the dependence of the viscosity (from viscous and inertial effects) on the volume fraction. As in the previous case, the value of $f_i(\phi)$-functions and especially their point of divergence is a very important, but poorly solved issue.

When $Ba >> 1$, the suspension is driven by particle inertia and behaves mainly like dry granular media. For example, it dilates, generating $P > 0$ (and $N_2 > 0$), when it flows. In that case, dimensional analysis shows that rheology is characterised by a single dimensionless number, the *inertial number* of the dry granular media, $I$ [76]:

$$I = \dot{\gamma} R_p \sqrt{\frac{\rho_p}{P}}$$  (1.10)

This number can be interpreted as the ratio between the time scale
required for a particle to be displaced by its own diameter by the pressure exerted by the other grains, \( t_{fall} = r \sqrt{\rho_p/P} \), and the time scale of the flow, \( t_{flow} = \dot\gamma^{-1} \). For given particles and boundary conditions, \( I \) only depends on the volume fraction \( \phi \). This also means that \( \tau \propto \dot\gamma^2 \) and \( \eta = \tau/\dot\gamma \propto \dot\gamma \). Thus, the Bagnoldian regime is then a mild continuous shear-thickening regime.

When compared to cement rheology data, Bagnold theory can be relevant for continuous-shear-thickening cement pastes, but fails to explain discontinuous shear thickening.

### 1.2.6 Conclusions on rheology

The rheology of dense suspensions in general and the rheology of dense cement pastes in particular are very complex (see Fig. 1.7). Many time and length scales are involved and various phenomena are competing. Due to extensive scientific work from the 1970s, this phenomenology has been largely rationalised.

Among the remaining open issues, shear thickening at high shear is one of the most puzzling. Bibliographical analysis shows that current theories (Hydroclusters and Bagnoldian regime) both converge on the idea
that the grains enter into close contact with their neighbours. Therefore, an understanding of the shear thickening of dense pastes requires the physics of the contact between the particles to be taken into account.
1.3 Lubricated contact tribology

In order to accurately describe the close contact between particles in a solution, the basics of the mechanics of static contacts between two solids, smooth and rough, are first given. Then we consider the case of when these solids begin to slide. Finally, this sliding contact is considered in the presence of a surrounding fluid and a classical tribological analysis of this lubricated contact is presented in terms of frictional dissipation and lubrication regimes.

1.3.1 Basics of static contact mechanics

Elastic spheres: the Hertz model

In the simplest model, two smooth solids are in contact at a single point, and only the elastic properties of the solid are taken into account (no adhesion, no friction, no plastic deformation). For the sake of simplicity and because of its relevance for the rest of the thesis, we will take here the example of two spheres (see Fig. 1.8) of Young’s modulus $E_1$ and $E_2$ and Poisson’s ratio $\nu_1$ and $\nu_2$, as Hertz did in his first article [94]. In the presence of a normal force $F_N$, the two spheres of radius $R_1$ and $R_2$, become deformed. The radius, $a$, of the contact area and the depth of indentation, $\delta$, can then be expressed by:

$$a = \left( \frac{3F_N R^*}{4E^*} \right)^{\frac{1}{3}}$$  \hspace{1cm} (1.11)

![Figure 1.8 – Elastic contact between two spheres](image)
\[ \delta \approx 1.04 \left( \frac{F_N^2}{R^*E^*} \right)^{\frac{1}{2}} \]  

(1.12)

where \( R^* \) is the effective radius, \( R^* = \frac{R_1 R_2}{R_1 + R_2} \) and \( E^* \) is the effective elastic modulus, \( E^* = \left( \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right)^{-1} \). Moreover, the normal force is spread over the contact area according to a quadratic law and the pressure at each point of the contact zone at a distance \( x \) from the centre is:

\[ P_c(x) = \frac{3F_N}{2\Pi a^2} \left( 1 - \left( \frac{x}{a} \right)^2 \right)^{\frac{1}{2}} \]  

(1.13)

Despite very many assumptions, Hertz’ theory is still useful for rough quantification of contact areas and pressures. More precise descriptions of the contact can be achieved by taking into account the adhesion forces in the contact area (JKR model) [108], outside of the contact (DMT model) [56, 147] or both (Maugis’ model) [140].

**Elastic/plastic rough spheres**

Most solid surfaces (and especially cement grains) are rough. In this case, Bowden and Tabor demonstrated [27] that only a very small fraction of the asperities of both surfaces actually come into contact. The real contact area, \( A_R \), represents only a small fraction of the apparent contact area, \( A_A \) and on these small spots, huge pressures are attained.

The real area of contact depends mainly on the topography of the surfaces and their mechanical properties. Many authors [9, 80, 86, 87] have assumed that the roughness can be modelled using half spheres on flat surfaces. For example Greenwood and Williamson [86, 87] showed that if the distribution of asperity heights is exponential, the area of each asperity contact is constant with load. On the other hand, if the distribution is Gaussian, the real area of contact is proportional to the load.

To summarize, if the solids are elastic at the studied loads and the number of asperities in contact is independent of the load, then \( A_R \propto F_N^{2/3} \). Nevertheless, the solid asperities are often in a plastic regime at these loads, which scales with \( A_A/A_R \), and in this case, the
real area of contact scales with $F_N$. There also exists a final case, in which the topography of the elastic asperities are such that when the load is increased, the area of each contact does not change but their number increases. In that last case also, $A_R \propto F_N$.

1.3.2 Friction between sliding objects

Dry friction

These findings on the real area of contact are extremely important in friction, because, as shown for example by Tabor, frictional dissipation takes place within the asperity contacts, which are proportional to $A_R$. Since the case where $A_R \propto F_N$ is very common, it explains why the frictional force, $F_F$, is usually found to be independent of $A_A$, proportional to the load and independent of the sliding speed. This set of three properties is referred as the Amontons-Coulomb model.

Lubricated friction

Lubricated contacts have been widely studied for their industrial interest, because they usually display lower dissipation than dry contacts. Indeed, the first and still pertinent description has been given for lubricated bearings [190]. In his work, Strubeck expressed the viscous coefficient of friction between the two cylinders of a journal bearing, $\mu = F_F/F_N$, and the distance between the two surfaces, $h$, as a function of a single parameter, called the Sommerfeld number.

$$s = \frac{\eta_f \omega}{P_c} \quad (1.14)$$

where $\eta_f$ is the viscosity of the lubricating fluid, $\omega$ is the rotational speed of the cylinders and $P_c$ is the pressure applied to the contact.

This Sommerfeld number has then been extended to other systems than bearings and defined as:

$$s = \frac{\eta_f v}{P_c L} \quad (1.15)$$
where $v$ is the relative speed of one surface compared to the other and $L$ a length scale of the contact.

The Sommerfeld number can be seen as the ratio of the viscous lift arising from the sheared viscous fluid in a convergent geometry and the load in the contact. This representation was then extended to small $h$ situations. Three regimes are then usually distinguished (see Fig 1.9):

- At high Sommerfeld number, the viscous lift dominates. There is a full layer of fluid between the two surfaces, which carries the load, and the coefficient of friction is relatively small due to the shear of this layer. In the case of rigid surfaces and low pressures ($< 100$ MPa), it is known as the hydrodynamic regime and $\mu$ is a linear function of $s$. At higher pressures ($>200$ MPa), the solid becomes deformed by the fluid pressure, and the lubrication regime is referred to as elastohydrodynamic. Nevertheless, in the case of concrete, due to the low viscosity of the aqueous solution, its low pressure-coefficient of viscosity and the rigidity of the suspended particles, in the rest of this thesis, high Sommerfeld number will only refer to the hydrodynamic regime (HD).

- As the Sommerfeld number decreases, the probability of direct contact between surface asperities becomes more significant. This usually corresponds to a film separation between surfaces of less than 3 times their typical roughness, $\sigma$. In this case the load is
carried by both the fluid and the asperities. This is an intermediate regime known as the mixed regime.

- When the Sommerfeld number and the film thickness between surfaces become even smaller (usually $h < \sigma/2$), the hydrodynamic lift becomes negligible and the load is entirely carried by the solid contacts between asperities. The coefficient of friction is then entirely controlled by the properties of the two surfaces (topography and physico-chemistry) and does not depend on $s$ anymore. This is referred to as the boundary lubrication regime (BL).

As it will be shown later (see Chapter 2), the particles can experience, depending on the shear, any of these three regimes. If the properties of the hydrodynamic regime with a Newtonian fluid are quite easy to describe, it is far more complicated to model the boundary regime, especially in the presence of an adsorbed polymer layer.
1.4 Tribology of comb polymer brushes

As we have seen in Section 1.2.3, the particles in dense cement slurries are usually covered by a thin layer of solvated polymer, called superplasticizer. This section describes the state of the art of the physics of comb polymers, which are commonly found in cement slurries, first in solution, secondly when adsorbed on surfaces. Finally, the consequences in terms of adhesion and friction in the boundary regime are detailed.

At each step, the physics of comb polymers is deduced from the physics of linear polymers, which is better understood.

1.4.1 Comb-polymer description

Superplasticizers are polymers that adsorb onto the cement grains due to their negative charge, reducing the grain-grain attraction because of their refractive-index matching with the solvent. Consequently, they improve the flowability of the cement slurry at low shear.

Here, we only address the case of the most recent superplasticizers. Since the 1980s a new generation of superplasticizers has been developed, in which the anchoring function and the index-matched spacer function are carried by different parts of the polymer. They are more efficient in terms of yield-stress reduction and, since they carry fewer calcium-binding groups, they interact less with the setting of the cement. These comb polymers are composed of two parts:

- a backbone, which carries the negative charges that will interact with the cement grains. They are usually polyacrylates, polymethacrylates or polymaleic acid. More rarely, the carboxylic groups can be substituted by sulfate or phosphate groups. The size of the backbones that are typically used is some tens of monomers.

- several non-charged side-chains, which confer the refractive-index-matched-spacer function. These almost always consist of polyethylene glycol (PEG) but can also be polypropylene glycol-polyethylene glycol copolymers with a typical size of a few kiloDaltons.

As before, the suspending solution is a salty alkaline solution that contains calcium ions. Thus the anchoring groups are totally dissociated
and the backbones carry a net negative charge.

### 1.4.2 Physics of comb polymers in bulk solution

#### Physics of linear polymers in bulk aqueous solution

In solution, a linear polymer tries to maximise its free energy under the following (entropic) constraints: the monomers are linked with each other and two monomers cannot be simultaneously in the same place. The enthalpic part of the free energy is linked with the solvent quality and the electrostatic interactions between charged groups.

For a neutral polymer, the polymer takes on a coil conformation (close to a self-avoiding random-walk), which is more or less swollen, depending of its short-range interactions with the solvent molecules compared to the interactions between monomers. This leads to a coil size, referred to as a radius of gyration, of:

\[
R_g \propto a_m n^{\nu_F}
\]  

(1.16)

where \(a_m\) is the size of a monomer and \(\nu_F\), the Flory parameter, which takes values between 1/3 for bad solvents and 2/3 for good solvents.

For charged linear polymers, the electrostatic repulsion between similar charges creates an additional rigidity. The prediction of the degree of this rigidity is still a debated issue. In order to provide orders of magnitude, the typical electrostatically-induced bending rigidity is given [155, 184], in the case of a distance between charges, \(d_q\) larger than a nanometre in aqueous solutions as:

\[
B_e \propto \frac{1}{32\pi N_A I d_q^3}
\]  

(1.17)

where, \(N_A\) is Avogadro’s number and \(I\) is the ionic strength of the solution. Nevertheless, for higher charge density it seems that the persistence length scales experimentally with \(I^{-1/2}\) [115, 123, 198], even if no theoretical formula has been obtained for this.

In the case of cement admixtures, the backbone of the comb polymer carries charge. The ionic strength of the solution surrounding cement is higher than 0.3 mol/L [214] and therefore the screening is so intense
that two neighbouring anchors essentially do not feel each other’s charge. Nevertheless, due to indirect effects of the ionic groups (e.g. the solvation of the ionic groups, the double layer forces), the charge of the polymer has a significant influence on its conformation. For fully deprotonated polyacrylic acid, the persistence length has been reported to be of the order of a few nanometres [115, 152, 198]. The electrostatic swelling effect is massively reduced when the ionic group is not directly on the backbone but connected to the backbone by a spacer [66].

**Physics of comb polymers in bulk solution**

The physics of a comb polymer is significantly different from that of linear polymers because the side chains can repel each other for entropic reasons and stretch the backbone, which may lose its flexibility as a result. Gay et al.[82] rationalised this problem by comparing the radius of gyration of each side chain with the radius of gyration of the backbone and the distance between the side chains. Some cases can be distinguished:
• When the side chains are short compared to their relative separation, the polymer behaviour is not significantly changed from that of a linear chain. This is known as the decorative chain regime (DC)

• When the side chains are long compared to the size of the backbone, the polymer takes a star conformation with the backbone as a core. Depending on the distance between each side chain, the backbone is stretched or not. These configurations are referred to as the stretched backbone star regime (SBS) and the flexible backbone star regime (FBS), respectively.

• When the side chains are long compared to their relative distance on the backbone but short compared to the size of the whole backbone, the polymer can be seen as blobs connected to each other, usually referred as a worm. Each blob behaves like star-like polymer (see above). Similarly, depending on the distance between each side chain, the backbone is stretched or not and the polymer conforms according to a flexible or a stretched backbone worm-like regime (FBW and SBW)

The configuration of the polymer in solution is important because it influences not only the physics of the solution but also the way in which polymers can adsorb onto a solid surface.

Most of the polymers that are used in cement slurries (and in the rest of the thesis) are in the worm-like regimes [74] according to Gay and Raphael’s model, but their backbone is additionally stretched by the effect of the charges, as previously described. The conformation of some PMAA-g-PEG polymers in a solution close to cement suspending fluid has been experimentally measured [25, 83] and corresponds to FBW chains of a few blobs with 3-5 nm radius.

1.4.3 Adsorption of comb polymers on solid surfaces

Driving forces

In the presence of solid surfaces, the comb polymer can adsorb onto the interface. The forces driving the adsorption are mainly of
two kinds: electrostatic and entropic. Hydrophobic interactions are a
common example of entropic forces [4, 12, 75, 124].

For salty aqueous solutions relevant to cement, the adsorption of the
comb polymers is driven by electrostatic attraction between oppositely
charged ions [72]. Indeed, cement particles are metal oxides and have
hydroxyl groups on their surface. These hydroxyl groups have an acid
activity leading to a pH-dependent surface charge. At such a high pH,
most of the particle surface is deprotonated and highly negatively charged.
This leads to the adsorption of a single calcium-ion layer onto the surface,
which therefore becomes positively charged [104]. The negative anchors
of the comb polymer can thus adsorb onto the calcium-covered surface.
For this reason, this anchoring process is commonly referred to as calcium
bridging.

Nevertheless, the role of entropy is not negligible. Indeed, in addition
to the obvious attraction between oppositely charged ions, when the
polymer adsorbs onto the solid surface, a large quantity of ions (and
subsequently water solvation molecule) that were previously trapped
in the Debye layers around the solid surface and around the polymer
ionic anchors, are released. This is entropically extremely favourable
and promotes adsorption. The entropic contribution to the adsorption
of PMAA-g-PEG often dominates over the electrostatic contribution
[54, 165].

Adsorption configuration and density

Once the adsorption process is complete, the polymer changes its
conformation due to the presence of the solid surface and due to the
presence of neighbouring polymer chains.

Conformation of linear end-anchored polymer chain. We start
with the simplest case, by reducing the comb-polymer to a single anchor
and a single chain.

In this case, the polymer can adopt different conformations depend-
ing of the grafting distance, \(d_g\), i.e. the distance between the anchoring
points of two neighbouring polymer chains and the relative affinity of the
polymer for the solvent and the solid surface. A balance will be achieved
between the chain entropy and the maximisation of the interactions with
the solid surface, the fluid, or the other polymer chains, depending of the relative affinity of the polymer for each of the three components.

In the dilute regime, i.e. when the grafting distance is large compared to the radius of gyration of the polymer \( d_g >> R_g \), the polymer spreads on the solid surface (pancake configuration) if it has less affinity for the solvent than for the surface or takes a mushroom-like configuration in the opposite case.

In the dense regime \( d_g < R_g \), the polymer starts interacting with its neighbours and forms, depending on the solvent quality, an entangled, non-solvated polymer layer at the surface (poor solvent) or a thicker layer of extended and solvated polymer chains (called a polymer brush) for a good solvent [52]. The brush-like regime is also characterised by a non-uniform density of polymer in the brush: the further away from the surface, the lower the density of polymer [10, 143].

For the specific case of the PEG chains in a salty alkaline solution, the affinity of the polymer for the salty alkaline solution is not really known, but it should take configurations that closely correspond to the good-solvent regime.

**Conformation of a comb-polymer.** The conformation of an absorbed comb-polymer is even more complex. Indeed, the distance between chains of the same polymer is constrained and the different parts of the polymer do not have the same behaviour. The charged backbone has a strong affinity (see Section 1.4.3) for the surface or, failing that, for the aqueous medium, and would take a pancake conformation. In contrast, the PEG chains, if not tethered, would energetically favour being in solution rather than at the solid interface. Depending of the polymer chain surface density, the comb polymer chains interact with each other by steric repulsion or not. These two regimes are respectively called brush and mushroom regimes by immediate extension of previous paragraph nomenclature even if their shape similarity is lost.
1.4.4 Repulsion & Friction

Repulsion

The compression of two polymer brush-coated surfaces against each other reduces the conformational freedom of each polymer chain and the polymer chains behave as entropic springs.

As written above, the precise elastic response of polymer brushes on cement grains is not fully known because their conformation is still poorly understood. Nevertheless, two approximations could be used.

On the one hand, they can be likened to end-anchored polymer chains in a good solvent with quite low grafting density ('grafting-to' techniques such as this never create brushes as dense as when the polymers are grown from the surface). In that case, the repulsive response, $F_r$, scales as follows [53]:

$$F_r \propto k_B T \frac{h_0}{d_g} \left( 7 \left( \frac{h}{2h_0} \right)^{-5/4} + 7 \left( \frac{h}{2h_0} \right)^{7/4} - 12 \right)$$  \hspace{1cm} (1.18)

where $h_0$ is the equilibrium thickness of each uncompressed brush and $h$ is the distance between the two surfaces.

On the other hand, Flatt et al. [74] have developed a model that extends Gay and Raphael’s model to adsorbed comb polymers. The adsorbed polymer is also seen as a series of blobs that are in a star-like regime. A strong assumption of this model is that these blobs are half spheres that implies that the surface is not crowded and would correspond more to a mushroom than a brush regime.

The size of the blob, which is also the thickness of the layer, is then given by:

$$R_c = \left( \frac{2^{3/2} (1 - 2 \nu_F)}{a_P} \frac{a_P}{a_N} \right)^{1/5} a_p P_s^{7/10} N_s^{-1/10}$$  \hspace{1cm} (1.19)

where $a_N$ and $a_P$ are the size of the backbone monomer and of the side-chain monomer, respectively, and $\nu_F$ is the Flory parameter. Moreover
the force between two approaching polymer-coated surfaces scale as:

\[
F_r \propto P_s^{-29/36} N_s^{-12/13} \left( \frac{5}{2^{1/3}} R_c^{2} \frac{h^{-1}}{2} \left( \frac{3h^{2} + 2^{8} R_c \left( \frac{R_c}{h} \right)^{1/3}}{3h} \right) \right) \tag{1.20}
\]

This formula efficiently fits AFM force-curve measurements for polycarboxylate-grafted PEG polymers.[74]

Friction

The friction between solvated polymer brushes has been reported to be extremely low [187]. On rough surfaces, they are commonly reported to be as low as $10^{-1}$ [150] and on model atomically-flat surfaces, they are even lower [187]. The friction coefficient has even been found to be virtually vanishing in the case of extremely well-solvated polyzwitterionic brushes in water [39].

The effective low friction of polymer brushes in a good solvent has been attributed to the entropic repulsion between the two brushes and the weak interpenetration of the brushes [117]. The entropic osmotic pressure supports the load and, because the chains are not entangled, the shear can take place in the plane between the two brushes, which is rich in water and consequently fairly fluid.

Moreover, these properties of polymer brushes are conserved for a long time because if any polymer is pulled out from the surface by shear, it (or another) polymer chain can desorb at the same spot from the solution. Such coatings are said to be self-healing [126].

Dependence on load  The very good lubricating properties are only valid for relatively low loads. At sufficiently high pressures, the polymer chains of the two brushes can interdigitate and begin dissipating severely [117]. This phenomenon is particularly strong in two cases: when the solvent is poor, promoting brush interdigitation [118] and when the brush monomers can bond to each other under pressure, such as the case of dextran brushes [174].

Dependence on solvent quality  The raison d’être for polymer brushes is that the polymer chains prefer being solvated than confronting other
polymer chains. Thus, when the quality of the solvent is reduced, the brushes swell less, the osmotic pressure is lower, and the effective friction increases. This phenomenon has been experimentally reported for a large variety of brushes [130, 146, 151, 153]. The affinity between the PEG chains and the salty alkaline solution that surrounds cement grains is poorly known but seems quite high.

**Dependence on surface roughness** The roughness of the substrate interferes with the brush lubricating properties when it has a length scale that is close to the size of the polymer chain. For example, it has been reported that the coefficient of friction increases significantly compared to that of the atomically flat case in the presence of silica nano-spheres with model roughness, providing its lengthscale is similar or smaller than the size of the adsorbed polymer [170].
1.5 Scope of the thesis

The creation of new concrete mixtures with lower carbon footprint is critical to control climate change but it also requires the use of very dense cement slurries. These cement slurries have a complex rheology and their flow is challenging to control. If the problem of yield stress has now been solved quite efficiently by the use of comb polymers grafted to the cement grain surface, the problem of shear thickening is still challenging, especially when it is discontinuous. Even if there exists no academic consensus on the physical cause of shear thickening, there is little doubt that the small gap between neighbouring particles plays a critical role. This has prompted us to understand the mechanics of two sliding solids in close contact in a lubricating aqueous salty solution, especially in the presence of comb polymers adsorbed onto the solid surface.

The main goal of this thesis is to understand the shear thickening of cement pastes and more generally of dense non-Brownian suspensions, in order to propose new ways to reduce it.

Since many experimental observations of continuous and discontinuous shear thickening on model system have been reported in the past, we decided to first propose an explanation that can rationalise these numerous observations and then test its validity on less-and-less model systems.

Thus, the rest of the thesis tries to provide a theoretical framework to explain the shear thickening by making a connection linking the local friction between grains and the macroscopic properties of the flow. The sufficiency of the model is then verified by computer simulations. Going toward industrial applications, the validity of our model is then tested for filler suspensions that mimick cement pastes and used to develop new admixtures for cement.

Chapter 2 describes the details of the physical parameters of the shear thickening of non-Brownian suspensions, and then describes our innovative framework that makes the link between the rheology of the non-Brownian suspensions and the tribological behaviour of a particle pair.

