IFPRI Critical Review of Tribology, Friction, and Contact Mechanics in Wet Systems

Introduction&Scope:

The mechanical response of particulate suspensions and of viscoelastic solids composed by said particles in a fluid is ultimately defined by two sets of interactions: the ones between the particles and the fluid, i.e., hydrodynamics, and the ones amongst the particles. While extensive literature exists on the hydrodynamics of solid particles under shear and the implications that hydrodynamic interactions have on the rheological response of wet systems, several recent developments have brought to question the classical view linking interparticle interactions to microstructure and hence to mechanical response. Over a century of colloidal science has thought us that the equilibrium and non-equilibrium phases of colloidal materials can be rationalized by central forces determined by pair-wise interaction potentials and by kinetics. However, this simple yet powerful assumption leaves us with some apparent contradictions, or at least with puzzling questions.

If one considers the case of two spherical particles in contact under the action of an attractive potential, i.e. with an interparticle distance approaching 2R, with R being the particle diameter, there is no work done against the attractive force when one particle orbits around the other one, and the only energy dissipation comes from interactions with the fluid. This furthermore indicates that "bonds" between particles correspond to minima of the interaction potential and can only be broken radially, i.e. by increasing the separation between the particles. There thus is no mechanical resistance (other than viscous forces) to sliding the motion between the particles. The further consequence of this argument is that mechanical rigidity can only be imparted to a material as a consequence of geometry and does not originate from pair-wise interactions. In other words, solid-like behavior (for rigid spheres) is caused by each particle having a sufficient number of contacts with neighbors such that sliding motion is restricted. Note that however, even in the situation where sliding between particles is prevented, there is no restriction to rolling (apart from topological constraints on the rolling direction deriving from hydrodynamic coupling) such that the relative motion between the particles' surfaces remains possible. This approach contrasts our experience with sticky or adhesive surfaces, which not only present a resistance to separation, but also to relative sliding and rolling. In this case, rigidity emerges not only from geometry but also from pair-wise particle interactions, which however can no longer be described by central forces.

This brief preamble serves the purpose of questioning which are then the relevant interactions that determine and define (together with microstructure) the mechanical response of particulate suspensions at high solids volume fraction. We strongly believe that in addition to interaction potentials, which are in any case present and play an important role, contact interactions are a determining factor for those materials where particles form bonds in a quiescent state, e.g. gels or attractive glasses, or where particles may come into contact under shear, e.g. in shear-thickening or shear-jamming suspensions.

The scope of this review is to critically question and assess the relevance of contact interactions in dense particulate systems, starting from their definition and mechanical interpretation, and followed by a comprehensive description of their measurement and characterization together with a list of strategies to modify them. Each of the sections of this part will both provide an assessment of the state of the art and a set of critical questions to guide further progress. After this initial more conceptual part, I will attempt to survey a range of different processes where interparticle contacts are dominant and to indicate how our fundamental understanding of contact interactions can help us design better materials for a broad range of applications, both for aqueous and non-aqueous systems.

Table of Contents

1) Introduction

- Motivation for this review. Brief review of relevant materials, i.e. suspensions and gels. Models for rheology that include contact forces, i.e. the Wyart-Cates model and its extensions.
- Brief review of applied processes of relevance, e.g. high solids paste processing, chemical mechanical polishing, filled polymer processing, slurry pumping and flow, additive manufacturing of gels.
- Challenges: If particle contacts are important in the materials and processes above, how do we optimize them to inform the design of better materials and processes? Give examples (a few first ones):
    - How can we control interparticle contacts to reduce restructuring times in colloidal gels for 3D printing?
    - How do we optimize interparticle contacts to delay the onset of shear thickening in dense slurries under pumping?
    - How do we select particles dispersed in a resin matrix to avoid clogging in the nozzle of a high-speed printer?
    - How do we enhance wear in the mechanical polishing of surfaces or in the milling of particulate fluids?
- The key is in understanding and engineering interparticle forces by surface modifications (topography, coatings and additives)

2) General framework: Central vs non-central forces & contact mechanics

Synopsis:
After the introduction, this chapter sets the stage for the most important concepts that will be discussed in the review. In particular, I will highlight the differences between central and non-central forces and provide a description of different contact mechanics models to explain adhesion and friction. For the case of adhesion, I will emphasize the importance of contact area and contact area calculations, as in contrast with standard approaches for particles that idealize the interactions as point contacts. I will also discuss what is the molecular origin of adhesion and ask the critical question of how and when is adhesion different from attraction. In the case of friction, I will start from a tribological approach to contacts and distinguish between boundary and hydrodynamic lubrication, drawing a connection with colloidal and hydrodynamic interactions. I will also describe elastohydrodynamic effects and define the regimes in which the various lubrication scenarios are relevant. I will end this chapter with a critical discussion of the differences between wet and dry systems to identify common aspects and differences.