Chapter 3 is dedicated to a proof of our framework based on computer simulations. Based on a contact-dynamics algorithm, in collaboration with Roman Mani (CPEM-ETHZ), we developed a proof of
sufficiency of our model. These numerical-simulation results are the first that reproduce the three flow regimes (Nw, CST, DST) of this kind of suspension and the transition between them.

Chapter 4 makes the link to industrial systems and goes in the direction of real cement pastes. It shows that the same framework is also relevant to describe the shear thickening of quartz-filler suspensions. Moreover, based on our theoretical knowledge, a new compressive-rheology technique is introduced, which quantifies the volume fraction at which discontinuous shear thickening appears. This technique is then applied to scan a large variety of suspensions, including different powders, suspending solutions and adsorbed polymers, in order to understand how the existing admixtures could be improved to reduce shear thickening.

Finally, since the previous chapters concluded that the friction between the suspended particles was a key parameter of the rheological behaviour, Chapter 5 is dedicated to the measurement of particle-pair friction. Based on AFM, we developed a direct, precise and robust technique to measure the friction coefficient between two microspheres in the boundary lubrication regime.
Chapter 2

Theoretical Framework

The main goal of this thesis is to understand how shear thickening arises in dense, non-Brownian suspensions, and in particular how it can arise for very simple rheological systems consisting only of a liquid loaded with a high fraction of particles. Since many experimental observations of CST and DST have already been reported in the past century, we propose here a framework that can explain these observations.

In Section 2.1, the rheological system and the relevant physical parameters are carefully described. Then, from a physical interpretation of the dimensional and dimensionless parameters, cases where the flow is in Newtonian, CST and DST regimes are identified. In particular, we define a local Sommerfeld number that determines the transition from Newtonian to shear-thickening flows. We then show that the suspension volume fraction and the boundary-lubrication friction coefficient control the nature of the shear-thickening transition.

The proposed framework also leads to a new definition of confinement that unifies DST and impact-induced solidification. Finally, we offer some extensions of this framework to two cases of special interest: the yield rate of attractive dense suspensions and the Cates & Wyart’s model for shear thickening of repulsive suspensions.
The section 2.1 is based on my personal work, under the supervision of J. Cayer-Barrioz, N.D. Spencer and L. Isa., and is published as a part of Ref.[65]:

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M. Mosquet, H. Lombois-Burger, J. Cayer-Barrioz,
H. J. Herrmann, N.D. Spencer & L. Isa.

*Microscopic mechanism for shear thickening of non-Brownian suspensions*
2.1 Our framework

2.1.1 A limited list of ingredients

As described in Section 1.2.5, steady-state shear thickening can occur in any dense suspension of small, non-attractive grains [13]. It thus seems that only liquid and solid grains are required. This is already a short list of ingredients for building a framework. Nevertheless, the system can be even further simplified by identifying which properties of these two components are essential for inducing shear thickening and which are only of secondary interest.

The Liquid.

It has been proven by Brown [33] that no transition from a Newtonian to a ST regime is observed in absence of a suspending liquid, for example for dry granular media in air. Indeed, in this case, the dry granular media shear thickens at any shear and no Newtonian behaviour is observed [76]. The liquid is thus an essential part of our system.

This immediately introduces two quantities: the fluid density $\rho_f$ and its viscosity, $\eta_f$. Since shear thickening happens for suspensions in which the suspending fluid is Newtonian as well as non-Newtonian [13], considering non-Newtonian fluids in our model would only lead to unnecessary complexity: the suspending fluid is considered as a Newtonian liquid. The same argument is valid for the compressibility of the fluid, since shear thickening happens with water suspensions (such as cement slurries!) even if water is incompressible, incorporating the fluid compressibility in the model would only generate additional and
unnecessary complexity.

In brief, the fluid parameters are its viscosity, $\eta_f$ and its density, $\rho_f$ and, for the sake of simplicity, we can suppose that the fluid is incompressible and Newtonian.

The Particles.

This work is restricted to non-Brownian particle suspensions.

Suspensions of particles of various shapes and polydispersity can experience shear thickening. Nevertheless, since this phenomenon can also be observed with monodisperse sphere suspensions, taking into account shape and polydispersity parameters as necessary condition in our model would lead to a lack of generality. Then, the particles are characterised only by their radius, $R_p$ and their density, $\rho_p$.

Moreover, it has been observed that soft-particle suspensions, such as emulsions, cannot experience shear thickening. A certain rigidity of the particle is needed. Since the particles that were used in reported experiments [13][34], such as corn-starch or silica, do not significantly deform under the shear stress that is applied (no more than some kPa), the value of the deformation of the particle should not be a critical parameter for the observed phenomenology and the particles can be assumed to be perfectly rigid.

All real particles also have surface properties. They are in general solvo-philic (if not, they would attract each other, see next paragraph) and rough. As a first consequence, there is no significant slip at the particle-fluid interface. The roughness can be quantified by a typical length scale normalised by the size of the particle, $R_p\varepsilon_p$. Their contact interactions with another particle lead to the definition of a coefficient of friction in boundary lubrication, $\mu_0$ (see Section 1.3.2).

In several situations, it has been demonstrated that too strong an attraction between particles extends the first shear-thinning regime to higher and higher shear stress and can obscure the shear thickening [13, 31, 203]. Nevertheless, having small attractive or repulsive forces between particles does not seem to prevent or promote shear thickening [31]. In the well-known case of corn-starch suspensions, no attraction or repulsion between particles has been found [32]. We can conclude that no colloidal interaction between particles is needed to see shear thickening.
In brief, the particles’ parameters are: their radius, $R_p$, their density, $\rho_p$, their surface roughness, $\epsilon_p$, and their boundary coefficient of friction, $\mu_0$. For the sake of simplicity, we can additionally suppose that they are monodisperse rigid spheres, as long as this does not lead to a loss of generality.

**Solid-Liquid Ratio** The shear thickening of non-Brownian suspensions is always reported for dense suspensions, i.e., very high solid volume fractions (around 50% and above for monodisperse spheres). In contrast to dry granular media, in suspensions, the volumes of suspending fluid and of particles are fixed. Consequently, in the limit of rigid-boundary effects (see Section 2.1.4), the volume fraction is fixed. Moreover, at these high volume-fraction values, the particles can create a percolating network throughout the entire suspension volume, meaning that both solid and liquid phases can be continuous.

A dimensionless parameter is introduced, the particle volume fraction, $\phi$.

### 2.1.2 Dimensional analysis: The need for inertia

We have set the limiting list of parameters that can be used to build a model for shear thickening. A dimensional analysis of these parameters is then useful. There are only 7 dimensional parameters: $\eta_f$, $R_p$, $\rho_f$, $\rho_p$, as well as the shear stress $\tau$, the confining pressure $P$ and the shear rate $\dot{\gamma}$. This leads, following Buckingham’s theorem, to 4 dimensionless parameters. First comes the normalised density $\tilde{\rho}_p = \rho_p/\rho_f$, the macroscopic friction $\mu_{\text{macro}} = \tau/P$. Then, the viscous number [28] can be defined, as:

$$I_v = \frac{\eta_f \dot{\gamma}}{P}$$ (2.1)

The viscous number, $I_v$, is simply a macroscopic version of the Sommerfeld number (see Section 1.3.2). Indeed, in a contact between 2 particles, $s = \eta_f v_{\text{sliding}} R_p / F_N$. The sliding speed, $v_{\text{sliding}}$, scales, on a macroscopic scale, with $R_p \dot{\gamma}$ and the normal force in the contact, $F_N$, scales with $R_p^2 P$. The Sommerfeld number controls the sliding distance between particles, $h$, which should be compared to the typical
roughness of the surface, in order to determine whether the contact is in hydrodynamic or boundary lubrication. As explained in the Section 1.3.2, the transition from hydrodynamic to boundary lubrication is a continuous process (known as the mixed regime). For the sake of simplicity, we define a critical Sommerfeld number, \( s_c \), which sets the transition between a regime dominated by hydrodynamic friction and a regime dominated by boundary friction (see Fig. 2.2). This critical Sommerfeld number is an increasing function of the roughness \( \epsilon_p \).

Thus, \( I_v \) should be compared to \( s_c \) in order to have some insights on the nature of the contacts between micro-particles.

![Figure 2.2](image)

**Figure 2.2** – Definition of a critical Sommerfeld number that set the transition from hydrodynamically lubricated to boundary-lubricated contact.

Finally, a Stokes number [8] can be defined:

\[
\lambda = \frac{\sqrt{\rho_p \tau} R_p}{\eta_f}
\]

This parameter can be seen as the ratio between the time scale of the viscous flow \( \eta_f / \tau \) and the time scale of the dry (i.e., inertia-driven) granular media flow \( R_p \sqrt{\rho_p / \tau} \). Thus, \( \lambda \) quantifies how much the inertial forces are important compared to the viscous forces for a given shear.

The importance of inertia in shear thickening is a hotly debated issue. In most experiments, the Reynolds number of the particles, \( Re_p = \frac{\rho_p R^2 \dot{\gamma}}{\eta_f} \), is less than 1, and in this case inertia is often presented as irrelevant.
Nevertheless, to the best of our knowledge, there is no proof that $Re_p$ is the most relevant quantifier of particle-inertia influence on the macroscopic scale (e.g., $\lambda$ is also a pertinent candidate as proposed by Ref.[8]) and there is even less proof that the transition between viscous and inertial flow happens at $Re_p = 1$ [113]. Care should be taken not to be misled by the formal similarity between $Re_p$ and the fluid Reynolds number, $Ref = \frac{\rho_f L^2 \dot{\gamma}}{\eta_f}$ (with $L$ the typical length scale of the flow), which is known to quantify inertial phenomena in Newtonian fluid flows and for which the critical values are well defined.

As previously noted by several authors [28, 179, 211], if inertia is disregarded (i.e., $\lambda << 1$ for any shear), the system does not have any shear-independent time scale or stress scale and thus $I_v$ as well as all the other parameters must be shear-rate independent. Consequently, because the occurrence of shear thickening is shear-rate-dependent, the inertia has to be taken into account in our framework.

### 2.1.3 Shear-dependent $\phi_{max}$ and the 3 flow regimes

#### Limit regimes

The behaviour of the suspension in the limit of infinitely low and infinitely high shear is easily recovered in a framework very close to that proposed by Bagnold [11].

At sufficiently low shear, inertial effects are totally absent. As previously stated, because there is no intrinsic timescale in the system, any dimensionless number in this regime is shear-rate independent. In particular, the relative viscosity, which is the ratio of the apparent viscosity of the fluid to the viscosity of the suspending fluid: $\eta/\eta_f$, is constant and the regime is Newtonian. For a long time, it was accepted that, in this regime, the vast majority of particle sliding contacts is hydrodynamically lubricated. This has been more debated recently [163, 199] and it seems that some solid contacts could exist. The viscosity in this regime depends only on the volume fraction and diverges at a specific jamming volume fraction $\phi_{max}^{NW}$. Several simulations and experiments report that the jamming volume fraction is close to that of random close packing, $\phi_{max}^{NW} \approx \phi_{RCP}$ [157, 176].

At infinitely high shear, inertia dominates and the suspension
behaves like dry granular media, exhibiting a so-called Bagnoldian regime. Dense granular flows with a fixed volume fraction follow a quadratic scaling of the normal and shear stresses, \( P \) and \( \tau \), with the shear rate \( \dot{\gamma} \) (so called Bagnold scaling) through a volume-fraction-dependent factor \cite{11}; this implies that the apparent viscosity rises linearly with \( \dot{\gamma} \) and that the system shear thickens continuously. This scaling can be expressed in terms of a dimensionless parameter, the inertial number \( I = \dot{\gamma}R_p\sqrt{\rho_p/\tau} \) \cite{76}, which is the ratio of the timescale of the flow, \( \dot{\gamma}^{-1} \), to the timescale of the dry granular media \( R_p\sqrt{\rho_p/\tau} \), which is the only shear-independent timescale in the system in the absence of viscosity. By the way, \( I \) could have been equivalently defined using \( \tau \) instead of \( P \) since both scale with each other. Here, we just follow the most commonly used convention. Using the set of dimensionless numbers defined previously, \( I \) can also be written as \( I = \lambda I_v/\sqrt{\mu_{macro}}. \)

Since there is only one shear-independent timescale in the system, \( I \) is shear-independent and only depends on the volume fraction, \( \phi \), and the BL local coefficient of friction, \( \mu_0 \), for rigid particles \cite{76}. It is actually a decreasing function of both \( \mu \) and \( \phi \). Moreover, since \( s \propto \eta_f\dot{\gamma}/P \) and \( P = \dot{\gamma}^2R_p^2\rho_p/I^2 \), the Sommerfeld number in the inertia-driven regime can be expressed as \( s \propto \eta_fI^2/\dot{\gamma}\rho_pR_p^2 \). This shows that at high shear rate, \( s \) is really small and it can be supposed that all the contacts in this regime are in boundary lubrication. This new regime where BL contacts dominate is also associated to another jamming volume fraction at which the viscosity diverges, \( \phi_{max}^{BL}(\mu_0) \), which is a decreasing function of the BL coefficient of friction \cite{41, 182}. Some values from Ref.\cite{182} are shown in Fig. 2.3. It follows that \( \phi_{RCP} \approx \phi_{max}^{NW} \geq \phi_{max}^{BL}(\mu_0) \).
Transition Newtonian - Shear Thickening

Quantifying the transition from a Newtonian regime to the inertia-driven regime requires setting a transition criterion. Here, we define it as the minimal speed at which a Bagnoldian regime with BL contacts is stable.

Assuming that the system is in this regime, the definition of $s$ leads to $s \propto \eta_f I^2 / \dot{\gamma}_p R_p^2$. Thus the Bagnold (CST) regime with BL contacts is possible as long as $\dot{\gamma}$ is larger than a critical shear rate:

$$\dot{\gamma}_c \propto \frac{\eta_f I^2}{s_c \rho_p R_p^2}$$

showing the link between $\dot{\gamma}_c$ and $s_c$ when particle contacts dominate. This transition was partially proposed, with macroscopic arguments, by Bagnold [11, 199]. Nevertheless, our microscopic analysis also accounts for volume fraction and roughness effects through the explicit inclusion of the inertial and the Sommerfeld numbers.

Discontinuous ST: The third regime

A main consequence arises from the fact that there are two different jamming volume fractions: this constitutes the major innovation of
our framework. Indeed, when \( \phi \leq \phi_{BL \max} \leq \phi_{NW \max} \), the transition from hydrodynamic to boundary-dominated flow is possible and the suspension exhibits CST, as reported above and predicted by Bagnold.

In contrast, when \( \phi_{BL \max} < \phi \leq \phi_{NW \max} \), the transition to a Bagnold regime is forbidden, and the shear rate cannot exceed \( \gamma_c \), which then appears as the maximum allowed shear rate for the system. In other words, the system undergoes DST. This situation is true as long as \( \phi_{BL \max} < \phi \leq \phi_{NW \max} \), so the DST is divergent (dDST). Since \( \phi_{BL \max} \) is the critical volume fraction for DST, it can be tuned by changing the particle BL friction coefficient. In this thesis, we will explore in detail the link between DST and BL friction.

![Figure 2.4](image)

**Figure 2.4** – \( (\phi; \dot{\gamma}) \) state diagram. On the right, two examples of flow curves for (green) a continuous shear thickening suspension and (orange) a discontinuous shear-thickening suspension.

### 2.1.4 A fixed volume-fraction framework

A significant characteristic of our framework is that it never refers to a need for stiff suspension boundaries, so called confinement, as some other authors have found necessary [33]. The only conditions that are required are a shear condition, \( \dot{\gamma} \geq \dot{\gamma}_c \), and a fixed-volume-fraction condition. This section explains why in steady-state rheology, our fixed volume-fraction condition is equivalent to confinement.

**Steady-state shear thickening requires confinement.** In a steady-state rheology experiment, the fluid is sheared for a long time in a con-
stant way and only the stable regimes are studied. Brown et al. [33] noticed the key existence of an upper stress boundary in steady-state shear-thickening flows, \( \tau_{\text{max}} \). It corresponds to the highest achievable stress in that regime before the fluid enters into a shear-thinning regime. In his experiments and in a very large set of other published rheology data, \( \tau_{\text{max}} \) scales with the stiffness of the boundaries of the suspension. For example in the ordinary case in which the sheared suspension has a free interface with the ambient air, \( \tau_{\text{max}} \approx 0.1 \gamma_{\text{surf}}/R_p \) with \( \gamma_{\text{surf}} \) the liquid-air surface tension, i.e. the pressure that is required for a particle to indent the interface. This correlation between shear at \( \tau_{\text{max}} \) and deformation of the air-fluid interface can even be observed with the naked eye (e.g., in Ref. [33]). The extension of this scaling to solid boundaries is straightforward using the Hertz indentation formula (see Section 1.3.1).

**Interpretation of \( \tau_{\text{max}} \) in term of fixed-\( \phi \).** As explained before, in the ST regime the suspension also dilates: the granular network applies a positive pressure to the boundary (see Section 1.2.5). If the boundaries are stiff enough, i.e. \( \tau < \tau_{\text{max}} \), they do not deform and the volume fraction remains constant. The fluid still behaves like volume-fraction-controlled granular media and ST continues forever. In particular, if \( \phi \geq \phi_{\text{max}}^{BL} \) DST can continue forever.

If the shear stress is increased above \( \tau_{\text{max}} \), the particles start to indent the boundary, the volume fraction of the suspension is reduced and the volume fraction condition is no longer fulfilled. In that case, the fluid no longer behaves like volume-fraction controlled dry granular media, but like pressure-controlled dry granular media. The confining pressure, \( P \) is then fixed by the stiffness of the boundary. Moreover, in this kind of fluid, the macroscopic coefficient of friction is almost constant, i.e., \( \tau \propto P \) [76]. Consequently, in the case of the liquid-air interface, \( \tau_{\text{max}} \) is sufficient to make the fluid flow at any speed greater than \( \hat{\gamma}_c \). The suspension enters a plastic regime. Or in other words, because the apparent viscosity \( \eta \) scales with \( \hat{\gamma}^{-1} \), the fluid enters into a shear-thinning regime.

*In brief, in the case of steady-state shear, confinement of the suspension is required because it leads to a fixed volume fraction. Moreover, our framework explains the existence and the value of \( \tau_{\text{max}} \) and of the following shear-thinning regime that is experimentally reported.*
2.2 Generalisation of the framework

As mentioned in Section 2.1.1, our framework addresses the steady-state flow of non-interacting particle suspensions. These conditions can be relaxed in order to describe other phenomena within the same framework. First, in the case of transient flow, our model predicts the possibility of transient DST in the absence of confinement, which corresponds precisely to some experimental observations. Secondly, if the particles are repulsive or attractive, some other steady-state DST-like phenomenon can also occur at low shear and without inertia. These phenomena have been described independently by Cates et al. [211] for repulsive particles and by us for attractive particles (such as cement grains). Both are slightly out the scope of this PhD thesis but show the potential of a Sommerfeld-number-based rheology for a large range of suspensions.

2.2.1 Transient shear thickening in the absence of confinement

There are some experiments [162, 200, 205] in which the solid-like behaviour of a corn-starch suspension has been observed, and the confinement does not seem to be critical. For example, many videos show people running on pools filled with corn-starch suspensions. These effects are clearly not following the same confinement scaling than the steady state flow rheology. Indeed, first, the runner applies an additional stress on the suspension that is around 40 kPa [34] when, according to Ref. [33], \( \tau_{\text{max}} \approx 1 \) kPa. Consequently, the runner should sink. Even more convincingly, Waitukaitis et al. [205] reported that a similar cornstarch suspension under impact becomes locally solid-like (phenomenon they called impact-induced solidification), even if the boundary is arbitrarily far or if the boundary stiffness is set to zero.

For this reason, some authors [205] have defined this phenomenon as a new one, and different from DST, calling it impact-induced solidification and for this they have developed an independent theory. We show, here, that this transient phenomenon can be described in exactly the same framework as steady-state DST.

In order to connect this phenomenon with the previously described
DST regime, we will show that a dense suspension, which would experience DST at high shear (i.e., $\phi \geq \phi_{BL}^{max}$) will also, and for the same reasons, experience a transient solidification upon a solid impact to its surface.

Indeed, at the exact moment of the impact, the shear conditions for the DST are fulfilled if the impact is really fast and leads to a high shear in the surrounding fluid ($\dot{\gamma} = \dot{\gamma}_c$); and providing the local volume fraction is high enough ($\phi \geq \phi_{BL}^{max}$). Under such shear, in the long term, the granular media will dilate and, since it is surrounded by un-sheared suspension (i.e., no boundary), the particles will migrate to the un-sheared regions, leading to the local reduction of volume fraction. But this migration of particles will take some time. The typical timescale for particle migration in granular media is actually $\dot{\gamma}^{-1}$ [63], i.e., the same timescale as the excitation. Consequently, for a brief instant between the impact and the moment when the granular network is locally expanded, $\phi \geq \phi_{BL}^{max}$ and the system experiences DST. DST is a dynamic jamming process, and as quantified directly in Ref.[19] and indirectly in Refs.[132, 201, 202], a fluid in the DST regime needs at least some fractions of second to relax. Thus, when the impactor shocks the fluid, the first layer of the fluid in front of the impactor dynamically jams and imposes a high shear to the next layer, which also jams. Thus, at the beginning of the phenomenon, the impactor experiences a negative acceleration arising from this added mass [145, 205]. If the relaxation time is long enough (e.g., $\phi$ is high enough according to [19]), the solidified region can extend from the impactor to the lower solid boundary of the tank, and this short-lived solid column can sustain almost any compressive load (in the limit of the stiffness of the particles) and in particular, the weight of the runner. This scenario is in agreement with the measurement of a solidification wave under the impactor, as observed in Refs.[145, 162, 205].

Thus, because our framework does not requires any stiff suspension boundaries, but only a fixed volume fraction, it can also describe impact-induced solidification, which appears to be none other than a transient DST.
2.2.2 Repulsive Particles

The proposed framework is only valid for particles that are sufficiently large to be non-Brownian and for which inertia dominates over viscous forces at realistic high shear. This is not the case for small particles, such as the silica nano-sphere slurries that are commonly used as model shear-thickening fluids [15, 110, 181]. Cates and Wyart [211], based on a simulation work from Seto et al. [136, 179], proposed extending the idea of a shear-rate-dependent jamming volume fraction due to the creation of BL contacts to any suspension of repulsive particles, including Brownian ones.

Cates’ model is in fact a mixture of the Hydroclusters theory (because it deals with the balance between a repulsive force and the viscous forces) and of our frictional framework (because it includes a HD/BL transition).

In brief, it assumes that the initial state is a dense suspension of colloidal particles, which interact with a short-range finite repulsive force $F^* = R_p^2 P^*$, which could be a double layer or Brownian force. At low shear stress, this repulsive force prevents any close contact between the particles, which would have been highly dissipative. In other words, in this case, the Sommerfeld number and the viscous number should scale as

$$ s \propto I_v \propto \frac{\eta \dot{\gamma}}{(P - P^*)} $$

(2.4)

Thus, at sufficiently small shear stress, all the contacts are hydrodynamically lubricated. As the shear stress is increased, the relative impact of the repulsive force is lowered. Indeed in a viscous regime $P \propto \tau$ [28]. At high shear stress, the system behaves as if there were no repulsive forces. If the volume fraction is high enough (as explained in Section 1.2.4) some of the contacts in the suspension could be boundary lubricated (even if the regime is still Newtonian) and this would lead to a higher dissipation and a higher apparent viscosity than at low shear. This model thus introduces a critical shear stress, $\tau^*$, which scales with $P^*$, at which the transition occurs from a purely hydrodynamically-lubricated regime to a regime in which some BL contacts are present. Similarly to our model, this higher dissipation is quantified by a lower jamming volume fraction. At low shear, Cates and Wyart forecast a maximum
volume fraction of $\phi_{RCP}$ and at higher shear, due to additional frictional contacts, the maximum volume fraction is $\phi_{RCP}^{max}(\mu_0) < \phi_{RCP}$.

Thus, in this model, shear thickening is seen as a transition between two Newtonian regimes of different viscosities and can be of 3 different kinds:

- if $\phi_{RCP} > \phi > \phi_{max}^{Nw}(\mu_0)$, the fluid experiences a divergent discontinuous shear thickening (dDST) at $\tau = \tau^*$.

- if $\phi \leq \phi_{max}^{Nw}(\mu_0)$, the fluid can flow at high speed and at this speed it experiences a Newtonian regime. Depending on the difference of viscosity between the two regimes and the parameters of the transition, this transition can be continuous (CST) or have an inflection point (sDST).

One can notice here a slight discrepancy between this model and our framework in the dependence of $\phi_{RCP}^{Nw}$ with the boundary coefficient of friction, $\mu_0$. The two models can be simultaneously true only if, for $\mu_0 \neq 0$:

$$\phi_{RCP} > \phi_{max}^{Nw}(\mu_0) > \phi_{max}^{BL}(\mu_0) \quad (2.5)$$

It is compatible with the fact that the behaviours of inertia-driven and viscous-driven flow of frictional spheres close to jamming differ in both nature and in scaling ([55] for theory and review). Nevertheless, significant work is still needed to predict more precisely the value of the jamming volume fraction of frictional rough suspensions in different regimes. The simulation presented in Section 3 constitutes a contribution in this direction that innovates in the way in which lubrication forces are modelled.

### 2.2.3 Attractive Particles

Simultaneously to Cates and Wyart, we developed a symmetrical model that applies to particles that attract each other, e.g. because of attractive interactions or because of collective confining pressure (e.g. density mismatch). This extension has specifically been developed to explain the phenomenon of yield rate that has been observed by Fall et al. [61] in cornstarch DST suspensions.
Thanks to an MRI-rheometer, Fall et al. observed not only the macroscopic behaviour of a DST cornstarch suspension but also its local behaviour. They reported that this suspension shows not only a yield stress but also a yield rate, i.e. a finite shear rate below which no flow seems to be possible. In their case \( \dot{\gamma}_{\text{min}} \approx 0.2 \text{s}^{-1} \), i.e. significantly more than their detection yield [61]. The existence of such a yield rate is, on the macro-scale, a lot more discrete than the existence of a maximum shear rate. Indeed, on the macro-scale, the fluid can flow at arbitrary small shear rates, if \( \dot{\gamma}_{\text{macro}} < \dot{\gamma}_{\text{min}} \), the flow becomes localised: a part of the fluid flows at \( \dot{\gamma}_{\text{min}} \) and the other part stays at rest. This localisation is only detectable by local measurements and hardly detectable on macro-scale flow curves.

This behaviour could be explained by a bifurcation model developed by Coussot for thixotropic fluids [46, 47], i.e. by incorporating a structuration timescale (see Section 1.2.3). Here, we propose a model that does not requires another timescale. Similarly to the previous section, we model the attractive force by setting \( P^* < 0 \) in Eq.2.5. Then at low shear, all the particle contacts are in the BL regime and at high shear some of them become hydrodynamically lubricated. Since in the case that Fall studied, the suspension is shear thickening discontinuously, it is probable that the suspension has an infinite viscosity in the low-shear/BL contact regime. This then sets a minimum local shear \( \dot{\gamma}_{\text{min}} \propto -P^*/\eta \).

This framework would additionally explain why in the same setup, the CST suspensions do not have any yield rate, even if they have a yield stress [60, 102]. Indeed in this last case, the low shear-BL contact regime can flow.

This point of view has to be challenged and its pertinence will have to be compared, using more local rheology data, with other existing yield rate suspension models [46, 47].
2.3 Conclusion

By carefully analysing the components and the physics of dense non-Brownian suspensions, we have identified the origin of both their continuous and discontinuous shear thickening as the consequence of the transition from a viscous-lubricated regime to an inertia-driven regime, as proposed by Bagnold.

Adding the concept of roughness to Bagnold’s original theory, we also identify that the modification of the driving force has important microscopic consequences. Indeed, in the viscous-driven regime, the sheared contacts are mainly hydrodynamically lubricated, whereas all the contacts are boundary-lubricated in the inertial shear-thickening regime. This difference in the lubrication regimes implies that the jamming volume fractions in the viscous regime $\phi_{max}^{NW}$ and in the Bagnoldian regime $\phi_{max}^{BL}(\mu_0)$ are not the same in general, the second being a decreasing function of the boundary lubrication coefficient of friction. Therefore two shear-thickening regimes can be distinguished. CST is found when $\phi_{max}^{NW} \geq \phi_{max}^{BL}(\mu_0) \geq \phi$ i.e. the suspension can flow in both regimes, while the suspension exhibits DST when the transition to the inertial regime is impossible because $\phi_{max}^{NW} \geq \phi > \phi_{max}^{BL}(\mu_0)$. Thus, in the absence of transient migration effects [63], the local volume fraction and friction coefficient determine the stable microscopic flow mechanism, which is either CST or DST [60, 61, 63].

Moreover, our model does not require any mechanical confinement at the boundaries to see shear thickening and can then reunify DST and impact-induced solidification. Finally, we showed how the concept of shear-dependent jamming volume fraction could be generalized to the low-shear behaviour of attractive and repulsive particles.
Chapter 3

Proof of Sufficiency by Computer Simulation

The previous chapter proposed a theoretical framework to describe and understand the shear thickening of suspensions. As often in soft-matter physics, the theoretical development proposed, involves assumptions, scaling laws and macroscopic averaging to make the link between the microscopic (local contacts) and the macroscopic (suspension flow) scales. This represents a potential theoretical weakness. The first step in the framework validation is thus to confirm that the simple set of ingredients defined in Chapter 2, is sufficient to describe and predict the rheological behaviour of non-Brownian suspensions.

Bringing microscopic and macroscopic scales together implies resolving the interdependent mechanical behaviour of a large collection of particles and is only possible with the help of computers. Section 3.1 explains the reason for choosing a contact dynamics algorithm from the large variety of computer-simulation algorithms and Section 3.2 explores its relevant features, in terms of implementation. In Section 3.3 & 3.4, the exact simulation conditions as well as the particle contact law are set and the greatest care is taken to involve only the simple set of ingredients defined in Chapter 2. Finally, in Section 3.5, exploring a wide range of shear, particle properties and volume fraction, we show that our framework indeed reproduces the rheological behaviour of dense non-Brownian suspensions, in terms of the Newtonian, continuous-shear-thickening and discontinuous-shear-thickening flow regimes, as well as the transitions between them.
This chapter is based on Ref. [65]:

N. Fernandez, R. Mani, D. Rinaldi, D. Kadau,
M. Mosquet, H. Lombois-Burger, J. Cayer-Barrioz,
H. J. Herrmann, N.D. Spencer & L. Isa.

*Microscopic mechanism for shear thickening of non-Brownian suspensions*


The two-scale modelling and the contact law are my contribution under the supervision of J. Cayer-Barrioz, N.D. Spencer and L. Isa. The simulations have been performed by R. Mani from CPEM (IFB-ETHZ) under the supervision of D. Kadau and H. Herrmann. The discussion and the physical interpretation were a common task.
3.1 Why contact dynamics simulation?

Besides resolving complex system behaviour, one of the advantages of computer simulation is that one can include only the desired physical phenomena, simplifying the problem to the key components. In our case, we are using it in order to demonstrate that the few ingredients of our theory (rigid particles, fixed volume fraction, lubricated contact law and particle inertia) are sufficient, in the logical sense of the word, to lead to shear thickening.

The most direct simulation would have been to use the Stokes law to directly describe the fluid around the particles, and to explicitly describe the roughness on the surface of the particles. Nevertheless, in terms of computation time, it is hardly possible. A precise description of the flow in the contact requires a very fine mesh because the zone of contact is extremely narrow, while at the same time, the description of the overall suspension rheology requires dealing with many-orders-of-magnitude larger volumes. Large volumes and fine meshes cannot work together.

Another option could have been to use one of the numerous molecular-dynamics methods [49]. In these algorithms, the viscous interactions are fairly well described. However, the contact forces are calculated explicitly as a function of the particle indentation. This introduces a coupling between forces and position and leads to a sharp divergence of the computing power as the granular media gets denser and the particles get stiffer. Since dense suspensions of rigid particles are precisely the object of our study, Molecular Dynamics is not the appropriate tool.

We finally decided to use a contact-dynamics algorithm [96, 107, 144] to simulate our granular media because it is especially designed to describe the case of infinitely rigid particles. Originally developed for dry granular media, this technique allows attraction and repulsion in the normal direction to be taken into account, as well as the tangential frictional forces between contacting rigid spheres.

Nevertheless, the hydrodynamic interactions are usually not included in contact-dynamics algorithms and we had to implement them by ourselves. Because most of the viscous dissipation appears in the nanometric gap between two neighbouring grains [78, 199], the problem can be split into two separated, spatial scales. On the larger scale, our suspension is a collection of rigid grains at a fixed volume fraction,
that are in contact or not, and that can be simulated according to a granular-media-simulation technique. On the smaller scale, in each contact, according to the local mechanical stresses, we can calculate the viscous and the frictional dissipation using a simplified Strubeck curve, which affects the granular media behaviour on the larger scale.
3.2 Principles of contact dynamics simulation

This section gives a quick overview of the contact-dynamics algorithm structure.

3.2.1 Newton’s Laws

Each particle follows 2nd Newton’s law, \( m\ddot{x} = \sum \vec{F}_i \) with \( m \) the mass of the particle and \( \vec{F}_i \) the forces applied to it. This equation is discretized in time into steps of duration \( \Delta t \). Thus for the time step \( (t + 1) \), one has:

\[
\begin{align*}
\vec{v}_{t+1} &= \vec{v}_t + \frac{\Delta t}{m} \sum \vec{F}_i^{t+1} \\
\vec{x}_{t+1} &= \vec{x}_t + \Delta t \vec{v}_{t+1}
\end{align*}
\]

(3.1) (3.2)

3.2.2 Contact Force Laws

The contact force is divided into its normal, \( F_N \), and its tangential component, \( F_T \). The dependence of \( F_N \) with the distance between particles is straightforward because the simulations avoid any overlap (see Fig. 3.1). The tangential force can follow a Coulombic law (as in the figure) or a more complex law (see Section 3.4.4).

![Figure 3.1 – (left) Normal force law. (right) Tangential force law in the case of Coulombic friction](image-url)
3.2.3 Contact Force Calculation

In short, if, due to the action of other forces, between the time step $t$ and the time step $(t + 1)$, the particles 1 and 2 tend to overlap, these two particles are considered in contact at the time step $(t + 1)$ and a repulsive normal contact force is created. Its value is set to exactly prevent any overlap:

$$F_{N_{t+1}}^{1 \rightarrow 2} = \frac{m_1 m_2}{m_1 + m_2} \frac{-d_{t}^{12} - \Delta t \, v_{t+1}^{12(free)}}{\Delta t^2}$$

with $d_{t}^{12}$ the distance between the particles at the time $t$ and $v_{t+1}^{12(free)}$ the relative speed of the particle 1 compared to that of the particle 2 if this contact force would not exist.

Regarding the tangential force, if $\sum_i \vec{F}_i.\vec{e}_T \leq \mu F_{N_{t+1}}^{1 \rightarrow 2}$, the particles should not slide and we set $F_{T_{t+1}}^{1 \rightarrow 2} = \sum_i \vec{F}_i$. If not, we set $F_{T_{t+1}}^{1 \rightarrow 2} = \mu F_{N_{t+1}}^{1 \rightarrow 2}$ and the particles slide on each other.

3.2.4 Algorithm implementation

As mentioned above, the forces in each contact depend on the forces in the other contacts. The determination of all the forces could have been achieved by solving a massive system of equations. In our implementation they are determined by iterative approximations: at each time step, the whole network of contacts is randomly swept in order to determine locally an approximation of the normal (with Eq.3.3) and then the tangential forces. The determination of the contact forces is then improved by iteration.

One can prove that the number of iterations for a single time step should scale with the square of the typical size of the system. Indeed, at each iteration, the information about one contact “diffuses” in the network of contacts; as in any diffusion process, the relevant time scale scales with the square of the relevant length scale. However, in practice, a convergence criterion is set and the iteration process is stopped when the change in the contact forces (normalised by their average) complies with this criterion.
3.3 Simulation conditions

We simulate stress-controlled, simple shear. The choice of a stress-controlled shear, compared to a rate-controlled shear, was both technically simpler and more relevant for observing DST that, by definition, corresponds to the existence of a continuum of possible viscosities for a single shear rate. The system is confined between moving and fixed rough walls (obtained by randomly glued particles) at a constant volume fraction [121, 160].

3.3.1 Shear box

The rectangular simulation box dimensions are \((L_x, L_y, L_z) = (25R, 10R, 27R)\), where \(L_z\) is the distance between the two walls and \(R\) the radius of the largest particle in the simulations. We use periodic boundary conditions in both \(x\) and \(y\) directions. The presence of hard confinement mimics experimental conditions. In order to confirm the role of the confinement, some simulations with Lees-Edwards boundary conditions, which are periodic in the three directions, have also been performed (see Section 3.5.4).

3.3.2 Granular media preparation

The granular media consist of a collection of particle whose radii are uniformly distributed between 0.8\(R\) and \(R\) to prevent crystallisation. At the beginning of the simulation, the right number of particles is created, in order to achieve the targeted volume fraction. They are glued randomly to the walls or positioned randomly in the shear box. In order to prevent any overlap at the beginning of the simulation, a repulsive force (proportional to the overlap) is introduced in each contact, the friction is switched off, and the system is left unsheared to relax until no overlap is measured.

3.3.3 Shear onset

Then a shear stress \(\tau\) is applied in the \(x\)-direction via a constant force on the wall, given by \(F_x = \tau L_x L_y\). The granular media starts
flowing and finally reaches a steady state that is characterised by a linear-flow profile. We then measure the time averaged velocity of the moving wall \( \langle v_{\text{wall}} \rangle \), thus \( \dot{\gamma} = \langle v_{\text{wall}} \rangle / L_z \) and the apparent viscosity of the suspension \( \eta \) is given by \( \tau / \dot{\gamma} \).

### 3.3.4 Dimensional analysis

When fixing \( \phi, \mu_0, R, \rho_p \) and \( s_c \), the physics of the system is characterised by a single dimensionless number, the Stokes’ number:

\[
\lambda = \frac{\sqrt{\tau \rho_p R}}{\eta_f}
\]  

(3.4)

As stated previously, \( \lambda \) can be understood as the ratio between the microscopic time scale of the lubricating fluid, \( \eta_f / \tau \), and of the granular medium, \( R \sqrt{\rho_p / \tau} \) \cite{76}. Increasing the shear stress \( \tau \) quadratically is equivalent to decreasing \( \eta_f \) linearly, which is why, in our simulations, we vary \( \eta_f \) and keep \( \tau \) fixed.

### 3.3.5 Parameter normalisation

The time scale of the problem is set by \( [T] = \sqrt{\rho_p / \tau R} \) and thus, we can introduce the dimensionless shear rate \( \dot{\gamma} \), velocity \( \tilde{v} \) and load \( \tilde{N} \) via

\[
\dot{\gamma} = \tilde{\dot{\gamma}} \frac{\sqrt{\tau / \rho_p}}{R} = \tilde{\dot{\gamma}} \lambda \frac{\eta_f}{\rho_p R^2}
\]  

(3.5)

\[
v = \tilde{v} \sqrt{\frac{\tau}{\rho_p}}
\]  

(3.6)

\[
N = \tilde{N} \tau R^2
\]  

(3.7)

The Sommerfeld number can be expressed as

\[
s = \eta_f \frac{vr}{\tilde{N}} = \eta_f \frac{\tilde{v}r}{\tilde{N} \sqrt{\rho_p \tau} R^2} = \frac{\tilde{v}r}{\tilde{N} R \lambda} = \tilde{\tilde{v}} \frac{\tilde{N}}{\tilde{N}} \lambda^{-1}
\]  

(3.8)

where \( r = \tilde{r} R \) is the normalised particle radius. For unequal spheres, we assume that we can replace \( r \) by the average radius \( 2r_c^{-1} = r_1^{-1} + r_2^{-1} \)
such that

\[ s = \tilde{r}_c \frac{\tilde{v}}{N} \lambda^{-1} \]  \hspace{1cm} (3.9)

Here, we readily see that for fixed $\phi, \mu_0, s_c$ the only control parameter is $\lambda$. In our simulations, we varied $\lambda$ to obtain $\tilde{\gamma}$ as the simulation output. From Eq.3.4 the stress $\tau$ is obtained via $\tau = \lambda^2 \tilde{\eta}^2/(\rho R^2)$ such that the apparent viscosity is given by

\[ \eta = \tilde{\gamma} = \frac{\lambda}{\tilde{\gamma}} \tilde{\eta} \]  \hspace{1cm} (3.10)

The quantities $\dot{\gamma}$, $\tau$ and $\eta$ are measured in units of $\eta_f/\rho_p R^2$, $\tilde{\eta}_f^2/\rho_p R^2$ and $\eta_f$.
3.4 Contact law

To determine the dissipation when two particles are in contact, we assume that the fluid layers between them are very thin compared to the particle radius and of the same order of magnitude as the amplitude of their surface roughness. This assumption permits us to create a local friction law that takes into account the lubrication effect of the suspending fluid in a simplified form of the well-known Strubeck curve (see Section 1.3.2 for details).

3.4.1 No mixed regime

A typical Strubeck curve shows two main lubrication regimes separated by a “mixed” zone: a boundary lubrication (BL) regime where the asperities on the two sliding surfaces are in contact and bear the load for low Sommerfeld numbers (i.e. \( s < s_c \)) and a hydrodynamically lubricated (HD) regime where energy dissipation emerges from the shear of the separating viscous fluid film for high Sommerfeld numbers (i.e. \( s \geq s_c \)). For the sake of simplicity, because we are looking for a proof of sufficiency and in order to minimise the number of parameters, the mixed regime is neglected. Moreover only one dissipative mechanism, either BL or HD, is taken into account in each contact. This constitutes the simplest physical description of a lubricated contact.

3.4.2 Boundary-lubrication regime

Implementing boundary lubrication is straightforward in simulations, since the boundary lubrication between two rough particles can be well described using Amontons-Coulomb friction, i.e. the coefficient of friction \( \mu_0 \) being independent of the load, the speed and the apparent contact area [188]. The novelty in our simulations is the implementation of the hydrodynamic regime in the particle-particle contact friction law.

3.4.3 Hydrodynamic regime

The hydrodynamic interactions between two similar neighbouring spheres in the HD regime are described by standard low-Reynolds-number
fluid mechanics with a lubrication hypothesis (i.e. inter-surface distance small compared to the radius of the particle) [14]. The drag force on one particle due to the other is given in the canonical reference frame of the contact by (for overall formula see Ref. [45] and for detailed calculations see: for the diagonal terms Ref. [114] and for the non-diagonal term Ref. [101]):

\[
\mathbf{F}_{1\rightarrow 2}^{HD} = \frac{\pi}{10} \eta_f R_p \begin{bmatrix}
-15 \tilde{h}^{-1} & 12 \tilde{h}^{-\frac{3}{2}} \\
0 & -10 \ln(\tilde{h}^{-1})
\end{bmatrix} \begin{bmatrix}
v_N \\
v_T
\end{bmatrix}
\] 

(3.11)

where \(\tilde{h}\) is the surface-to-surface distance normalised by \(R_p\), \(\eta_f\) is the fluid viscosity and \(v_N\) and \(v_T\) are the normal and tangential components of the local relative speed, respectively. By definition of the reference frame: \(v_T \geq 0\). Please note that spinning around the normal direction is neglected because other components of the drag dominate for small \(\tilde{h}\) since the normal spinning drag does not diverge when \(\tilde{h} \rightarrow 0\) [186].

Newton’s 2\(^{nd}\) law on one of the spheres, projected on the normal and tangential axis of the contact gives then:

\[
a_n + \frac{9}{8} \frac{\eta_f}{\rho_p R_p} \left( \frac{\dot{\tilde{h}}}{\tilde{h}} - \frac{12}{15 R_p \sqrt{\tilde{h}}} v_T \right) + \frac{3}{4\pi} \frac{F_N^{ext}}{\rho_p R_p^3} = 0
\] 

(3.12)

\[
a_t + \frac{3}{4} \frac{\eta_f}{\rho_p R_p^2} \ln(\tilde{h}^{-1}) v_T + \frac{3}{4\pi} \frac{F_T^{ext}}{\rho_p R_p^3} = 0
\] 

(3.13)

with \(a_n\) and \(a_t\) the normal and tangential component of the particle acceleration, \(\rho_p\) the density of the particle and \(F_N^{ext}\) and \(F_T^{ext}\) the sums of external forces applied on the sphere by means of other contacts projected respectively on the normal and tangential axes. This nonlinear differential equation system is not easily solvable analytically.

Nevertheless, here, the Reynolds number of the particle \(Re_p = \rho_p R_p^2 \dot{\gamma} / \eta_f\) is small for the range of shear rates that we investigate experimentally. Then we can assume that the acceleration terms are negligible. Moreover, the time scale of the normal speed damping, \(t_N \propto \eta_f R_p^2 / F_N^{ext} \propto I_v / \dot{\gamma}\), is small compared to the time scale of the flow, \(\dot{\gamma}^{-1}\), since \(I_v\) is small for dense suspensions. Consequently, the stabilisation of the lubrication conditions is fast compared to the time scale of the evolution of the system. Transient effects in the contact are thus negligible and only the steady-state lubrication is relevant.
Moreover, the particles cannot interpenetrate each other and the existence of a long-lived contact itself implies that \( v_N = 0 \), given that for \( v_N > 0 \) the particles separate from each other. This hypothesis is justified by prior simulation studies, in which the contact duration between particles in dense granular media was long compared to \( \dot{\gamma}^{-1} \) [76]. As an additional consequence of this hypothesis, the shear-thickening behaviour that we could observe in the results of our simulation cannot be due to hydroclusters arising from attractive viscous forces in opening contacts [24, 30].