- Definitions:
    - Central and non-central forces
    - Contact geometry
    - Degrees of freedom
- Contact mechanics models with and without adhesion
    - Hertzian contacts
    - JKR & DMT
    - Molecular origin of adhesion
    - When is it adhesion and when is it attraction?
- Friction
    - The Stribeck curve and the Sommerfeld number: different friction regimes:
        1. Boundary lubrication:
            a. Amonton-Coulomb law with and without adhesion
            b. Bagnold scaling
            c. Friction and contact area
            d. Sliding and rolling friction
            e. The molecular origin of friction
            f. Static and dynamic friction
        2. Hydrodynamic and elastohydrodynamic lubrication
- Comparison between wet and dry systems
    - Friction in dry powders and different flow regimes
    - Force chains: clearly visible in dry systems. Do they exist in wet ones?

3) Measuring friction and adhesion for particulate systems

Synopsis:
After having defined friction and adhesion, I will provide an extensive review of the methods currently in use to measure the tribology of particles, starting from macroscopic methods from which these quantities can be inferred and then moving to methods that characterize directly single-particle contacts. The shortcomings and advantages of these methods will be described together with a critical analysis of the challenges for the development of new methods to fill in current gaps.

- Macroscopic friction and adhesion:
    - How a tribometer works
    - Force sensors for adhesion measurement
    - Challenges for downscaling to particulate systems
- Microscopic friction:
    - Macroscopic measurements to extract single-particle friction
        1. Shear and extensional rheology
        2. Capillary pressure measurement under shear
        3. Rheoconfocal
        4. Challenges and perspectives (polydisperse systems, adhesive systems, spatial and temporal resolution)
    - Microscopic measurements

1. Atomic force microscope: colloidal probe and lateral force microscopy
2. Tuning fork
3. Optical tweezers
4. Other types of force sensors
5. Challenges and perspectives (force and rate ranges, sliding and rolling, from single to multiple contacts)

- Challenge: how do we connect macroscopic and microscopic friction measurements?

4) Modifying friction and adhesion for particles

Synopsis:
After having discussed how to measure contact interactions, I will now describe different ways in which they can be regulated. The most commonly used strategies for particles act during synthesis or post-modification, where the former approach leverages control of the particle shape, topography and surface chemistry during synthesis, while the latter enables the modification of some of these characteristics afterwards by the addition of coating elements ex-situ, i.e. prior to use. Finally, additives can also be employed in-operando and used to regulate lubrication. The field of tribology modifiers is vast, with a wealth of application- and materials-specific strategies being constantly developed. The aim of this section is to provide an overview of the general approaches for tribology modification illustrating the relevance for particulate suspensions.

- Controlling particle surface roughness:
  - Milling
  - Direct synthesis of rough particles
  - Roughness modification by heteroaggregation and smoothing
  - Model systems vs real systems: what do we learn and what can we use?
- Particle surface functionalization:
  - Electrostatic stabilization
  - Surface coatings
    1. Surface modification
    2. Polymer brushes: grafting to and grafting from
    3. Polymer brushes: why are they so good to reduce friction?
    4. Smart coatings (friction and adhesion control on demand)
- Additives:
  - Surfactants: surface adsorption and micelles
  - Nanoparticles are friction modifiers
- Challenges and perspectives
  - Roughness and coatings: what do they do to friction and adhesion and what is their interplay?
  - How do we design coatings and additives for target contact interactions?

5) Case studies (to be discussed)

<u>Synopsis:</u>
In this last section I would like to present some hypothetical case studies, based on the examples listed in the introduction and use them to discuss a potential design-based approach for the optimization of contact properties for a targeted application. This section has the goal to illustrate which aspects of the rheological response of concentrated particulate suspensions, which define their use in a given process, can be influenced by engineering contact mechanics. The idea is to stimulate the reader to reflect on a new set tools at their disposal, in addition to the classical ones given by colloidal science and hydrodynamics, which can be used to optimize, improve or develop new systems and formulations. A few examples are listed below, but I would be very happy to receive feedback on which other cases could be of interest for the readership of the review from the perspective of IFPRI

- Shear thickening fluids for impact absorption:
  - How can I maximize the viscosity jump across the shear-thickening transition?
  - How can I minimize the solid loading?
  - How do I control relaxation?
- Extrusion of dense pastes of particles in a polymeric matrix:
  - How can I prevent clogging but ensure a percolating network of particles?
  - How do I maximize the solid loading?
- 3D printing of colloidal gels:
  - How do I control the yield stress of the material?
  - How can I minimize the restricting time?
  - How do I ensure low creep?

6) Conclusions and outlook

<u>Synopsis:</u>
In the conclusions I will summarize the main points discussed in the review and provide a collection of critical questions that I consider crucial to advance this field.