With these hypotheses, Eq. 3.12 and 3.13 become:

\[
\frac{6\pi \eta_f R_p}{5\sqrt{h}} v_T + F_{N}^{ext} = 0
\]  

(3.14)

\[-\pi \eta_f R_p \ln(\tilde{h}^{-1}) v_T + F_{T}^{ext} = 0\]

(3.15)

and the steady state is given by:

\[
\|F_{N}^{ext}\| = \frac{6\pi \eta_f R_p}{5\sqrt{h}} \|v_T\|
\]

(3.16)

\[
\|F_{T}^{ext}\| = \pi \eta_f R_p \ln(\tilde{h}^{-1}) \|v_T\|
\]

(3.17)

At this stage, following standard hydrodynamic lubrication analysis [188], the minimum thickness of the fluid layer between the contacting particles is given by equation (3.14):

\[
\tilde{h} = \left(\frac{6\pi \eta_f R_p \|v_T\|}{5 \|F_{N}^{ext}\|}\right)^2 = \left(\frac{6\pi}{5} s\right)^2
\]

(3.18)

with \( s = \eta_f v_T R_p / F_{N}^{ext} \), the Sommerfeld number as defined in Section 1.3.2. The ratio between the tangential viscous drag and the normal load gives the coefficient of friction \( \mu \):

\[
\mu = \frac{\|F_{T}^{ext}\|}{\|F_{N}^{ext}\|} = 2\pi s ln\left(\frac{5}{6\pi s}\right)
\]

(3.19)
This formula is valid only for small $s$ because the lubrication hypothesis is valid only for $\tilde{h} \propto s^2 << 1$. We fixed the validity limit of Eq. 3.19 at $s_{\text{lim}} = 10^{-1}$ and $\mu(s) = \mu(s_{\text{lim}})$ for $s > s_{\text{lim}}$. This limits the range of our simulation excluding the non-dense pastes and/or too low shear; these cases are, anyway, outside of the targeted regimes. In any case we have experienced in the numerical simulations that there are less than 0.5% of the contacts with $s > 10^{-1}$ in the considered range of shear stresses and that the resulting forces are weak.

### 3.4.4 Friction law

The friction law used for the simulations is then (see also Fig.3.4b):

$$
\mu(s) = \begin{cases} 
\mu_0 & \text{if } s < s_c \\
2\pi s \ln \left( \frac{5}{6\pi s} \right) & \text{if } s_c < s \leq s_{\text{lim}} \\
2\pi s_{\text{lim}} \ln \left( \frac{5}{6\pi s_{\text{lim}}} \right) & \text{if } s \geq s_{\text{lim}}
\end{cases}
$$ (3.20)

### 3.4.5 Normal restitution

Finally, as an additional consequence of the long-lived contact hypothesis, the normal restitution coefficient, $e_N$, is zero for both lubrication regimes. It can be seen physically as the result of the intense damping of any normal speed when two particles are near each other, as seen in Eq.3.11. Moreover, the normal restitution coefficient is known to have a minor impact on the behaviour of dense granular media [50].

### 3.4.6 Comparison with other simulations

In some other simulations [136, 163, 179, 199], the lubrication between spheres is implemented in a radically different way. Two major differences can be pointed out. First, the particles can interact viscously with any close neighbours while, in our simulation, only the particles that are in contact for the Contact Dynamics algorithm can interact with each other. This is an important limit of our model for dilute suspensions but in the limit of dense suspensions, this should not change the results significantly.
Another important difference is the way the hydrodynamic lubrication forces are approximated. Starting from Eq.3.11, these authors decided to neglect the non-diagonal term, i.e. the sliding lift. This is a correct approximation for the short term effects because \( v_N \) and \( v_T \) should have similar values before contact and consequently \( v_N/h \gg v_T/\sqrt{h} \). However, as shown in the previous paragraphs, this lift term is critical to determine the long-term sliding distance between the two spheres. Indeed, as soon as the spheres are close to each other, the normal velocity goes to any arbitrary small value in a short time \( t_N \propto I_v \hat{\gamma}^{-1} \). In the absence of this lift force, two rough spheres will then touch and start experiencing elastic repulsion and boundary lubrication. For this reason, removing the lift term would lead to an overestimation of the proportion of boundary lubricated particle contacts in dense suspensions. This could explain why other authors report [136, 163, 179] that the jamming-volume fraction for a viscously lubricated suspension of rough spheres is the same as for a dry granular media, \( \phi^{NW}_{max} \approx \phi^{BL}_{max} \) in contrast with our results.
3.5 Results

The goal is to determine if our framework is setting sufficient conditions to recover the different flow regimes and the transitions between them. We will first explore the transition between the Newtonian regime and the shear-thickening regime, showing that it does not exist in the absence of lubrication and elucidating the role of $\dot{\gamma}$, $\phi$ and $s_c$. Then we explore the transition from continuous shear thickening to discontinuous shear thickening and the role of $\phi$ and $\mu_0$.

In order to observe a shear thickening in realistic conditions, the simulations were mainly performed with volume fractions around 0.58 that are close to that reported experimentally for example in Refs. [33, 63]. In the absence of measurements of friction coefficient between particles in these publications, values were chosen between 0.01 and 1 that correspond to the frictional properties of most hard materials.

3.5.1 Differences from the case of dry granular media

In order to confirm the robustness of our simulation algorithm and in order to distinguish our results from shear-induced jamming of granular media [21], we first performed simulations with a constant coefficient of friction i.e. $\forall s, \mu(s) = \mu_0$ (no HD regime).

Fig.3.3 shows data from the suspension simulations, superimposed on simulations where lubrication is disregarded, i.e. $\mu = \text{const}$, or in other words, all contacts are always in the boundary lubrication regime. Here, we see that the curve $\mu = 0.2 = \text{const}$ exhibits pure and stable Bagnoldian scaling for any shear rate $\dot{\gamma}$.

Furthermore, the vertical solid line indicates that the system is jammed at any applied stress for $\mu = 0.4 = \text{const}$ as opposed to lubricated contacts, where flow is possible at sufficiently low $\dot{\gamma}$ (see $\mu_0 = 0.4$). Note that as we consider infinitely hard particles in our simulations, the jamming point does not depend on the applied stress as opposed to soft sphere simulations, as discussed in Ref. [41].

In contrast, the flow curves of the suspensions exhibits both a Newtonian and a shear-thickening regime. This confirms that the existence of
these regimes and of the transition between them relies on the presence of a lubricating fluid.

Figure 3.3 – Shear stress $\tau$ as a function of $\dot{\gamma}$ for two different friction coefficients. Stars and squares correspond to data where the lubrication is taken into account in the numerical model, whereas filled circles correspond to a constant $\mu$, i.e. lubrication is disregarded. The solid line schematically shows the jammed state, where no flow is possible at any applied stress when lubrication is disregarded.

### 3.5.2 Newtonian to ST transition with $\dot{\gamma}$

In Fig. 3.4a, the viscosity of a suspension with $\phi = 0.58$, $\mu_0 = 0.1$ and $s_c = 5 \times 10^{-5}$, is plotted. The flow curve shows a clear transition between a Newtonian plateau at low shear stress ($\tau < 10^2$) to a continuous-shear-thickening regime at higher shear stress. This transition also corresponds to a modification of the lubricating regime in the sliding contacts as shown in Fig.3.4 b&c. During the Newtonian regime, most of the sliding contacts are hydrodynamically (HD) lubricated. When the shear stress is increased, the distribution of local $s$ goes toward smaller values (see Fig.3.4b). This finally leads to an increase of the BL sliding
contacts proportion and the virtual disappearance of any HD contact. Fig. 3.5 shows an example of the geometrical repartitioning of these contacts (for $\phi = 0.59$), increasing the shear stress. The particles in BL contacts start creating strings and then, at the highest shear, a percolating network appears, very similar to that is seen in dry granular media. Thus, as proposed in our model, the transition toward a shear-thickening regime corresponds to an increase in boundary lubricated (BL) sliding contacts.

Nevertheless, our simulation is not totally able to fit the data quantitatively. If the viscosity of the suspension take credible values, the onset of the shear thickening happens at normalised shear rates that are several orders of magnitude higher than the values reported in Refs. [31, 32, 63, 134].

**Effect of $s_c$.**

Lootens et al. [134] have previously reported that rough particles shear thicken at lower shear rates than smooth ones. This phenomenon is explained in our framework by the fact that a rough particle enters into BL contact at lower loads than smooth ones.

To validate the impact of the roughness of the particles in our model, we increase the value of $s_c$ from $5 \cdot 10^{-5}$ to $4 \cdot 10^{-4}$. Fig.3.6 shows that, also in our simulation, the critical shear rate is a decreasing function of $s_c$, i.e. of the surface roughness.

Moreover, in the previous chapter (Section 2.1.3), we used our model to propose a scaling law of the critical shear rate:

$$\dot{\gamma}_c \propto \frac{\eta_f I^2}{s_c \rho_p R_p^2}$$  \hspace{1cm} (3.21)

For a given $\mu_0$ and $\phi$, $\eta_f I^2/\rho_p R_p^2$ is a constant. The relevance of the scaling in Eq.3.21 is proved by observing the collapse of the data when the horizontal axis is rescaled by $\dot{\gamma}s_c$ in Fig. 3.6b.

This helps us to reconsider the difference in term of critical shear rates between our simulation and the experimental results that we observed in the previous paragraph. Indeed, this difference could be due to the very low value of roughness that we took: $s_c = 10^{-5}$ represents ex-
Figure 3.4 — (a) The viscosity as a function of shear rate. (b) Friction law chosen for numerical simulation (black line) and probability distributions of $s$, $P(s)$, for all sliding contacts at several shear stresses as defined in b. (c) Frequencies of BL sliding contacts, $P_{BL}$, and HD sliding contacts, $P_{HD} = 1 - P_{BL}$, as a function of $\dot{\gamma}$ for the stresses defined in a. The simulations data in b-c-d are performed with $\phi = 0.58$, $\mu_0 = 0.1$ and $s_c = 5 \times 10^{-5}$.
Figure 3.5 – Simulation snapshots for $\phi = 0.59$, $\mu_0 = 0.1$ at $\tau = 10^2$, $10^4$ and $10^8$ from top to bottom left to bottom right. Lines indicate the forces: line thickness scales with the force magnitude and are normalised by the mean normal force. Red lines correspond to boundary-lubricated contacts, whereas blue lines correspond to hydrodynamically lubricated contacts. At low shear, most of the contacts are hydrodynamically lubricated. Increasing of the shear stress, more and more contacts become boundary lubricated. For $\tau = 10^6$, the particles in BL contacts form some chains and at even higher stress , $\tau = 10^8$, they create a percolating network.
tremely smooth particles. For comparison with experimental rheological results, \( s_c \approx 10^{-2} \) is more relevant and this choice would lead to orders of magnitude smaller \( \dot{\gamma}_c \), which fits better with the reported values.

Nevertheless, in our simulation, low values of \( s_c \) are a technical constraint. Our simulation is only valid if the value of \( s \) in each contact stays below \( s_{lim} = 10^{-1} \). If \( s_c \) is too close to \( s_{lim} \), the hydrodynamic lubrication regime would just be disregarded.

**Effect of \( \phi \).**

Fig.3.7, shows the Nw-ST transition for two different volume fractions. An increase in \( \phi \) results in an increase in the Newtonian plateau viscosity, and the shear-thickening-regime viscosity. Our results are also compatible with a shift of the transition between these two regimes towards lower shear rate when increasing the volume fraction as reported in numerous experimental studies (for review: Refs.[13, 34]).

### 3.5.3 CST-to-DST transition

The most innovative part of our framework is the prediction of the discontinuous shear thickening of our suspensions. According to Section 2.1.3, it happens when \( \phi > \phi_{max}^{BL}(\mu_0) \). Since \( \phi_{max}^{BL}(\mu_0) \) is a decreasing function of \( \mu_0 \) [41, 182] this case is reached, in our simulation, by increasing \( \phi \) or \( \mu_0 \).

**Effect of \( \phi \).**

The transition from CST to DST is known to occur when increasing \( \phi \). This phenomenon is reproduced in our simulation. For example, in Fig.3.8, the system experiences CST at \( \phi = 0.58 \), \( \mu_0 = 0.3 \) but experiences DST for \( \phi = 0.59 \) and the same \( \mu_0 \). Moreover, as predicted in our theoretical model, the CST-DST transition occurs when \( \phi \) is increased above a \( \phi_{max}^{BL}(\mu_0=0.3) \), compatible with Ref. [182].
Figure 3.6 – (a) The apparent viscosity $\eta$ as a function of the shear rate $\dot{\gamma}$ for $\phi = 0.58$, $\mu_0 = 0.1$ and different critical Sommerfeld number, $s_c$. (b) The same dataset where the shear rate has been rescaled via $\dot{\gamma} \rightarrow s_c \dot{\gamma}$
3.5 Results

Figure 3.7 – The viscosity as a function of the shear rate for $\phi = 0.58$ and 0.59, $\mu_0 = 0.1$ and $s_c = 5.10^{-5}$.

Effect of $\mu_0$.

The transition from CST to DST also occurs when increasing $\mu_0$. Keeping the volume fraction fixed, $\phi = 0.58$, in the Fig.3.8, we tuned the value of $\mu_0$ within a realistic value range, from 0.01 to 0.5. We first observed that the viscosity of the Newtonian regime is not significantly affected by the value of $\mu_0$ at this volume fraction. The scenario changes at higher shear rate.

- For the lowest values of $\mu_0$, i.e. 0.01 or 0.1, the system experiences a direct transition between from a Newtonian to a Bagnoldian continuous shear thickening.

- For $\mu_0$ between 0.1 and 0.3, the shape of the transition becomes sharper as $\mu_0$ increases (see inset), but the granular media can still flow at the highest shear rate at which it still exhibits Bagnoldian behaviour. One can notice that the transition extends over several orders of magnitude. Because of the limitations of the experimental setup, the highest shear rates are not realistic and the inset cor-
responds to the maximum range of shear that can be accessed experimentally.

- For $\mu_0 \geq 0.35$, finally, the apparent viscosity diverges vertically at the critical shear rate and no shear faster than $\dot{\gamma}_c$ can be achieved irrespective of the shear stress. The system shear-thickens discontinuously.

![Figure 3.8](image)

**Figure 3.8** – Apparent viscosity versus $\dot{\gamma}$ for different $\mu_0$ and $s_c = 5 \cdot 10^{-5}$ in simulations. In the Newtonian regime, the viscosity does not depend on $\mu_0$ but on $\phi$. At $\phi = 0.58$, for $\mu_0 \leq 0.3$, the system experiences CST, where the viscosity depends on the friction coefficient. For $\mu_0 \geq 0.35$, the system jams at sufficiently large $\dot{\gamma}$. Data points for $\phi = 0.59$ show DST for $\mu_0 = 0.3$. Inset: Zoom of the transition zone.

### 3.5.4 Effect of the confinement

We investigate the influence of the confining walls to confirm, first, that the phenomena we observe are not a shear-induced jamming arising from the confinement of the granular media between the two walls [21]
and, secondly, that our framework does not requires a stiff boundary but only a constant volume fraction, as stated in Section 2.2.1.

We modified the boundary conditions in the vertical $z$-direction by removing the walls and using Lees-Edwards [3] boundary conditions instead. Shear in the $x$-direction is induced by considering moving (in $x$-direction) mirror images of the simulation box. Briefly, particles at the bottom of the simulation box interact with particles at the top of the box, with an $x$ coordinate displaced by an amount $\delta_x = tv_{\text{shear}}$ where $v_{\text{shear}}$ is the shearing velocity and $t$ is time. When particles cross the boundaries in the $z$-direction, the $x$-velocities are corrected by an amount $\delta_x = v_{\text{shear}}$. As in the solid wall case, we simulate stress-controlled shearing at a mean stress $\tau_0$, where the shearing velocity $v_{\text{shear}}$ is measured. In order to keep a constant mean stress, $v_{\text{shear}}$ is adjusted via the equation of motion $\dot{v}_{\text{shear}} = (\tau_0 - \tau)$ [156], where $\tau = -1/V \sum_i F_i r_i$ is the actual shear stress of the sample. The sum runs over all contacts $i$ having contact force $F_i$ and distance vector $r_i$ connecting the two centres of the spheres. The effective viscosity of the suspension is given by $\eta = \tau_0/\dot{\gamma}$ where $\dot{\gamma} = v_{\text{shear}}/L_z$ and $L_z$ is the system size in the $z$-direction.

Fig.3.9 shows $\eta$ as a function of $\dot{\gamma}$ for different boundary lubrication friction coefficients $\mu_0$ and volume fraction $\phi = 0.595$. As seen previously, we observe two transitions, from Newtonian to Bagnoldian as $\dot{\gamma}$ is increased, and from continuous to discontinuous shear thickening as $\mu_0$ is increased. These calculations indeed suggest that a friction law is responsible for both the different, observed flow regimes and the transitions between them. In particular, the DST transition is not due to the presence of confining walls. The critical volume fraction and the $\mu_0$ at which the system experiences DST are slightly larger compared to the values in the wall-confined case, but no qualitative differences are found. This quantitative difference is due, at least partially, to the fact that the presence of hard walls has the effect of reducing the accessible volume to the particles in the system [41]. Some direct, but small, effects of the confinement itself on the exact value of $\dot{\gamma}_c$, $\phi_c$ or any other critical parameters are also possible.

In any case, the overall picture is conserved, showing that the boundary conditions are not critical.
Figure 3.9 – Effective viscosity as a function of the shear rate for different $\mu_0$ at $\phi = 0.595$ for a system with periodic boundary conditions in all three spatial dimensions.
3.6 Conclusions

In brief, we have constructed, based on a contact-dynamics algorithm, and on the restricting set of ingredients described in Chapter 2, a computer simulation dedicated to the modelling of very dense suspensions. This simulation was able, for the first time to the best of our knowledge, to predict the three main rheological regimes of a granular suspension that are reported in the literature (Newtonian, CST and DST), as well as the transitions between them.

The results also confirm that our theoretical framework sets sufficient conditions to explain the Newtonian-Shear Thickening transition as a function of shear rate. Moreover, as previously theoretically forecast, this transition appears to result from a transition between a viscous regime, in which hydrodynamic lubrication dominates and an inertial regime, in which boundary-lubricated contacts dominate. We also determined that an increase in volume fraction or an increase in roughness of the particles results in a lower critical shear rate, because both promote boundary-lubricated contacts. All these observations are in agreement with our theoretical studies, as well as with the reported experimental results [13, 34].

Additionally, our simulation results confirm that the nature of the shear-thickening regime depends on the ability of the granular media to flow with only BL contacts between particles (i.e. \( \phi \leq \phi_{BL}^{max}(\mu_0) \)). As a consequence, the transition between continuous and discontinuous shear thickening depends on the volume fraction and on the boundary lubrication coefficient of friction.

Finally, quantitatively speaking, the values of viscosity and maximum volume fractions that we found in simulation seem to be compatible with the reported experimental results. Only the critical shear rate is less precisely addressed, due to the technical impossibility of simulating realistic roughness.
Chapter 4

Validation for Filler Suspensions

The main goal of this thesis is to understand and control the shear thickening of cement slurries. Thus, testing our framework only with a model system of sphere suspensions cannot be sufficient. This chapter explores the relevance of our model for industrial slurries and discusses prospects to improve cement admixtures.

As described in Section 4.1, in order to prevent any chemical reactions, the tests were performed on quartz and calcite filler suspensions that are chemically inert but have physical and mechanical properties close to those of the cement grains. The surface properties of the grains, especially the coefficient of friction in the boundary regime, is modified by adsorption of comb-polymer brushes. In this section, the details of the experimental protocols are also described.

In Section 4.2, the relevance of our framework for quartz filler suspensions is challenged by comparing the lubricating properties of four different polymers on quartz surface and the shear-thickening behaviour of suspensions of quartz particles coated with the same polymers. This also led us to develop a quantification method based on compressive rheology that allows easy and robust measurements of the main parameter of the shear-thickening regime, $\phi_{max}^{BL}$, for any paste.

In Section 4.3, we finally address the control and reduction of shear thickening in industrials slurries by the identification of the relevant polymer architectural characteristics.
The section 4.2 is based my own contribution, under the supervision of J. Cayer-Barrioz, N.D. Spencer and L. Isa., to Ref.[65]:

N. Fernandez, R. Mani, D. Rinaldi, D. Kadau,
M. Mosquet, H. Lombois-Burger, J. Cayer-Barrioz,
H. J. Herrmann, N. D. Spencer & L. Isa.

*Microscopic mechanism for shear thickening of non-Brownian suspensions*


A part of the experimental results reported in Section 4.3 were obtained by E. Marini during his bachelor project in LSST under my supervision.
4.1 Materials and methods

Testing the validity of our framework on cement-like pastes requires powders, lubricating polymers to change the powder grain surface properties and different rheometric and tribometric techniques. This section describes the characteristics of the materials and the details of the protocols that were used for this purpose.

4.1.1 Polymers

All the polymers were kindly provided by Lafarge LCR as neutral-pH concentrated solution ($\approx 25\%_{mass}$). Most of them were synthesised by Lafarge LCR. Two polymers are commercial concrete additives.

Nomenclature of the tailored polymers

These comb polymers are synthesised by radical polymerisation in water according to Refs. [109, 172] of poly(ethylene glycol) methyl ether methacrylate and (only one of the following) methacrylic acid or ethylene glycol methacrylate phosphate. This leads to random comb polymers with carboxylic or phosphate anchors, respectively.

![Chemical structures of polymers](image)

**Figure 4.1** – Chemical composition of the random comb polymers: (right) PMAA-g-PEG, PMAA-g-EGPh-g-PEG. The counter-charges are sodium ions.
The nomenclature for the carboxylic-anchor comb polymers is: PMAA-g(X₁)-PEG(X₂) with X₁ the grafting ratio, i.e. number of carboxylic groups per PEG chain and X₂ the length of the PEG side chains in kDa.

The nomenclature for the phosphate-anchor comb polymers is: PMAA-g-EGPh-g(X₁)-PEG(X₂) with X₁ the grafting ratio, i.e. number of phosphate groups per PEG chain and X₂ the length of the PEG side chains in kDa.

The lengths of the polymer backbones were chosen around 4 kDa. The grafting ratios were between 0.8 and 4. The lengths of the PEG chains were 0.5, 2 or 5 kDa. The details of the polymers that are used in this chapter are provided in Table 4.1.

<table>
<thead>
<tr>
<th>Grafting Ratio</th>
<th>PEG Side-Chain Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 kDa</td>
</tr>
<tr>
<td>0.8</td>
<td>Ø</td>
</tr>
<tr>
<td>1.0</td>
<td>PO₃⁻</td>
</tr>
<tr>
<td>1.5</td>
<td>COO⁻</td>
</tr>
<tr>
<td>2.3</td>
<td>Ø</td>
</tr>
<tr>
<td>4.0</td>
<td>Ø</td>
</tr>
</tbody>
</table>

Table 4.1 – Characteristics of the polymers used in this chapter. “PO₃⁻” means that a polymer with these architecture parameters and phosphate anchors (PMAA-g-EGPh-g-PEG) has been used. “COO⁻” means that a polymer with these architecture parameters and carboxylic anchors (PMAA-g-PEG) has been used. Both kind of anchors are never mixed in a single polymer. “Ø” means that no polymer of this architecture has been used.

**Nomenclature of the commercial polymers**

Two commercial polymers were used. Glenium 27 from BASF (Ludwigshafen, Germany), which is essentially composed of PMAA-g(1.5)-PEG(1.1) and Optima 100 from Chryso (Issy-les-Moulineaux, France), which is essentially composed of a linear polymer: a 2kDa-long hydrophilic side-chain with an N-iminobis(methylphosphonic acid) group
at one of the ends.

4.1.2 Rheology

Powders

The powders were chosen in order to mimic the mechanical and physical properties of cement grains without any chemical activity. Filler powders appear to be a valuable choice in this context. Two different filler powders were used for these experiments: a calcite filler and a quartz filler. Both have similar grain size and specific surface area to cement grains. They mainly differ from each other by their roundness and their surface properties.

Limestone filler. The limestone filler is finely ground natural calcite of high purity (more than 99% CaCO₃ with traces of MgCO₃ and Fe₂O₃) from Orgon, France and sold under the name BL200 (Omya SAS, France). The size and the shape of the grains are reported in Figs. 4.2 & 4.3. It has a BET specific surface area around 860 m²/kg and a density of 2.7g/cm³.

Quartz filler. The quartz filler is finely ground natural quartz of high purity (more than 99% SiO₂ with traces of Al₂O₃, K₂O, Fe₂O₃ and CaO) from Compiègne, France and sold under the name C400 (Sibelco,
Figure 4.3 – Retained mass proportion of the BL200 limestone (grey) and the C400 quartz particles by laser sizing (the line is a guide for the eye).

France). The size and the shape of the grains are reported in Figs.4.3 & 4.4. It has a BET specific surface around 620 m²/kg and a density of 2.65g/cm³.

Shear Rheology

The shear rheology experiments were performed only on quartz filler suspensions with a tailored rheometer geometry.

Geometry. The use of standard rheology geometries, such as plate-plate (P-P), cone-plate (C-P) and Couette (i.e. cylinder in cylinder), is poorly applicable for dense filler pastes. Indeed, the grains would migrate promptly in any geometry in which the shear is not homogeneous (such as P-P or Couette). The polydispersity of the powder also prevents the use of small gap geometry (especially C-P) because the gap must be significantly larger than the largest particles (≈ 10²μm). Additionally, in any geometry that is vertically extended, the filler grains also quickly sediment. This leads to a vertical heterogeneity and an overestimate of the viscosity in a Couette geometry due to the denser suspension in the bottom part and an underestimate of the viscosity in a P-P because only
the less dense top part is sheared.

In order to measure the rheological properties of cement suspensions, several dedicated tools are described in the literature [44]. Within this large collection, we chose a double helix geometry that consists of two ribbons making a single turn around a common axis. This geometry is constraint to rotate around its own axis in a rough cylinder as shown in Fig.4.5. This geometry maintains efficiently the homogeneity of the pastes by creating a torus-like flux in the cylinder. Because it combines also a large unsheared volume (inside and above the ribbon) and zones of high shear (on the outer edge of the ribbon), it mimics well the industrial flow situations, such as mixing. Nevertheless, this geometry also has some drawbacks. The most important one, in our case is the lack of the possibility to measure the dilatancy. Indeed, the horizontal stick at the bottom of the helix is thin, leading to a small vertical force signal in the case of dilatancy and additionally the helix rotation generates by itself a vertical force that has an unknown dependence on the fluid rheological properties.

The rheometer measures torques and rotation speeds. For the standard rheometric geometries, the conversion of these data to shear stress and shear rates is straightforward. The calibration of our geometry is a much more complex problem. Because the ribbon geometry shape is close to a Couette design, the calibration was done using the Couette Analogy technique as described in Refs. [2, 26]. In these papers, Bousmina proved that such a geometry can be approximated by a Couette geometry with inner and outer radii ($r_i$ and $r_o$) that can be deduced from couple and ro-
Figure 4.5 – Picture of the helicoidal geometry
(a) Inner cylinder diameter (50 mm)
(b) Outer helix diameter (49 mm)
(c) Distance for the helix to the cylinder bottom (0.5 mm)
(d) Ribbon width (5.0 mm)
(e) Helix height (75 mm)
(f) Suspension filling level (85 mm)
Not represented: Thickness of the ribbon (1.0 mm)

...rotation speed data obtained in simple experiments. Additionally, because even in a Couette geometry, the shear rate is not uniform, Bousmina also proved that, in such a geometry, there always exists a cylinder of radius $r^* \in [r_i; r_o]$ on which the shear rate and the shear stress can be calculated from the torque-rotation data with accuracy and with very little dependence on the properties of the fluid. A calibration of the geometry is performed to measure the shear stress and rate values on this cylinder.

The Couette-analogy calibration of our geometry has been performed by Fabrice Toussaint’s team in Lafarge LCR using 3 Newtonian glucose-water mixtures (80, 83 and 87%\text{mass} of glucose) of different viscosities and a shear-thinning Carbopol gel.

**Protocol.** The rheological measurement was performed, with an Anton Paar MCR 301 rheometer, on suspensions of ground quartz with volume fraction, $\phi$, between 0.47 and 0.57. The suspending fluid was a solution of K$_2$SO$_4$ (20 mmol/L). An excess of Ca(OH)$_2$ (6 mg/g$_{SiO_2}$) was added as a powder to maintain saturation of the suspending solution, even after the reaction of OH$^-$ with the surface of the quartz grains and the adsorption of calcium ions. Under similar conditions, the $\zeta$-potential of silica surfaces has been reported to be around 6mV [166]. A drop of Surfynol MD-20 (antifoaming Gemini surfactant, from Air Products, USA) was also added to prevent air trapping during the mixing.

Before mixing, the polymer solution was added. It was found that any addition of small quantities of adsorbing polymers decreases the viscosity, both in the low-deflocculation and high-shear-rate (ST) regimes. Above a certain mass of polymer per unit mass of quartz, further addition of polymer no longer changes the suspension viscosity. This saturation...
takes place at polymer concentrations in the solution below 2 \%_{\text{mass}}, i.e. far below levels that could change the viscosity of the suspending fluid. All the rheology experiments were thus carried out with excess polymer relative to the saturation mass ratio. The working polymer mass ratios were $r(A)= 3.1 \text{ mg/}g_{\text{SiO}_2}$, $r(B)= 3.1 \text{ mg/}g_{\text{SiO}_2}$, $r(C)=1.5 \text{ mg/}g_{\text{SiO}_2}$ and $r(D)=4.0 \text{ mg/}g_{\text{SiO}_2}$. These working concentrations have not been precisely optimised. Nevertheless the small value of $r(C)$ can be explained by polymer C shorter side chains that create a thinner brush layer and thus a lower adsorbed mass per unit surface [161].

Even if the reduction of viscosity due to adsorption of the polymers was immediate, the experiments were performed at least 10 min after the initial mixing. During this period the suspension can settle, the suspension is therefore homogenised before the start of the experiments by mixing and pre-shear (increasing logarithmic stress ramp from 0.01 to 700 Pa in 100 s).

The rheological data are then acquired during a decreasing logarithmic stress ramp from 700 to 0.01 Pa in 100 s. The temperature is kept constant at 23°C using a temperature-controlled water-circulation system. The suspension is renewed after each test.

**Compressive Rheology**

**Protocol.** The compressive-rheology tests have been performed on both quartz and limestone fillers. The different components of each sample were added into a 25mL PTFE beaker (VWR international, USA) in the following order: Filler, Ca(OH)$_2$ as powder, K$_2$SO$_4$ solution, MilliQ water, Polymer as a dense solution ($\approx 25\%_{\text{mass}}$), Antifoam: Tri-iso-Butyl Phosphate (TiBP). The quantity of each constituent varies with the experiments.

The components are mixed with a PTFE spatula until complete homogenisation. To ensure that the adsorption equilibrium state in the suspension is reached, each solution was left to settle for ten minutes. The suspensions were then homogenised, poured in 10 mL glass measuring flasks (Hirschmann, Germany), homogenised for 2 min on a whirlly mixer\footnote{This step is removed in the Section 4.3 to improve the reproducibility in case of multiple experimenters.} and centrifuged for 20 minutes at 4000 rpm (Rotafix 32 from Hettich}
Laborapparate, Switzerland). In the centrifuge, the flask was kept in position by a home-made PDMS shape adapter. The distance to the rotor axis was between 6 cm (top of the flask) and 15 cm (bottom of the flask) leading to a centrifugal acceleration of around 2000 $g$ and compressive extra-pressure on the granular network around of $10^5$ Pa. The flask During preliminary tests, we found that the sediment achieved a stable compaction in the first few minutes.

After centrifugation, some of the supernatant was employed to rinse the PTFE beaker and poured back in the flask. Each flask was centrifuged a second time in the same way. Only the samples for which the supernatant-sediment border was in the flask neck were used further. Since the flask neck is a cylinder of diameter 7 mm, the volume of the sediment can be calculated by measuring the position of the supernatant-sediment border compared to the ring graduation marking (see Fig. 4.6). The jamming volume fraction was then calculated by dividing by the volume of filler introduced. The use of a glass measuring flask, compared to ordinary centrifuge tube, allows a precise measurement of the sediment volume to the naked eye.
Figure 4.7 – Quartz suspensions for Glenium 27 (2mg/\text{g\_filler}) in aqueous solution ([K_2SO_4] = 80 mmol/L and saturation of Ca(OH), 90mg) with (a) and without (b) whirly mixing

**Impact of the whirly mixing.** During the tests, we noted that the whirly mixing step led to an increase in the sediment volume fraction for quartz suspensions (see Fig. 4.7). This phenomenon is very similar to the reduction of the viscosity during long periods in the shear-thickening regime noted in Section 4.2.3. Moreover the whirly mixing effects can depend on the exact way in which the experimenter holds the flask, and we found that removing the whirly mixing step led to better reproducibility in case of multiple experimenters.

For the experiments reported in Section 4.3, the protocol has been modified by suppressing any whirly mixing. To prevent any gravitational sedimentation before the centrifugation, each flask is centrifuged immediately after its filling. This improvement of the protocol leads to the sediment volume fraction being shifted to lower values (by around 0.005) in the second part of this chapter. The differences of sediment volume fraction between polymers are conserved in any case.

**Reproducibility.** We performed independently 6 identical tests on calcite with Glenium 27 (7mg/\text{g\_filler}) in aqueous solution ([K_2SO_4] = 80 mmol/L and [KOH] = 53 mmol/L). The average of sediment volume fraction was 0.643 and the standard deviation was 2.10^{-3}. Such high precision is rare for jamming-volume-fraction measurements. The dispersion of the data is similar with quartz suspensions and stays small compared to the difference of sediment volume fraction for different
polymers, which is on the order of $10^{-2}$.

**Independence on the initial volume fraction.** The initial volume fraction of the suspension is limited by flask geometry. Indeed the sediment-supernatant border must be located in the flask neck to allow a precise measurement of the sediment volume fraction. In the range of possible initial volume fractions, no impact of the volume fraction has been observed.

### 4.1.3 Tribology

The lubricating properties of different polymers on quartz surface in the boundary-lubrication regime were measured separately as follows.

**CSM Nanotribometer**

Tribological experiments were performed with a ball-on-disc NTR2 tribometer (CSM Instruments, Peseux, Switzerland). A detailed view of the measuring head is provided in Fig 4.8. The ball is rigidly embedded into a mobile stage, which is itself connected to the main part of the tribometer by a set of blade springs. In this configuration, the displacements of this mobile stage compared to the basis of the tribometer in vertical and horizontal directions are proportional to the normal and frictional forces that are applied on the ball. These displacements are measured via capacitive sensors. The forces are then calculated with help of spring and capacity calibration parameters.

The position of the disc relatively to the ball is adjusted by a servo-loop during the measurement to follow the targeted track, speed and load by a linear motor (laterally) and a piezo-actuator (vertically).

**Sample preparation**

**The ball.** The ball was a 2 mm diameter borosilicate sphere (Sigma-Aldrich, USA) cleaned for 20 min using Piranha solution (7:3 concentrated $H_2SO_4/30\% H_2O_2$). Between two measurements, the sphere was renewed.
The disc. The disc was prepared from a rose quartz stone (Cristaux Suisses, Switzerland). The stone was polished using a set of SiC polishing papers and diamond pastes down to 1μm-grade (from Struers, Denmark). The final topography of the surface is shown in Fig.4.9. Then the polished stone was cleaned for 20 min using Piranha solution. Between two measurements, the quartz surface was washed using a large volume of neutral pH buffer solution and then pure water (Milli-Q system from Millipore, 18.2 MΩ.cm) in order to desorb and remove the polymer without modifying the quartz surfaces by aggressive chemical and thermal cleaning procedures. After this cleaning procedure, the tribological properties of the surface was found to be identical to the freshly polished surface.

The tracks of the different tribotests were parallel and separated by several millimeters.

The lubrication solution. The lubricated solution is a freshly prepared salty alkaline solution (20mM K₂SO₄ and saturation of Ca(OH)₂) with 5 %mass of the lubricating comb-polymer.
Figure 4.9 – Topography of the quartz surface by white light interferometry. Image size 1.3 x 0.95 μm. The RMS roughness = 100 ±10 nm.

**Protocol.** The sliding surfaces were immersed without contact between each other in the drop of the lubricating solution (100 μL) for 10 min before the beginning of the measurement. The polymers from the lubricating solution are adsorbed on both surfaces via calcium bridging under alkali conditions.

In addition, in order to prevent acidification of the solution by CO$_2$ dissolution, the measurements were performed under a N$_2$ atmosphere at room pressure and temperature. Neither modification of pH nor CaCO$_3$ precipitation was observed during the experiments.

The experiments were carried out at a sliding velocity of 640, 70 and 17 μm/s under a constant load of 100 mN over a 2-mm-long track under reciprocating conditions. Under these conditions, according to Hertz’s theory [188], the average local pressure is around 0.1 GPa and the expected contact radius is 16μm, which remains small compared to the sliding distance. The average friction coefficient is then calculated over a distance of 1.2 mm.
4.2 Validation on quartz filler pastes

4.2.1 Description of the system

The test of the relevance of our framework on cement-like slurries requires the measurement of the boundary-lubrication tribological properties of the surfaces and the rheological properties of polymer-coated particle slurries.

In order to prevent any impact of chemistry on the results, the particles were chosen to be inert in the salty alkaline solution. Among the different possibilities, a quartz filler was chosen for this test because this material was available both as a micron-scale powder for the rheology and as macroscopic block for the tribology. Moreover, the quartz filler we chose has the advantages of exhibiting almost no yield stress and a very intense shear-thickening regime.

In order to quantify the impact of the particle coefficient of friction on the filler-slurry flow curves, the surface properties of the grains have been tuned by adsorption of a comb polymer. In this study, we chose a set of 4 PMAA-g-PEG polymers that are currently used in the concrete industry. For the sake of simplicity, they have been designated with a single letter and a color code as follow:

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Backbone size</th>
<th>Grafting Ratio</th>
<th>PEG size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer A</td>
<td>4.3 kDa</td>
<td>4.0</td>
<td>2.0 kDa</td>
</tr>
<tr>
<td>Polymer B</td>
<td>3.4 kDa</td>
<td>2.3</td>
<td>2.0 kDa</td>
</tr>
<tr>
<td>Polymer C</td>
<td>4.3 kDa</td>
<td>4.0</td>
<td>0.5 kDa</td>
</tr>
<tr>
<td>Polymer D</td>
<td>5.0 kDa</td>
<td>1.5</td>
<td>2.0 kDa</td>
</tr>
</tbody>
</table>

Table 4.2 – Nomenclature and characteristics of the polymers used in this section

4.2.2 Tribology

The friction between quartz filler microparticles cannot be directly and accurately measured due to their complex and irregular shapes. It is actually extremely difficult to carry out tribotests on any crystalline solid microparticles, because they are polyhedrons. Indeed it is not even possible to make tribotests between their polyhedral flat faces because
Figure 4.10 – Friction force for the 3 sliding speeds and a constant load of 100 mN on one cycle of amplitude 2mm for polymer C. Each value was recorded over a 8µm sliding distance (due to time resolution of the apparatus) but only 50 values per speed (equally spaced) are plotted.

the smallest angle between them would lead to a bias in the BL friction force due to a viscous lift, and it is hardly possible to measure the friction between a face and an edge because the latter will become rounded by wear during the test.

In order to establish the difference between the lubrication ability of the four tested polymers, the friction force was measured on a model tribosystem: a borosilicate glass sphere with a radius \( R_{ball} = 2 \) mm and a polished quartz plane. In this system, the geometry of the contact is well defined and fairly stable during the tribotest. The properties of both surfaces are close to those of the quartz filler grain surfaces and in the presence of the alkaline salty polymer solution, both surfaces become coated by a lubricating polymer brush.

The experiments were carried out using a CSM Nanotribometer in an \( N_2 \) atmosphere with a load \( F_N \) of 100mN at sliding velocities \( v_{sliding} \) between \( 10^{-5} \) and \( 10^{-3} \) m/s after careful cleaning of the surfaces and adsorption of the polymer brush. The details of the surface preparation are described in Section 4.1.3.

As shown in Fig.4.10, the friction force does not depend on the sliding velocity. This confirms that the system is in the boundary-
lubrication regime, in agreement with the low value of the Hershey number $H = \frac{v_{sliding} \eta_f}{\langle P \rho_{RMS} \rangle} \in \left[10^{-7}; 10^{-9}\right]$. Moreover, after a short transient regime, the friction force was also found to be stable for more than twenty cycles. The value of the boundary coefficient of friction for the 4 polymers are reported in the Table 4.3:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Coefficient of Friction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.6 ± 0.08</td>
</tr>
<tr>
<td>B</td>
<td>0.9 ± 0.05</td>
</tr>
<tr>
<td>C</td>
<td>0.9 ± 0.05</td>
</tr>
<tr>
<td>D</td>
<td>1.1 ± 0.06</td>
</tr>
</tbody>
</table>

Table 4.3 – Coefficient of friction in boundary lubrication in the presence of each polymer measured with the Nanotribometer

These coefficients of friction are significantly higher than the reported values for such contact, especially in the presence of polymer brushes. This could be explained by the composite roughness of the tribosystem. It could also be due to the wear of the surfaces that we observed. By optical microscopy after the tribotest, we measure 35 $\mu$m-large tracks, in agreement with the expected radius of contact.

These results also show that, by adsorbing comb polymers with different architectural parameters, we can significantly tune the friction coefficient in the boundary regime of the quartz surface. The relation between the polymer architecture and the frictional behavior is explored in more detail in Section 4.3.

4.2.3 Rheology

A strong prediction of our model is that the minimum volume fraction at which the suspension can experience discontinuous shear thickening corresponds to $\phi_{max}^{BL}$, the jamming volume fraction of the granular media in the absence of any hydrodynamic lubrication and therefore this volume fraction is a decreasing function of the boundary-lubrication coefficient of friction.

First, the jamming volume fractions, $\phi_{max}^{BL}$, of filler suspensions with the four different polymer coatings were measured by compressive
rheology. Secondly, the shear thickening of the same suspensions was studied by means of shear rheology.

**Compressive Rheology: Measurement of \( \phi_{max}^{BL} \)**

\( \phi_{max}^{BL} \) corresponds to the maximum volume fraction that can be obtained in the absence of fluid lubrication. We approximate this volume fraction by measuring the sediment volume fraction after an intense centrifugation of the suspension.

Due to the large density mismatch between the grains and the suspending fluid (here, \( \Delta \rho = 1.65 \text{g/cm}^3 \)) and to the large centrifugal acceleration (\( \approx 2000 \text{g} \)), during the centrifugation, the grains readily sediment, creating a loose sediment at the bottom of the flask. Then, due to the pressure they apply on each other (of the order of \( 10^5 \text{ Pa} \)), this sediment is slowly compressed until it reaches a jamming volume fraction. Since the pressure that is applied on the grains is high and the velocity of the grains compared to each other is geometrically limited in the sediment, we can suppose that most of the contacts are boundary lubricated during the sediment compression. Thus, the sediment jamming volume fraction provides us with an approximation of \( \phi_{max}^{BL} \).

To the best of our knowledge, this technique has rarely been reported in the scientific literature before. Some centrifugation tests have been reported for measuring the yield stress of cement pastes [116, 159] but in these cases, the compression pressure were only on the order of \( 10^2-10^3 \text{Pa} \). A few tests with compressive pressure similar to the one used here have been shortly reported by Kjeldsen et al. [116]. In those experiments, all the PMAA-g-PEG coated magnesia particle suspensions sedimented at the same volume fraction independently of the polymer architecture parameters in apparent contradiction with the results we reported here. This apparent disagreement could be explained by the significant differences between Kjeldsen’s and our system in term of Hamacker constant, particle surface hardness and roughness, polymer grafting ratio and dosage, or sample preparation even if the role of each of these parameters is still unclear.

Experimentally, fairly dilute (\( \phi = 0.47 \)) suspensions of quartz fillers in an alkali aqueous suspending fluid with an excess of lubrication polymer were realized, poured into 10mL flasks, briefly whirly-mixed and
centrifuged at high speed (see Section 4.1.2 for details). Fig. 4.11 shows the flasks obtained after centrifugation. Knowing the common initial mass of filler and the height of the sediment in the cylindrical neck of the flasks, the sediment volume fraction is calculated. The results for the four polymers are the following:

![Figure 4.11](image.png)

**Table 4.4** – Sediment volume fraction after centrifugation of quartz suspensions in the presence of different polymers

<table>
<thead>
<tr>
<th>Sediment Volume Fraction (±0.005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer A 0.578</td>
</tr>
<tr>
<td>Polymer B 0.560</td>
</tr>
<tr>
<td>Polymer C 0.555</td>
</tr>
<tr>
<td>Polymer D 0.545</td>
</tr>
</tbody>
</table>

**Shear Rheology**

The rheological analysis was performed on quartz suspensions with φ between 0.47 and 0.57 in the alkali polymer solution using a helicoidal paddle geometry. The data that are presented here were obtained in a descending logarithmic stress ramp after pre-shear (from 700 to 0.01 Pa in 100s) in the presence of an excess of lubricating polymer (see Section 4.1.2 for details).
Yield Stress. As shown in Fig. 4.12, no yield stress was measured for any of the reported experiments even at the highest volume fraction. This is first due to the intense pre-shear of our pastes and the relative short duration of our shear test that limit the thixotropic effects. Moreover, the absorbed polymer brushes create a repulsion between grains and limit the yield stress. Finally, it is also due to the relatively low volume fractions used here. This value is around 20% lower for shear thickening suspensions of spheres [63] or of our calcite filler [197]. This ability to experiences intense shear thickening at relatively low volume fraction is probably due to the fact that the quartz grains are angular [13].

Low-shear behaviour. In absence of yield stress, at low shear, the suspension exhibits a Newtonian behaviour with a viscosity that depends on the volume fraction, as shown in Fig. 4.12 & 4.13. Additionally, we found that this Newtonian viscosity, \( \eta_{Nw} \), was independent of the polymer coating (see Fig. 4.13 & 4.14). This seems to confirm that a large majority of the contacts between grains are hydrodynamically lubricated and that the boundary coefficient of friction does not play any role in this regime.

These observations contrast with some previously reported measurements such as Refs. [100, 197], in which the polymer coating seems to play a role in the value of the viscosity plateau. This difference can be explained by the flocculation and the volume fraction of the suspensions. Indeed, the reported "Newtonian viscosity" often refers to the viscosity in a short range of shear between the shear-thinning and the shear-thickening regime. It is then difficult to know if this short plateau is a viscous dominated regime or just an extended transition from shear-thinning to shear-thickening regimes. The volume fractions that we used, which are small compared those reported in some other experiments can also explain why \( \eta_{Nw} \) is polymer independent, since high volume fractions promote BL contacts between grains, even in the Newtonian regime.

High-shear behaviour. For high shear rates, the fluid shear-thickens. At moderate volume fractions, the system undergoes CST with \( \tau \propto \dot{\gamma}^2 \) (Bagnoldian regime) as observed in Ref. [63], while for the highest volume fractions in our experiment, the abruptness of shear thickening increases quickly at a critical \( \phi \) (see Fig. 4.12 for Polymer A). Above this threshold,
**Figure 4.12** – Viscosity $\eta$ vs shear rate $\dot{\gamma}$ with adsorbed polymer A for various volume fractions $\phi$ of quartz filler suspensions. In dotted line, an example of the determination of $\dot{\gamma}_c$ with $\phi = 0.516$.

**Figure 4.13** – Viscosity in the Newtonian regime, $\eta_{N_w}$, as a function of the volume fraction $\phi$. The Newtonian viscosity does not depend on the polymer coating (Symbols are the same as in Table 4.2). The low values of the viscosity confirm that the studied volume fractions are far from $\phi_{N_w}^\text{max}$. The slight dispersion of the results, the distance to the divergence and the variety of parametric formulae proposed in the literature [45] do not allow us to provide a pertinent fit of $\eta_{N_w}(\phi)$. 
the suspensions display DST.

Experimentally speaking, the shear-thickening regime is stable and reversible in the time scale of our experiment. Nevertheless, one can observe when keeping the suspension in the shear-thickening regime for several minutes that the viscosity slowly decreases. Since this viscosity decrease is not reversible by re-homogenization or long rest of the suspension and consequently not a consequence of particle migration or polymer desorption, it is probably due to plastic damages at the grain level (probably due to wear during BL contacts).

In order to quantify the DST critical volume fraction, the flow curves for the various $\phi$ in the ST regime are fitted by an Oswald-De Waele power law: $\eta \propto \dot{\gamma}^n$.

In Fig. 4.15, we show that $n(\phi)$ diverges at the polymer-dependent $\phi_{\text{BL}}^{\text{max}}$ that we measured independently by centrifugation, as predicted by our model. Moreover, the data from the different polymer coatings collapse onto a single master curve as a function of a reduced volume fraction $(\phi_{\text{BL}}^{\text{max}} - \phi)/\phi_{\text{BL}}^{\text{max}}$ that does not depend on surface properties.

One can notice that a very similar collapse was also observed for particles of different convex shapes by Brown et al. [36]. This would support the idea that the scaling of the divergence of the viscosity
(jamming) when $\phi$ is approaching $\phi_{max}^{BL}$ is similar for a large variety of suspensions independently of the shape, the mechanical properties and the surface properties of the solid suspended particles. The generality of this feature could become a major fascinating subject of study for theoreticians.

We also notice that further away from the divergence volume fraction, the Oswald-De Waele exponent seems to stabilise close to a value of 1 (Balnold scaling), which is compatible with our framework. Nevertheless, due to the low viscosity of the Newtonian regime for volume fraction lower than 0.47, it was not technically possible to prove experimentally that this stabilisation occurred because of the expulsion of the fluid from the geometry.

In terms of critical shear rate, as shown in Fig.4.16, it also seems that the relevant parameter is not the volume fraction but the reduced volume fraction. Indeed with this rescaling, the data for the four different polymers collapse. Nevertheless, the little extension of the data on the critical shear rate does not allow us to confirm either the theoretical scaling we found in Section 2.1.3: $\dot{\gamma}_c \propto I^2 \propto \left(\frac{(\phi_{max}^{BL} - \phi)}{\phi_{max}^{BL}}\right)^2$ or the scaling proposed by Fall et al. [63] $\dot{\gamma}_c \propto \frac{(\phi_{max}^{BL} - \phi)}{\phi_{max}^{BL}}$. 

**Figure 4.15** – Oswald-de Waele exponent, $n$, versus the reduced volume fraction. Inset: Same data as in the log-log plot. The solid line is a power-law fit for $(n - 1)$ versus reduced volume fraction. (Symbols are the same as in Table 4.2).
4.2 Validation on quartz filler pastes

Figure 4.16 – Critical shear rate, $\dot{\gamma}_c$, versus the reduced volume fraction. (Symbols are the same as in Table 4.2).

4.2.4 Conclusions

By adsorbing different comb polymers on quartz filler grains, we change their coefficients of friction in boundary contacts. This allows us to show that in the Newtonian regime, most of the dissipation is viscous and, since we used only a single type of grains, the pertinent parameter is the volume fraction, independent of the polymer coating. In contrast, in the shear-thickening regime, the polymer coating radically modifies the flow behaviour of the pastes. In particular, we show that the DST critical volume fraction is controlled by the BL coefficient of friction, similarly to what our framework predicts (see Fig.4.17). Moreover, we observed that the sharpness of the shear thickening, as well as the critical shear rate are directly linked to the reduced volume fraction $(\phi_{\text{BL}}^{\text{max}} - \phi)/\phi_{\text{BL}}^{\text{max}}$. Thus, $\phi_{\text{BL}}^{\text{max}}$ appears to be the most relevant parameter to predict the behaviour of a given suspension in the shear-thickening regime. Finally, we also prove that $\phi_{\text{BL}}^{\text{max}}$ can be approximated with good precision by the volume fraction of the sediment, when this suspension is centrifuged at high speed.

At this point, we can underline two industrial outputs of this study. First, modifying the nature of the polymer brush on the cement grains to reduce its BL coefficient of friction is a solution to increase $\phi_{\text{BL}}^{\text{max}}$ and thus
reduce the shear thickening for a fixed volume fraction. Secondly, an easy and rapid compressive rheological test is able to give an approximate of $\phi_{\max}^{BL}$ for any cement slurries.
4.3 Optimisation of polymer chemistry

The previous section also stated that our compressive rheology technique allows for a rapid and easy quantification of this control parameter for dense suspensions of hard particles. Compressive rheology is a handy tool to measure the impact of different polymer coatings on the reduction of shear thickening. In this section, we apply this technique to various filler suspensions (quartz and calcite) with a large variety of polymer coatings in order to determine the effects the polymer architecture. In this section, the concentration of sulfates ions in the suspending fluid is higher than in the previous one. These ions are known to compete with the adsorption of the carboxylic anchors and, to a smaller extend, of phosphate anchors [51, 212].

4.3.1 Impact on the yield stress

Since we would like to use this technique with calcite filler suspensions, which can exhibit a yield stress, it is important to verify that the existence of a yield stress does not modify the measurement. The centrifugal pressure during the compression is on the order of $10^5$ Pa, significantly larger than the yield stress of filler pastes and consequently, no significant effect of the yield stress is expected. To prove it experimentally, we compare three suspensions of calcite with respectively Glenium 27 only, Optima 100 only and a mix of the two polymers. The shear-rheology tests, carried out under similar conditions as previously and presented in Fig.4.18, reveal that the suspension with the polymer mix behaves as the first one at low shear (deflocculation) and as the second one at high shear rate (shear thickening). The results of the centrifugal tests show that the suspension with the polymer mix behaves, in compression, similarly to the that with Optima 100. This seems to indicate that our technique is not sensitive to the presence of yield stress.

Even if the yield stress has no major impact on the measurement itself, the suspensions with the highest yield stress cannot be measured for practical reasons. Indeed the filling of the flask implies a double-flow process (suspension downward and air upward). Since the thickness of the suspension layer flowing due to its gravity is an increasing linear function of the yield stress [135], the most flocculated suspensions plug the thin neck of the flask and block the air counter-flow. This issue can
be solved easily by designing tailored glassware.

### 4.3.2 Saturation

It is important to know the impact of the polymer-to-particle-mass ratio on the sedimentation, i.e. the dry mass of polymer compared to the mass of powder. The results for PMAA-g-EGPh-g(1.5)-PEG(2) on calcite and for Glenium 27 on quartz are reported in Fig.4.19 and 4.20. The suspensions without any polymer cannot be measured, because they cannot flow. Increasing the quantity of polymer, the sediment gets denser until it achieves a saturation value, $\phi_s$. Above this saturation quantity, any further addition of polymer has no significant effect. For all the polymers tested, the saturation quantities of polymer correspond to a surface density of 60-90 ng/cm² of powder BET surface, similar to the maximum surface density found in adsorption tests for similar fillers [54, 165].

### 4.3.3 Impact of the PEG chain length

The results presented in Section 4.2 seem to show a positive dependence of the sediment volume fraction with the side chain length for quartz suspensions (Polymers A and C). Nevertheless the contrary effect was found when comparing PMAA-g(1.5)-PEG(0.5) ($\phi_s = 0.54$)
4.3 Optimisation of polymer chemistry

Figure 4.19 – Sediment volume fraction of suspensions of calcite with PMAA-g-EGPh-g(1.5)-PEG(2) in aqueous solution ([K$_2$SO$_4$] = 80 mmol/L and saturation of Ca(OH)$_2$ (90 mg))

Figure 4.20 – Sediment volume fraction of suspensions of quartz with various concentrations of Glenium 27 in aqueous solution ([K$_2$SO$_4$] = 80 mmol/L and saturation of Ca(OH)$_2$, 90 mg)
and PMAA-g(1.5)-PEG(2) ($\phi_s = 0.522$).

The results are different for calcite. In Fig.4.21, the sediment volume fraction for suspensions of calcite is reported in the presence of an increasing quantity of PMAA-g-EGPh-g(4)-PEG(2) and PMAA-g-EGPh-g(4)-PEG(5). No difference between the effects the two polymers has been found. Similar results were found for PMAA-g-EGPh-g(1)-PEG(0.5) et PMAA-g-EGPh-g(1)-PEG(2) (see Fig.4.22).

4.3.4 Impact of the grafting ratio

In Fig.4.23, the sediment volume fractions for calcite suspensions in the presence of increasing concentrations of phosphate-anchor comb polymers with same side chain length (2kDa) and different grafting ratios are plotted. In addition to the previously stated effect of the polymer concentration, we see that the polymers with the highest grafting ratio give the densest sediments.

This effect seems robust since it was also observed for quartz suspensions with phosphate-anchor polymers (see Fig.4.24) and calcite
Figure 4.22 – Sediment volume fraction of calcite suspensions for various concentration of PMAA-g-EGPh-g(1)-PEG(0.5) or PMAA-g-EGPh-g(1)-PEG(2) in aqueous solution ([K$_2$SO$_4$] = 80 mmol/L and saturation of Ca(OH)$_2$, 90 mg)

Figure 4.23 – Sediment volume fraction of suspensions of calcite with different concentrations of various phosphate-anchor polymers in aqueous solution ([K$_2$SO$_4$] =, 80 mmol/L and saturation of Ca(OH)$_2$, 90 mg)
suspensions with carboxylic-anchor polymers (see Fig. 4.25).

Moreover the phosphate-substituted polymers are significantly more efficient, i.e. they produce denser sediments, than their carboxylic equivalents. Since the polymers are attached to the surface by calcium bridging, we propose to interpret the data using not only the grafting ratio, $g$, but also the binding energy between a single anchor and a calcium ion. This binding energy can be quantified by $\log(K_B)$ with $K_B$, the binding constant of the fully dissociated anchor with a calcium ion. These specific binding constants are not directly tabulated in the literature, thus we approximate their values by referring to similar chemical compounds. The carboxylic anchor is approximated by the propanoic acid, the phosphonic anchor by the ethylphosphonic acid and the N-iminobis(methylphosphonic) anchor by N-Methyliminobis(methylphosphonic acid). The values we used are reported in Table 4.5 and are representative of the values tabulated in Refs. [137, 169] for room temperature and an ionic strength of 0.1.

Figure 4.24 – Sediment volume fraction of quartz suspensions at saturation of polymer, $\phi_s$, for various phosphate-anchor polymers in aqueous solution ($[K_2SO_4] = 80$ mmol/L and saturation of Ca(OH)$_2$, 90 mg)
Figure 4.25 – Sediment volume fraction of calcite suspensions at saturation of polymer, $\phi_s$, for various carboxylic-anchor polymers in aqueous solution ([K$_2$SO$_4$] = 80 mmol/L and saturation of Ca(OH)$_2$, 90 mg)

Table 4.5 – Values of the binding constant of the different anchors with a calcium ion.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Log ($K_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COO$^-$</td>
<td>0.45</td>
</tr>
<tr>
<td>PO$_3^{2-}$</td>
<td>1.6</td>
</tr>
<tr>
<td>N-(CH$_2$-PO$_3^{2-}$)$_2$</td>
<td>4.6</td>
</tr>
</tbody>
</table>

In Fig.4.26 and 4.27, the sediment volume fraction at polymer saturation as a function of $\tilde{E} = g \cdot log(K_B)$, for various polymers with 2kDa side chains is plotted for quartz and calcite. The connection between the data on quartz seems to confirm that $\tilde{E}$ is a pertinent parameter to quantify the effect of a given polymer.

The rescaling is similar for the calcite suspensions but the data are slightly more dispersed. Indeed, for calcite, in addition to the binding energy, the geometry of the anchor can play a role since the calcium ions are already included in a crystalline network [171].
Figure 4.26 – Sediment volume fractions of suspensions of quartz at polymer saturation for various polymers with 2kDa PEG chain in aqueous solution ([K₂SO₄] = 80 mmol/L and saturation of Ca(OH)₂, 90 mg). Symbols are the same as in Figs. 4.24 & 4.25 and the orange circle represents Optima 100.

Figure 4.27 – Sediment volume fractions of suspensions of calcite at polymer saturation for various polymers with 2kDa PEG chain in aqueous solution ([K₂SO₄] = 80 mmol/L and saturation of Ca(OH)₂, 90 mg). Symbols are the same as in Fig.4.26.
4.3.5 Conclusions on compressive rheology

Compressive rheology can provide a good estimate of $\phi_{\text{max}}^{BL}$. This section shows that it is also a precise and versatile technique that can be applied for various fillers and comb polymers. The short duration of the test also allows us to test the polymer architecture parameters that lead to denser sediment. While the influence of the side-chain length is unclear, the binding energy per PEG chain clearly appears to be the most relevant parameter: the more numerous and the stronger the anchors, the denser is the sediment. Moreover, we did not experience any correlation between the shear-thickening behaviour and the yield stress. Since the latter is known to be directly correlated to the mass surface density of PEG (in case of partial coverage) or thickness of the PEG layer (in case of full coverage) [67], it seems that the condition to reduce the friction between grains is not only to adsorb a large amount of polymer, but also to adsorb them firmly. An higher affinity of the comb polymer for the surface seems to be critical, probably because it leads to polymer brushes that are denser and keep more efficiently their conformation during the boundary-lubricated contact between grains.

Nevertheless, from an industrial perspective, increasing the concentration of calcium-binding chemical groups in cement slurries can significantly delay the setting. Thus a balance between flowing and setting properties will have to be found for each application.
4.4 Conclusions

The experimental validation of our framework aimed at producing particle suspensions, in which we can tune the particle-pair coefficient of under boundary lubrication. We achieved this by adsorbing different comb polymers onto quartz grains. In shear rheology, in addition to the well-known transition from CST to DST with increasing volume fraction, we have also observed a similar transition with increasing particle BL coefficient of friction. Both observations fit with our theoretical framework and with the simulation results. In addition, we confirmed that the distance to the critical volume $\phi_{max}^{BL}$ determines the intensity and the onset of shear thickening.

We propose a novel compressive rheology technique based on intense centrifugation to provide an estimate of $\phi_{max}^{BL}$. This technique combines many advantages compared to the usual measurement of the ST critical volume fraction (several shear rheology tests with increasing volume fractions and a power law fit of $n$-divergence). It is experimentally easier because it does not require manipulation of very high volume fraction pastes. It is faster because accurate results are obtained in a single experiment. If some shear-thickening cement pastes become commercialised, this technique could become the equivalent of the slump test for high-shear behaviour.

Moreover, we applied this technique to a large variety of pastes in order to determine the impact of the comb polymer architecture on the shear thickening of quartz and calcite fillers. The most important parameter seems to be the binding energy per side chain, showing that a low boundary coefficient of friction is only achieved when the dense adsorbed PEG brush can maintain its conformation at the surface during the boundary-lubricated contact between grains.
Chapter 5

Toward a Precise Measurement of Inter-particle Friction

In the previous chapters, we explored the link between the macroscopic flow of granular media and the frictional properties of the particle contacts. We especially emphasised the case of the shear thickening of non-Brownian suspensions, but also noted the importance of friction for other media and flow regimes.

For this reason, a precise measurement of the frictional properties of particle-particle contact appears to be a crucial requirement in order to understand unsolved granular media rheology issues. In the case of suspensions, since the hydrodynamic regime is well understood, especially for Newtonian fluids, the main obstacle is the measurement of the properties of a boundary lubricated contact between two particles. Until now, this has been poorly addressed.

In this chapter, we explain how, by means of AFM-Tribometry, the mechanical properties of a particle-particle contact can be explored (Section 5.1) and we propose a new, precise and robust method, based on lateral force microscopy, to measure the coefficient of friction between microspheres quantitatively and without complex data processing (Section 5.3). Finally, in Section 5.4, we apply this method to the contact between silica microspheres in liquid, with and without polymer coatings.
This chapter is based my personal work, under the supervision of J. Cayer-Barrioz, L. Isa and N.D. Spencer, that will be published as:


*A Direct, Robust Technique for Measurement of Friction between Microspheres*

Submitted to Langmuir (2014)
5.1 Relevance of AFM-tribometry

There are very few techniques that allow a robust and reliable measurement of friction for particles below the millimetre range. For a long time, the microscopic scale could not be accessed via standard tribometric measurements.

Some important steps forward were taken by the introduction of the surface forces apparatus (SFA) (by Tabor [106, 194] and by Georges [141, 196]), which allows contact forces to be measured in micrometre-scale contacts. Unfortunately, this is restricted to specific solid surfaces (mica for Tabor’s SFA) or non-aqueous lubricating liquids (for Georges’s SFA - molecular tribometer). Moreover sphere-on-sphere contacts are not readily implemented in an SFA and consequently these instruments are not really suited to the investigation of microparticle tribology.

These limitations are overcome by the recent development of AFM-based tribometry [139]. This technique has already been used to characterize the adhesion between particle pairs [91–93] and the interaction potential between charged particles in electrolyte solutions [43, 167, 168, 177, 195]. It is also commonly used to measure the friction between a “colloidal probe” and a flat surface [6, 20, 213], but its extension to particle-on-particle friction measurements is far from trivial.

In fact, for particle-friction measurements, the complexity does not only arise from the small size of the objects, but also from their shapes; the exact geometry of the contact deeply influences friction measurements [120, 142, 192]. To date the most successful friction measurement between pairs of microspheres has been demonstrated by Ling and co-workers [131]. In their seminal work, these authors attached a 3-4μm silica sphere onto an AFM cantilever and measured its friction in air against other identical silica microparticles attached to a flat surface as a function of various preparation protocols. Their measurements are based on a pixel-by-pixel analysis of the LFM images. This requires complex image post-processing to produce a local map of the point-by-point friction between the two surfaces in contact.

However, the high level of symmetry of a sphere-on-sphere contact can be exploited to design a much simpler technique that readily allows the measurement of the average friction between the two spherical surfaces in relative motion, which is, ultimately, the friction coefficient that is relevant for e.g. comparing with rheological experiments.
5.2 Materials and methods

5.2.1 AFM tribometry

General features of Lateral Force Microscopy.

![Figure 5.1 – Schematic view of the optical setup of a 4-quadrant AFM (modified from [208])](image)

Atomic force microscopy (AFM) and derived techniques have been, from the 80’s, predominantly used as a tool for the characterisation of surfaces and manipulation of micron-sized objects. All these techniques rely on the conversion of the desired parameter (topography, force, electrostatic charge...) into a motion of the extremity of a micron-sized cantilever. A laser beam is reflected from the back of the cantilever toward a position-sensitive photodetector (PSD), which converts incident light power into electrical voltage signals. The interpretation of these voltage signals then leads to the quantification of the desired parameter. In our case, we want to measure the normal and frictional forces that are applied in the contact between a microsphere glued to the cantilever and a microsphere glued on the sample (see Fig. 5.4).

We chose to work with an MFP 3D Instrument (Asylum Inc., Santa Barbara, USA), which has a 4-quadrant PSD (see Fig. 5.1). As illustrated in Fig. 5.1, the difference between the voltage signal (1+2) and (3+4), called normal deflection, can be converted into the bending of the cantilever, $\theta_N$, and thus into the vertical force applied on the
scanning particle with optical, geometrical and mechanical parameters of the system. The difference between the voltage signal \((1+3)\) and \((2+4)\), called lateral deflection, can be converted into the torsion of the cantilever, \(\theta_{tor}\) and thus into the lateral force experienced by the scanning particle (see next section for calibration details).

In order to keep the load in the contact as constant as possible, the AFM is operated in contact mode, where the sample is moved horizontally according to a defined path and the vertical position is controlled by a feedback loop in order to keep the normal deflection constant.

**AFM tribology calibration.**

The normal and lateral signals, measured with AFM, were converted to forces using appropriate calibration constants. The cantilever normal spring constant calibration was carried out using the thermal-noise method [103] before the attachment of the colloidal probe. The torsional spring constant was estimated using Sader’s method [85] with the help of Sader’s online calibration applet\(^1\). The normal sensitivity was directly measured by contact with the flat glass surface. The lateral sensitivity (SL) of one cantilever was estimated using the test-probe method, as described by Cannara et al. [37] for rectangular cantilevers (see Fig.5.2). The lateral sensitivity of all the other cantilevers was estimated from the measured lateral sensitivity of the test cantilever.

### 5.2.2 Materials

The major interest of this chapter is to use particles that are of relevance in rheology. For this reason, we worked this silica microspheres.

**Particles**

The soda-lime glass Petri dishes (Duran Group, USA) were sonicated in Milli-Q water and then immersed in Piranha solution (70% sulphuric acid, 30% hydrogen peroxide solution (30%) for 20 min under stirring and then rinsed in Milli-Q water 10 times. Monomodal Stöber silica particles with a mean diameter of 9.78 \(\mu m\) and a standard deviation

\(^1\)www.ampc.ms.unimelb.edu.au/afm/calibration.html#torsional
of 10.8% (Whitehouse Scientific Limited, UK) were spread on the glass surface. The first layer was immobilised by sintering the surface of the glass (600°C, 3 hours). Because the glass transition temperature of the amorphous silica is higher than that of soda-lime glass, this thermal treatment does not sinter the spheres. Indeed, no bridging between two spheres was observed.

The Petri dishes were then sonicated in Milli-Q water to detach the particles, forming the second and upper layers. After treatment, the monolayers covering the Petri dishes were used in AFM as scanned particles. The particles that detached under sonication were collected, glued on the cantilever and used as scanning spheres.

**Scanned spheres** The Petri dish with a particle monolayer attached on it was cleaned in Piranha solution (same protocol as previously) in order to remove any organic contaminant and restore silanol groups at the silica surface. Due to the absence of organic compound in the sample, the risk of contamination of the contact is lowered compared to previous techniques [131]. Moreover the glass surface between particles provides a clean, flat, rigid surface that can also be used for the normal cantilever calibration.

**Scanning spheres** The particles that detach themselves during the Petri dish sonication were collected from the surrounding fluid by centri-
Figure 5.3 — (Top) High-resolution AFM topography of the surface of a particle after sintering and Piranha cleaning. The main curvatures of the spherical surface have been removed by image processing. The roughness was $R_a = 10.4nm$ and $R_q = 12.7nm$. (Bottom) Example of topography along a line (the position of extraction is marked by an arrow on the main image)
fugation. The sediment is cleaned in Piranha solution (same protocol as before with centrifugation between rinsing steps) and dried for 2 days at low pressure (50 mbar, static, in air). One of these spheres was glued onto a tipless cantilever (NSC 36 copper-gold coated, Spring constant around 1N/m, from MikroMasch, Tallinn, Estonia) using a small amount of epoxy glue Araldite standard (Huntsman, The Woodlands, Texas) by means of a micro-manipulator (DC-3K from Märzhäuser, Wetzlar, Germany) under an optical microscope.

Lubricating fluid.

A salty alkaline solution ([K$_2$SO$_4$] = 80mmol/L and saturation of Ca(OH)$_2$) was used as lubricating fluid. Due to the calcium hydroxide, the solution pH is around 13. From 50mL of stable K$_2$SO$_4$ aqueous solution, before each experiment day, a fresh solution was produced by adding 90mg of Ca(OH)$_2$ in a polypropylene centrifuge tube (TPP, Switzerland). The tube was agitated for 10 min and then centrifuged to separate the solid lime grains. Neither pH change nor CaCO$_3$ crystals were detected upon storing the lubricating fluid in a centrifuge tube for several days.

Polymers.

The two comb polymers that are discussed in this chapter are similar to that used in previous chapters. They were diluted at 0.1%$_{mass}$ in the salty alkaline solution in order to create adsorbed polymer layers and have the following chemical architecture:

- A random copolymer of polyethylene glycol (2kDa) methacrylate (22.7%) and ethylene glycol methacrylate phosphate (77.3%). The backbone length is estimated by gel permeation chromatography around 4kDa. This polymer is referred as PMAA-g-EGPh-g(4)PEG(2).

- A random copolymer of polyethylene glycol (2kDa) methacrylate (22.7%) and methacrylate (77.3%). The backbone length is estimated by gel permeation chromatography around 4kDa. This polymer is referred as PMAA-g(4)-PEG(2)
As previously stated, due to their anionic anchors, these two polymers adsorb from solution onto silica surfaces by calcium bridging at high pH (see Section 1.4.3). Moreover, they are also representative of the ordinary admixtures that are used in the cement and ceramics industries. The polymer was diluted to 0.1% \(\text{mass} \) in the same salty alkaline solution.

Both polymers were synthesised and kindly provided by Lafarge LCR, France.

**Tribotest**

The surfaces were immersed in the lubricating solution (with or without polymer) 30 min before starting the tribotest. The whole measuring system was maintained under a \( N_2 \) atmosphere in order to prevent the reaction of \( Ca^{2+} \) with dissolved \( CO_2 \). In this way, the pH was kept around 13 (measured by pH indicator) and no calcite crystals could be seen in the bulk solution.

The cantilever particle was positioned on top of the centre of the target-scanned particle. An image of this particle obtained by the second one was recorded in contact mode with a scanning speed of 6\( \mu \text{m/s} \) (i.e. a contact point speed of around 3\( \mu \text{m/s} \)), perpendicular to the cantilever axis. The resolution of the image was set to 64x64 pixels. The size of the image was 6x6 \( \mu \text{m}^2 \), so the scanned region on each sphere was 3x3 \( \mu \text{m}^2 \) (see Fig.5.6). Since the radius of the contact between the two spheres was estimated from 10 to 30nm according to Hertz’ theory [188], the

**Figure 5.4** – Schematic view of the tribotest. The scanning sphere (glued on the cantilever) and the scanned sphere (fixed on the glass flat surface) were immersed in an aqueous solution and coated with a polymer layer. When they are maintained in contact and moved laterally compared to each other, the modification of the laser reflection allows the normal and frictional forces in the contact to be measured.
friction tracks (i.e. the scanning lines) did not significantly overlap but the full area was scanned.

Another original experimental characteristic of this sphere-on-sphere contact is that the contact point moves during the test on both surfaces. A local contamination of the cantilever sphere can then be easily detected as an area of anomalous friction or topography in the image. Moreover, since a given point of one sphere is always in contact with the same point of the other sphere, it is unlikely that any contamination spreads over the whole friction area. By comparison, in the traditional sphere-on-plane test, the contact only takes place on the top of the ball. In this case, contamination of the top of the ball cannot be detected (except by referring to external data) and this contamination will be spread over the full scanned area.

For a single particle, the scanning process was repeated several times with different normal loads, successively from low loads to high loads and back to low loads. No history dependence of the friction could be detected. A 2x2µm image of the top of the particle was manually cropped and used for the friction-coefficient calculation.
Figure 5.6 – Schematic view of a friction image (5x5 pixels) in the case of non-overlapping tracks and identical spheres: (a) Position of the friction tracks (A to E) on the sample sphere (lower sphere) and the cantilever sphere (upper sphere). In grey, the centre of the contact. The dotted lines represent the spatial sampling of the measurement. Top left: Position when measuring point A3. Bottom left: Position when measuring point C3. Right: Position when measuring point E3. NB: A given point on the sample sphere can be in contact only with its symmetric point on the cantilever sphere. (b) Projection of the friction tracks in the (x,y) framework of the cantilever. The mesh in background represents the pixel size. The areas in white were not scanned. (c) Final image. The value of each pixel corresponds to the average value of the vertical/horizontal forces for a given part of a friction track (example for E3 in pink). Due to the discretization, the area of each pixel and the area of the corresponding part in the friction track are different.
5.2.3 TlnAS

Principles of TlnAS.

Transmission interferometric adsorption sensing (TlnAS)[95] is an interferometry technique that allows measurements of adsorbed films on transparent surface (in our case, on sputtered silica, 8 nm RMS roughness with some 10-100 nm grains). The operating principle is shown in Fig.5.7, from the wavelength of the fringes' peaks formed when light is transmitted through a film adsorbed onto a special multi-layered TlnAS sensor, the software deduces the dry adsorbed mass, assuming the refractive index of the adsorbate,. The sensitivity is of the order of 1ng/cm² and the temporal resolution is 1s [138].

![Illustration of the operating principle of TlnAS.](image)

**Figure 5.7** – Illustration of the operating principle of TlnAS. White light passes through a custom multilayer sensor, and multiple partial reflections interfere to produce modulation of the transmitted light intensity with wavelength. (From Ref.[84])

Sample preparation

The silica-coated sensor was cleaned by successive sonifications for 10 minutes in four solvents (toluene, isopropanol, salty water ([K₂SO₄] = 80mM) and MilliQ water). The sensor was then enclosed in a dedicated sealed cell that was filled and maintained under a constant flux (100 μL/h) of the salty alkaline solution overnight, by the mean of a peristatic pump. The chemical stability of the surface was verified by the stability of the optical signal for an hour before the measurement. Then the polymer (0.5%_{mass} in salty alkaline solution) was injected in the cell. A constant flux of polymer solution was maintained during the adsorption.
5.3 Theory

We first derive a mathematical relation between the measured signal, the location, and the forces in the contact in a system consisting of two spheres and the AFM cantilever. Subsequently, we will show how this relation can be simplified, exploiting the symmetry of the problem.

As shown in Fig.5.8, the system is composed of two rigid homogeneous spheres in contact: Sphere 1, or scanned sphere, is glued to the sample holder and Sphere 2, or scanning sphere, is glued to the AFM cantilever. With a proper and accurate calibration of the cantilever (see Section 5.2.1 for detail), the deflections of the AFM laser can be converted into mechanical stresses on the cantilever in both vertical and horizontal directions.

5.3.1 Mechanical Analysis

For simplicity’s sake, the problem is described in the frame of reference of Sphere 1 in an orthonormal coordinate system $(O_1, e_x, e_y, e_z)$, in which $O_1$ is the centre of the scanned sphere, $e_x$ is in the trace scanning direction, $e_z$ is in the upward vertical direction and $e_y$ is chosen in order to have a right-hand coordinate system. The average radius of the spheres is defined as: $R_a = (R_1 + R_2)/2$. The position of the centre of the moving sphere, $O_2$, is $O_2 = (x \cdot R_a, y \cdot R_a, z \cdot R_a)$ with $(x, y, z)$ being its dimensionless position parameters. For geometrical reasons, the following calculation is restricted to $x^2 + y^2 + z^2 < 4$ (see the following dedicated paragraph for a stricter definition). The distance between $O_2$ and the torsional axis of the cantilever is called $\alpha R_2$. In the case studied here, there is no spacer (e.g., tip or excess of glue) between the colloid and the cantilever, so $\alpha = 1 + \frac{t}{2R_2}$ with $t$ being the thickness of the cantilever.

Sphere 2 experiences two contacts. The contact with Sphere 1 is a frictional point contact, and thus it transmits a repulsive force that is normal to the surface, $F_N$, and a friction force, $F_F$. In this nomenclature $F_N$ is not corrected from the adhesion. The direction of $F_F$ can be unambiguously determined by noting that $F_F$ is antiparallel to the velocity of Sphere 2 and therefore, perpendicular to $e_y$ and $F_N$. The impact of the cantilever torsion on the position of the contact point is
neglected. The contact with the cantilever has no degree of freedom and therefore can transmit not only a force $\mathbf{F}_C = (F_x, F_y, F_z)$ but also a moment $\mathbf{M} = (M_x, M_y, M_z)$.

In contrast to the sphere-on-plane case, the relations between these forces and moments depend on the relative location of the spheres and $F_N$ and $F_z$ are almost never equal. In order to clarify this dependence, the mechanical equilibrium of Sphere 2 at the contact point with Sphere 1 can then be projected on $\mathbf{e}_x$ and $\mathbf{e}_z$ for the forces and on $\mathbf{e}_y$ for the moment:

$$F_x = \frac{\pm \cos \phi}{\sqrt{1 - \sin^2 \phi \sin^2 \theta}} F_F - \sin \phi \cos \theta F_N$$  \hspace{1cm} (5.1)

$$F_z = \frac{\mp \sin \phi \cos \theta}{\sqrt{1 - \sin^2 \phi \sin^2 \theta}} F_F - \cos \phi F_N$$  \hspace{1cm} (5.2)

$$\frac{M_y}{R_2} = - \sin \phi \cos \theta F_z + (\alpha + \cos \phi) F_x$$  \hspace{1cm} (5.3)

With $\theta$ and $\phi$, the polar and azimuthal angles as defined in Fig.5.8, $\pm$ means “+” in the trace direction and “−” in the retrace direction and
\(\mp\) means the opposite. By substitution of \(F_x\) and \(F_z\) in Eq.5.3 using Eq.5.1 and 5.2, a direct link between the measurable quantities (\(F_z\) and \(M_y\)) and the forces in the contact (\(F_N\) and \(F_F\)) can be written as:

\[
\begin{bmatrix}
\frac{M_y}{R_2(\alpha+1)} \\
F_z
\end{bmatrix} = 
\begin{bmatrix}
\pm\frac{(1-\sin^2\phi \sin^2\theta)+\alpha \cos\phi}{(\alpha+1)\sqrt{1-\sin^2\phi \sin^2\theta}} & -\frac{\alpha \sin\phi \cos\theta}{(\alpha+1)} \\
\frac{\sin\phi \cos\theta}{\sqrt{1-\sin^2\phi \sin^2\theta}} & -\cos\phi
\end{bmatrix}
\begin{bmatrix}
F_F \\
F_N
\end{bmatrix}
\]

(5.4)

We define \(\gamma = \frac{-M_y}{(\alpha+1)R_2 F_z}\). \(\gamma\) immediately gives the friction coefficient in the sphere-on-plane case. Indeed, in this case, \(R_a = R_1 = +\infty\) then \(\phi = \theta = 0\) in Eq.5.1 & 5.3 and finally \(F_N = F_z\) and \(F_F = \frac{-M_y}{(\alpha+1)R_2}\). By definition of the sliding coefficient of friction \(\mu\): \(F_F = \mu(F_N) F_N\). By using Eq. 5.4 and the basic trigonometric relations:

\[
\sin \theta = \frac{-y}{\sqrt{x^2 + y^2}}
\]

(5.5)

\[
\cos \theta = \frac{x}{\sqrt{x^2 + y^2}}
\]

(5.6)

\[
\sin \phi = \frac{\sqrt{x^2 + y^2}}{2}
\]

(5.7)

\[
\cos \phi = \sqrt{1 - \sin^2 \phi}
\]

(5.8)

one obtains:

\[
\gamma = \frac{-\alpha x \sqrt{4 - y^2} \pm (2\alpha \sqrt{4 - x^2 - y^2} + 4 - y^2)\mu(F_N)}{(\alpha + 1)(\sqrt{4 - x^2 - y^2}\sqrt{4 - y^2} \pm 2x\mu(F_N))}
\]

(5.9)

In order to take advantage of the symmetry of the problem and the homogeneity of the surfaces, we define an average value of \(\gamma\) over a square area. The difference between trace and retrace signals is not strictly needed. Nevertheless, it is commonly used in order to remove any offset in the lateral deflection that can arise from initial setting and from
the position of Sphere 2 on the cantilever. It also significantly reduces
the error coming from a miscentered image.:

\[ \Gamma = \frac{1}{8a^2} \int_{-a}^{a} \int_{-a}^{a} \left[ \gamma_{\text{Trace}}(x, y) - \gamma_{\text{Retrace}}(x, y) \right] \, dy \, dx \]  

(5.10)

with \( a \), the half-length of the image section normalised by \( R_a \). Since
\( M_y \) is proportional to the lateral deflection and since \( F_z \) is kept constant
during the experiment, \( \Gamma \) is experimentally obtained by averaging the
trace and the retrace lateral deflection image, and dividing by the targeted
load.

Summarising, the friction coefficient \( \mu \) is calculated using Eq. 5.9
from the measured averaged value of \( \gamma \), as obtained from Eq. 5.10. This
constitutes a major difference with the technique proposed by Ling et al. [131] in which the coefficient of friction is calculated on each single
measurement point at the cost of a complex image processing.

5.3.2 Necessary requirements for the image size.

Because of the specific geometry, the scanned area cannot be arbit-
rarily large. In this paragraph, the size limit will be expressed in terms
of the image size, which is the relevant experimental parameter. One can
notice that, due to the curvature of the particles, the point of contact
moves less than the centre of the scanning sphere, \( O_2 \), (see Fig.5.6) and
thus the real scanned area is not the image size, i.e. \((2aR_a)^2\), but \((aR_1)^2\).

\( \Gamma \) is a function of \( \alpha \), \( \mu \) and \( a \). To maintain the contact between
the spheres, we must keep \( a < \sqrt{2} \). Moreover, \( a \) can be chosen to be
arbitrarily small in the limit of the AFM scanning capabilities. The
choice of \( a \) is affected by several requirements.

From an experimental point of view, the scanned area should be
large enough to average out the local heterogeneity of the surface. It is
also important to ensure that the size of the image is large compared
to the contact radius. Moreover, the range of \( z \) and \( z \)-speed that can be
reached by the cantilever is usually limited. Therefore, depending on
the particle size, only the topmost part of the spheres can be used. In
addition, far from the top of the particle, the contact sliding speed starts
differing from half of the scanning speed and also starts depending on
the position, due to the sphere curvature.
From a theoretical point of view, the validity of the formulae that will be provided in the following paragraphs is restricted to $a < 1$, to limit the coupling between normal force and local geometry, and to $a \mu \ll 1$, to limit the nonlinear coupling between normal and frictional force.

According to the range of particle radii that can be used with the present technique ($10^0$ to $10^2\mu m$), the most relevant scan size is in the range of $a \in [0, 0.4]$, which corresponds to scanning areas from 400x400nm$^2$ to 40x40\mu m$^2$, depending on the particle size. We note that $a$ can easily be reduced after the experiment by cropping the image.

### 5.3.3 Determination of the friction coefficient

In this part, the coefficient of friction is assumed to be constant over the range of normal forces that is applied during a single scan, where $\frac{\Delta F_N}{F_N} < \frac{a(8\mu + 5a)}{8}$. Indeed, even if the vertical force, $F_z$ is kept constant by the control loop of the AFM, the normal force changes due to the contact geometry and the friction force. The range of applied normal force is approximated from Eq.5.2 using $F_F = \mu F_N$. The case of variable coefficient of friction, which can occur in the case of high adhesion or during a transition between lubrication regimes, is addressed in the Section 5.3.5.

10 Due to the complexity of the mathematical relation, the link between $\Gamma$ and $\mu$ cannot be analytically expressed. Consequently, in the rest of the paper, $\Gamma$ will be approximated by its $(x, y)$-Taylor series in $(0; 0)$. After integration, $\Gamma$ can then be developed as a Taylor’s series of $a \mu$ that is arbitrary small (i.e. $a \mu \ll 1$). The errors arising from this approximation are detailed in the dedicated paragraph below. This leads to two formulae, depending on the value of the friction coefficient as described below: high and low friction.

#### High friction

Without further hypotheses concerning $\mu$ and keeping the second order in $a \mu$, one can determine the friction coefficient by solving the
For Centering  | For Normal Force  | For Friction Force
---|---|---
Topography  | Normal Defl. trace  | Lateral Defl. trace  
6 μm  | 500 nm  | 1.6 μm  
3  | 4.4 V  | 2.8 μm  
6  | -1.0  | 0.4 V  
3  | Average  | Average  
6  | Average  | Average  

\[ \mu , F_L \]  

Eq 11/12

**Figure 5.9** – Example of friction test results between bare spheres: a) Topography for selecting the area used for the friction analysis (red scale) b) Normal Deflection in trace for calculating normal force c-d) Lateral Deflection in trace (c) and retrace (d) for calculating the friction force.

following relation numerically with experimentally measured values:

\[
\left(1 + \frac{(3\alpha + 1)a^2}{24(\alpha + 1)}\right)\mu + \frac{a^2}{12}\mu^3 = \Gamma \tag{5.11}
\]

**Low friction**

If, in addition, the friction coefficient is low (i.e. \( \mu \ll 1 \)), Eq. 5.11 becomes:

\[
\mu = \left(1 - \frac{(3\alpha + 1)a^2}{24(\alpha + 1)}\right)\Gamma \tag{5.12}
\]

Due to the restrictions on the image half size \( a \) and because \( \alpha \gtrsim 1 \) if the colloid is directly glued on the cantilever, these equations also show that even the first-order relative correction is very small (\( \sim 10^{-2} \)). Consequently, this correction is often smaller than the common uncertainties arising from the cantilever calibration and can often be neglected (i.e. \( \mu \simeq \Gamma \)).
5.3.4 Determination of the additional errors

In this section, the link between the experimental errors and the uncertainty of the final results due to the sphere-on-sphere geometry, is detailed in the limit of small errors. Except for the error originating from the radius of the scanning sphere, these errors are specific to the technique. They only refer to the conversion from vertical and horizontal forces to the coefficient of friction and are cumulative with, for example, the errors from cantilever calibration, which converts the deflections into the vertical and horizontal forces. These errors have to be added to the classical AFM-tribology errors, especially the tip-calibration error, which can be very large compared to those mentioned in the following.

Scanned-sphere radius. Due to the presence of a large particle on the cantilever instead of a sharp tip, the radius of the scanned particle is not always precisely known. Since $R_1$ only plays a role in the length normalisation, this error in $R_1$, $\epsilon_{R_1}$, is equivalent to an error in $a$ in the Eq.5.12 or 5.11. Then, the relative error in the coefficient of friction due to $\epsilon_{R_1}$ is (highest non-zero order in $a$), in the low-friction case:

$$
\frac{\epsilon_{R_1}}{\mu} = \frac{3\alpha + 1}{24(\alpha + 1)} a^2 \frac{\epsilon_{R_1}}{R_a}
$$

(5.13)

and in the high-friction case:

$$
\frac{\epsilon_{R_1}}{\mu} = \left( \frac{3\alpha + 1}{24(\alpha + 1)} + \frac{\mu^2}{12} \right) a^2 \frac{\epsilon_{R_1}}{R_a}
$$

(5.14)

In our experimental case, the standard deviation of the particle radius is 1.15μm and so $\frac{\epsilon_{R_1}}{\mu} \approx 10^{-3}$.

Scanning-sphere radius. An error in $R_2$, $\epsilon_{R_2}$, is much more problematic, since Sphere 2 also plays the role of a lever. Nevertheless, Sphere 2 has been intensively manipulated under microscopy in order to be glued on the cantilever and can, during this process, be precisely measured. The relative error on the coefficient of friction due to $\epsilon_{R_2}$, independently
of the friction coefficient, is (highest non-zero order in $a$):

$$\frac{\epsilon R_2}{\mu} = \frac{\epsilon_{R_2}}{R_2}$$

(5.15)

In our experimental case, the precision of our optical microscope ($\approx 500\text{nm}$), $\frac{\epsilon_{R_2}}{\mu} \approx 10^{-1}$. This error is not characteristic of our method but common to all colloidal lateral force microscopy. This error can be further reduced by measuring the size of the scanning sphere more accurately by means of electron microscopy.

**Miscentered gluing of scanning sphere.** An error in the position of Sphere 2 relative to the longitudinal axis of symmetry of the cantilever (miscentered gluing) generates a coupling between the normal force and the flexion of the cantilever [133]. Nevertheless, since this artefact is constant during the measurement and since we subtract the trace image from the retrace image, this does not have a significant impact on the measured friction in this technique.

**Image miscentering.** An error in the position of Sphere 1 relative to Sphere 2 (miscentered image) is equivalent to integrating $\gamma$ over a non-zero centred interval. For an error of $\epsilon_x R_a$ in the trace direction in the other direction in low friction case:

$$\frac{\epsilon_x}{\mu} = \frac{2\alpha + 1}{8(\alpha + 1)} \epsilon_x^2$$

(5.16)

and for high friction case:

$$\frac{\epsilon_x}{\mu} = \frac{2\alpha + 1}{8(\alpha + 1)} \left(1 + \frac{2(\alpha + 1)}{2\alpha + 1}\mu^2\right) \epsilon_x^2$$

(5.17)

For an error of $\epsilon_y R_a$ in the other direction, independently of the friction coefficient:

$$\frac{\epsilon_y}{\mu} = \frac{\alpha}{8(\alpha + 1)} \epsilon_y^2$$

(5.18)
In our experiments, keeping the top of the particle in the centre quarter ($\epsilon_x, \epsilon_y < \frac{a}{2}$) of the image was a straightforward task. Then, in this case, $\frac{\epsilon_x^2 + \epsilon_y^2}{\mu} \approx 5 \cdot 10^{-3}$.

**Neglected terms in the theory** Due to the restriction to the lowest orders of the $a\mu$-Taylor series, the coefficient of friction, using the Eq.5.11 or 5.12, is underestimated by less than 1%. The highest error is achieved for large scanned areas and low friction.

### 5.3.5 Variation in the coefficient of friction

The assumption that the coefficient of friction is independent of the normal force in the range of force that is applied during a single test ($\frac{\Delta F_N}{F_N} \approx \frac{a(4\mu + a)}{4}$), leads to an additional error. This paragraph will present the detailed derivation in this case.

According to Equation 5.2, at any point:

$$F_z = -(\cos \phi \pm \mu(F_N)\frac{\sin \phi \cos \theta}{\sqrt{1 - \sin^2 \phi \sin^2 \theta}})F_N$$  \hspace{1cm} (5.19)

Since the relative normal-force change in the image will remain small in the scanned area ($\frac{\Delta F_N}{F_N} \approx \frac{a(4\mu + a)}{4}$), the local friction coefficient is approximated by the first-order approximation relative to an arbitrary point $A = (x_A, y_A)$:

$$\mu(x, y) = \mu_A + (F_N(x, y) - F_N(A)) \frac{d\mu}{dF_N}\bigg|_A$$  \hspace{1cm} (5.20)

and, because $F_z$ is kept constant, using Eq.5.19:

$$\mu(x, y) = \mu_A + \left(\frac{\sqrt{4 - y^2}}{y_A} \sqrt{4 - (x_A^2 + y_A^2)} \sqrt{4 - y_A^2} \pm 2\mu_A x_A \right) F_N(A) \frac{d\mu}{dF_N}\bigg|_A$$  \hspace{1cm} (5.21)

One can note that $F_N(A) \frac{d\mu}{dF_N}\bigg|_A = \tilde{\mu}_A - \mu_A$. With $\tilde{\mu} = \frac{dF_c}{dF_N}\bigg|_A$, the differential coefficient of friction.

Following the same process as in the constant coefficient of friction case, we expand $\Gamma$ as a Taylor’s series of $(a\mu_A, a\tilde{\mu}_A)$ that is arbitrary small.
Since the goal is to measure $\mu_A$ as independently as possible from the value of $\tilde{\mu}_A$, the point A is chosen in order to minimise the dependence of $\Gamma$ with $\tilde{\mu}_A$. We choose $A=(0, \frac{a}{\sqrt{2}})$. Then, $F_N(A) = -\left(1 + \frac{a^2}{8}\right)F_z$. The value of $\mu$ for this corrected normal force is:

$$\left(1 + \frac{(3\alpha + 1) a^2}{24(\alpha + 1)}\right)\mu + \left(\frac{3\tilde{\mu}}{\mu} - 2\right)\frac{a^2}{12}\mu^3 = \Gamma$$

(5.22)

The Equation 5.22 shows that the correction due to the variation of the coefficient of friction is also small. Nevertheless, this equation can be used only if $a\mu_A$ and $a\tilde{\mu}_A$ are small compared to 1, which may require cropping the experimental image and focusing on a smaller area.

From a practical point of view, one can also interpret the variation of the coefficient of friction as a source of error. The differential coefficient of friction and $\delta_\mu = |\tilde{\mu} - \mu|$, the error in the measured coefficient of friction is given by

$$\frac{\delta_\mu}{\mu} = \frac{a^2}{4} \mu \delta_\mu$$

(5.23)
5.4 Results

Using the technique described in Section 5.2.1, we measured the frictional properties of a pair of silica microparticles. The silica particles are immersed in a solution that mimics the suspending solution in cement slurry. The scanning speed is 6 \( \mu m/s \) and the loads are between 20 and 400nN.

In the following we perform particle-on-particle friction measurements in the presence and in the absence of some of the lubricating polymers.

5.4.1 In the absence of polymer

In order to extract the effect of the polymer and to verify the validity of our analysis, some tests on bare-bare particle contacts have been performed.

Contaminated Particles

The friction between objects that have been exposed to ambient air for a long time is surprisingly stable and almost always around 0.2-0.3 [164]. After exposition to ambient air for days (see Section 5.2.1 for details), the friction force between silica microsphere pairs, in pH-neutral salty buffer, has been found to be nicely linear with the load with a coefficient of friction around 0.26 (see Fig.5.12). Moreover, no adhesion has been detected. These values are in agreement with the value reported for the dry and contaminated case for similar spheres by Ling et al. [131].

This shows that our technique is able to measure ordinary coefficients of friction under standard conditions.

Clean Particles

If, on the other hand, we thoroughly clean the particle surface (by Piranha and UV-Ozone cleaning, see Section 5.2.1 for details) before exposing the particles to the reference salty alkaline solution, the results change significantly. First an adhesion of some nanonewtons (see Fig.5.11) is measured after each of the tribotests. Secondly, the friction between the
particles is considerably higher, with a coefficient of friction of 0.9. This value could be seen as surprising. Nevertheless, one should remember that the surface of amorphous silica at pH 13 is chemically active. It is possible that the friction leads to additional dissolution of silicic acid in the media that would contribute significantly to the friction (as proposed in Ref. [148]). Moreover, this value is close to the value reported in Ref. [131] for clean and fresh Stöber silica microparticle pairs and this is, to the best of our knowledge, the only other publication reporting silica-microsphere-pair AFM friction data.

5.4.2 In the presence of polymer

In a $Ca(OH)_2$ solution, the copolymers that have been used are known to adsorb on the surface via calcium bridging of their phosphate anchors, forming a hydrophilic polymer brush and reducing the coefficient of friction [127, 128]. We quantify the adsorbed layer of each polymer onto amorphous silica using TInAS interferometer at $77\pm3$ ng/cm² for PMAA-g(0.2)-PEG(2kDa) and $86 \pm 5$ ng/cm² for PMAA-g(0.8)Phosphate-g(0.2)PEG(2kDa). No confirmation of these results has been obtained by AFM because of the high roughness of the surfaces. Nevertheless, these quantities are rather consistent with the comb copolymer adsorption model recently proposed by Flatt et al.[74]. In order to know the configuration of the polymer chain at interface, the average distance between chains, $L$ should be compared to the radius of gyration of each chain $R_g$ (see Section 1.4.3). In absence of precise measurement of PEG in the presence of $Ca(OH)_2$, we assume that $R_g$ is around 1.6
Figure 5.11 – (Top) Example of force-distance curve in approach (red) and retraction (blue) for clean bare particle pair in the alkaline salty lubricating solution. The inset is a zoom at the contacting point. (Bottom) Same experiment in the presence of PMAA-g(4)-PEG(2). The polymer coating removes any adhesion between the spheres.
nm as reported by Ref.[112] in a K$_2$SO$_4$ solution. So $L/2R_g < 0.7$ and we confirm that the polymer is in the brush regime. Furthermore, the difference in PEG surface density between the two brushes is small and should not play an important role in the lubrication.

In our case, the adhesion tests revealed that both spheres repelled each other in close proximity, confirming the presence of the polymer at the surface (see Fig.5.11).

The friction results that are reported in Fig.5.13 reveal several interesting features. As previously stated in the literature [187], the polymer brushes reduce the friction force considerably. Moreover, the coefficients of friction that we found were of the order of previous values reported for silica colloids on nano-rough silicon surfaces with similar polymer coatings [170]. We also confirm that phosphate-substituted comb polymers exhibit an even greater reduction of the friction, in line with the effects described in Chapter 4.3. Since the grafting ratio and PEG surface density is similar for the 2 polymers, this difference in friction is probably due to the nature of their anchors (phosphate Vs. carboxylic).

Two other features can be then pointed out. First, the data are more dispersed than in the bare case. This is partially the consequence
Figure 5.13 — Friction force Vs. normal force between several microparticle pairs in the salty alkaline solution in presence of PMAA-g-EGPh-g(4)PEG(2) in red and PMAA-g(4)-PEG(2) in green. Each data symbol corresponds to a different particle pair (respectively 4 and 5 repetition for each set).

of the accuracy of the measurement for such low friction forces, but it also illustrates the strong dependence of the brush properties on the precise local nanotopography [170].

Finally, the friction law differs from an Amontons-Coulomb law since the frictional force is not a linear function of the load, especially for PMAA-g(0.8)Phosphate-g(0.2)PEG(2kDa). The accuracy of our data for the lowest forces (below 5nN) does not allow us to determine if our system exhibits a normal friction law in the presence of a repulsive force or if we see here the transition from the low-pressure/low-friction regime to the high-pressure/high-friction regime, in which the brushes start entangling [117, 174], since this transition is moved toward lower pressure by the roughness [170].
5.5 Conclusions

Based on the mechanical analysis of a sphere-sphere contact, we propose a novel method to quantify the sliding friction between homogenous rigid microspheres in both dry and liquid environments. We have applied this technique to bare and polymer-coated particles in aqueous medium. The technique is simple and robust, with respect to the most common experimental errors.

Our method therefore offers the opportunity to significantly extend the characterisation of frictional contacts at the single-particle-pair level and thus to further our understanding of a host of rheological phenomena in which such microscale contacts play a crucial role. This includes most of the rheological behaviour of dense non-Brownian suspensions but also dry granular media rheology.
Chapter 6

Conclusions & Outlook

Shear thickening of suspensions is a very complex issue that simultaneously raises theoretical, instrumental and practical problems. Despite about a century of theoretical studies, the underlying mechanisms are still unclear and the understanding of the phenomenon remains fragmented. Experimentally speaking, despite recent instrumental developments, measuring particle interactions or the viscosity of very dense suspensions, even in simulations, is still highly challenging. In parallel, shear thickening appears with increasing frequency in industrial suspensions, such as low-carbon footprint concrete. This thesis has tried to address these three aspects of the problem simultaneously.

Understanding shear thickening

The bibliographic study revealed that the main open theoretical question was not the occurrence of continuous shear thickening, but the existence of a discontinuous shear thickening regime, which to date had not been explained. Building on the work of Bagnold on continuous shear thickening, we determined that the transition from a Newtonian regime toward an inertia-driven flow had tremendous consequences on the contacts between grains. In the inertial regime, the collective pressure of the grains leads to the rupture of the lubricating fluid layer between them, leading to boundary lubrication. Thus, not only the driving force changes, but also the particle interactions and consequently the jamming volume fraction. In this regime, the jamming volume fraction $\phi_{max}^{BL}$ is smaller than that in the Newtonian regime, $\phi_{max}^{NW}$. Bagnold theory is then pertinent if $\phi < \phi_{max}^{BL}$, and the suspension exhibits continuous shear thickening, while
for $\phi_{max}^{\text{NW}} > \phi > \phi_{max}^{\text{BL}}$, the viscosity of an inertial/boundary lubricated flow regime is infinite and the suspension exhibits discontinuous shear thickening.

Our model clearly required experimental evidence, especially concerning its most innovative assertion: the key role of the coefficient of friction between grains. This was obtained by two different strategies. On the one hand, we showed using quartz suspensions that the coefficient of friction and the volume fraction control the nature of shear thickening. On the other hand, we developed computer simulations, which recover the three flow regimes of such dense non-Brownian suspensions. In addition, these simulations also reproduce the transitions between the three regimes, in term of shear rate, coefficient of friction and volume fraction.

**Outlook** - This extension of Bagnold’s theory obtained by forging a connection to the mechanics of granular media, and thus incorporating steady-state Newtonian, CST and DST flows is an improvement by itself. Nevertheless, the details of the transitions between these regimes pose fascinating theoretical problems. Are there shear rates for which NW and ST regimes are both stable? Are there fundamental reasons why the divergence of the viscosity of the ST regime approaching $\phi_{max}^{\text{BL}}$, follows a common pattern, independently of the particle properties (see Fig.6.1)?

While we believe that our model could also explain the transient behaviour of DST suspensions, extensive theoretical work is still required to explore this regime. Both the jamming front propagation and the jamming relaxation mechanisms remain unclear. Finally and more generally, our approach to considering the jamming volume fraction as function of the shear rate can also be fruitfully applied to many other unsolved issues.
Measuring shear-thickening parameters

While testing our framework, we have also developed new experimental tools that could help future measurements of the important parameters that influence shear thickening.

In collaboration with R. Mani, we have developed a radically new way to simulate the rheological behaviour of dense suspensions by taking into account that in dense suspensions the contacts are long-lived and that in such contacts, the dominant forces are not the same as in short-lived ones. Its success in simulating shear thickening is promising for wider use in the rheology of dense suspensions.

Through this project, it appears clear that the improvement of our knowledge about shear thickening involves a more precise measurement of particle interactions and, in particular, the coefficient of friction in boundary lubrication between two particles. To this end, we developed a technique to measure this parameter with an AFM. Even if some experimental dexterity is still required, as is often the case for experiments at the microscale, this new technique enables the measurement of the friction coefficient without any complex data processing, while maintaining excellent robustness towards most experimental errors.

For similar reasons, in the absence of an efficient technique to measure $\phi_{\mathrm{BL}}^{\mathrm{max}}$, we developed a compressive rheology experiment that provides a very good approximation of $\phi_{\mathrm{BL}}^{\mathrm{max}}$ with low requirements regarding the nature of the suspension, and with excellent reproducibility.

**Outlook - All of these tools can still be improved.** There is little doubt that our tribometry technique will move towards more convenient protocols, following the current general trend in AFM techniques. We also hope that our demonstration of the importance of the viscous-lift term in suspension simulation will lead to the development of algorithms in which the full hydrodynamic interactions will be implemented. Improvements in these tools would be useful elements in shedding light on a decade-long experimental quest: determining precisely the jamming volume fractions in the different flow regimes and the influence of the particle-pair interactions.
Controlling shear thickening on an industrial scale

As stated in the introduction, industrial applications were one of the main driving forces for our project. Our results contribute to the reduction of the viscosity of low-water-content cement pastes.

The compressive rheology determination of $\phi_{\text{max}}^{BL}$ is also an important contribution to concrete mix design. While the slump test reveals most of the low-shear properties of a cement paste, the centrifugation of a flask gives most of the information needed on the high-shear-rate behaviour of a cement paste. It is simultaneously faster, easier, more reproducible and more universally applicable than previous techniques that relied upon an incremental increase of the paste volume fraction until the suspension exhibited DST.

We have already applied this technique to a large variety of polymers in order to isolate the architecture parameters that influence their lubricating properties and their ability to reduce shear thickening. For this purpose, the number of anchors and their affinity to the calcium-coated surface appear to be the most promising “knobs to turn”.

**Outlooks** - *Our research mainly focused on the reduction of shear thickening by tuning the particles’ polymer coating. Numerous others methods remain unexplored, such as tuning the particle roughness during grinding, adding a small amount of well-lubricated particles or modifying the suspending-fluid properties.*

![Figure 6.2 - Impact of addition of well-lubricated particles (A) in a DST suspensions of poorly-lubricated particles (B) ($\mu_0^{AA} = 0.01$, $\mu_0^{AB} = 0.2$, $\mu_0^{BB} = 0.4$, $\phi = 0.58$).](image)

Finally, by introducing the concept of boundary-lubricated contacts as a component of shear thickening and the cause of DST, this research has proposed new concepts to understand the shear thickening of dense non-Brownian pastes and new tools to measure and reduce it. It paves the way to addressing numerous fascinating problems and open questions in future work.
## Nomenclature

<table>
<thead>
<tr>
<th>Name</th>
<th>Unit</th>
<th>Definitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_a$</td>
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<td></td>
</tr>
<tr>
<td>$A_0$</td>
<td>[J]</td>
<td>Hamaker constant</td>
</tr>
<tr>
<td>$A_A$</td>
<td>[m$^2$]</td>
<td>Apparent area of contact (cf p.37)</td>
</tr>
<tr>
<td>$A_R$</td>
<td>[m$^2$]</td>
<td>Real area of contact (cf p.37)</td>
</tr>
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<td>[m]</td>
<td>Size of the contact (cf p.36)</td>
</tr>
<tr>
<td>$a^*$</td>
<td>[m]</td>
<td>Local radius of curvature of the particle surface (cf p.22)</td>
</tr>
<tr>
<td>$a_m$</td>
<td>[m]</td>
<td>Size of a monomer (cf p.42)</td>
</tr>
<tr>
<td>$a_N$</td>
<td>[m]</td>
<td>Size of a backbone monomer (cf p.47)</td>
</tr>
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<td>[m.s$^{-2}$]</td>
<td>Normal component of the particle acceleration (cf p.81)</td>
</tr>
<tr>
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<td>[m]</td>
<td>Size of a side-chain monomer (cf p.47)</td>
</tr>
<tr>
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<td>[N.m$^2$]</td>
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<td>[1]</td>
<td>Bagnold number (cf p.33)</td>
</tr>
</tbody>
</table>
\( Dd \)
\( d \quad [m] \) Particle diameter (cf p.14)
\( d_g \quad [m^{-2}] \) Surface grafting density (cf p.45)
\( d_q \quad [m] \) Distance between two charged group on a linear polyelectrolyte (cf p.42)

\( E_e \)
\( E^* \quad [Pa] \) Effective elastic modulus of two contacting solids (cf p.36)
\( e_N \quad [1] \) Normal restitution coefficient (cf p.83)

\( F_f \)
\( F^* \quad [N] \) Short-range finite repulsive force between particles (cf p.66)
\( F_{ext} \quad [N] \) Sum of the external forces applied on a particle excluding the studied contact (cf p.81)
\( F^{HD} \quad [N] \) Lubrication force in the lubricated contact of two spheres (cf p.81)
\( F_N \quad [N] \) Normal force in a contact (cf p.36)
\( F_r \quad [N] \) Repulsive force between two surface (cf p.47)
\( F_T \quad [N] \) Tangential force in a contact (cf p.38)
\( F_x \quad [N] \) Force applied on the simulation box wall (cf p.77)
\( F_{N}^{ext} \quad [N] \) Component of \( F_{ext} \) that is normal to the studied contact (cf p.81)
\( F_{T}^{ext} \quad [N] \) Component of \( F_{ext} \) that is tangential to the studied contact (cf p.81)

\( G_y \)
\( G \quad [Pa] \) Elastic Modulus
\( g \quad [1] \) Comb-polymer grafting ratio (cf p.99)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<td>$Hh$</td>
<td>Distance between two particle surfaces</td>
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<td>Equilibrium thickness of an uncompressed brush</td>
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<td>Surface-to-surface distance normalised by the particle radius</td>
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<td>[kg]</td>
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<td>Number of backbone monomer per segment in a comb polymer</td>
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<td>Number of segment in a comb polymer</td>
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<tr>
<td>Symbol</td>
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<td>[Pa]</td>
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<td>Effective radius of curvature of two contacting surfaces (cf. p.36)</td>
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<td>[m]</td>
<td>Polymer radius of gyration (cf. p.42)</td>
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<td>[K]</td>
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<td>Upper deformation limit of the elastic regime (cf p.23)</td>
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<td>Liquid-air surface tension</td>
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<td>$\dot{\gamma}$ [s$^{-1}$]</td>
<td>Shear rate (cf p.20)</td>
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<td>$\dot{\gamma}_c$ [s$^{-1}$]</td>
<td>Shear-thickening critical shear rate (cf p.61)</td>
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<td>$\dot{\gamma}_{macro}$ [s$^{-1}$]</td>
<td>Macroscopic apparent shear rate (cf p.67)</td>
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<td>$\dot{\gamma}_{min}$ [s$^{-1}$]</td>
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<td>Viscosity in the Newtonian regime</td>
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<td>Reduced viscosity (cf p.26)</td>
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<td>Yield stress contribution to the apparent viscosity (cf p.26)</td>
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<td>$M\mu$</td>
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<td>Boundary lubrication coefficient of friction (cf p.38)</td>
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<td>Macroscopic coefficient of friction of a granular media (cf p.57)</td>
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<td>$T_\tau$</td>
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<td>Critical shear stress for a repulsive particle suspension (cf p.66)</td>
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<td>Solid volume fraction</td>
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<td>Solid volume fraction at which the viscosity diverges in Krieger-Dougherty model (cf p.27)</td>
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<td>$\phi_{max}$</td>
<td>Solid volume fraction at which the suspension viscosity diverges (cf p.59)</td>
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<td>$\phi_{BL_{max}}$</td>
<td>Solid volume fraction at which the granular media viscosity diverges when the particles experience only boundary lubrication (cf p.59)</td>
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<td>$\phi_{Nw_{max}}$</td>
<td>Solid volume fraction at which the suspension viscosity diverges in the Newtonian regime (cf p.59)</td>
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<tr>
<td>$\phi_{YODEL_{max}}$</td>
<td>Maximum packing volume fraction of the YODEL model (cf p.24)</td>
<td></td>
</tr>
<tr>
<td>$\phi_{RCP}$</td>
<td>Random Close Packing solid volume fraction</td>
<td></td>
</tr>
<tr>
<td>$\phi_{RLP}$</td>
<td>Random Loose Packing solid volume fraction</td>
<td></td>
</tr>
<tr>
<td>$\phi_s$</td>
<td>Sediment volume fraction in compressive rheology (cf p.105)</td>
<td></td>
</tr>
<tr>
<td>$\Omega \omega$</td>
<td>Rotational speed</td>
<td></td>
</tr>
</tbody>
</table>
Bibliography


