IFPRI Research Project Brief

Wetting and Dispersion of Organic and Biologically-Derived Powders

The International Fine Particle Research Institute (IFPRI) wishes to fund a project in the broad area of dispersion and dissolution of organic particles. The overall objective of the project is to develop systematic understanding of wetting, imbibition, dispersion, and dissolution to facilitate proactive design of powder formulations for optimal dispersibility.

The project should explore and demonstrate approaches to control, design, and engineer nano to meso scale particle surface topology and surface chemistry of organic and biologically-derived materials to promote wetting and dissolution, in concert with addition of surface modifiers (surfactants, ions, polymers, etc.). Dispersion by liquid incorporation into powders and powder addition to liquids should *both* be investigated. A mechanistic model for dispersion and dissolution should be developed and validated. This model should describe both modes of dispersion.

IFPRI's interest is in dispersion of powders common in food and pharmaceutical applications, with an emphasis on water dispersible, bio-derived materials of which, fully soluble particles and mixed soluble/insoluble particles are explored. A phenomenological mechanistic model of the particle/powder wetting, dissolution and dispersion kinetics should be developed and validated as a predictive tool for assessing wetting/dissolution issues of powders/powder beds in both confined and unconfined vessels. The model should address powder to liquid ratios that are representative of localized conditions in transforming a wetted bed of powder having capillary or even funicular wetting at liquid-particle interfaces to a fully dispersed suspension of particles in excess liquid. An understanding of the development of films, gelatinous layers, and fish eyes should be considered, as these are some of the most common issues encountered with reconstitution of powders. Systems where little to no agitation is available to promote wetting and dispersion, such as gravimetric liquid incorporation are of particular interest.

Reconciling Surface Energetics to Electrical Double Layer Manipulation for Soft Fine Particle Dispersion in Water
to
International Fine Particle Research Institute

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James H. Adair
Materials Science & Engineering
Penn State University
University Park, PA 16803
Jha3@psu.edu

Introduction

Dispersion of particles in liquid is one of the critical scientific and engineering foundations that permit the reliable production and utilization of fine particles. In general, the development of particle dispersion in liquids has followed two parallel paths; the first based upon surface energetics and the relationships shown for the work of wetting or adhesion as shown in Figure 1(a) and a second approach associated with the dispersion of hard sphere fine particles using surface speciation and van der Waals attractive interactions to control the repulsive and attractive interaction energies between two or more interacting particles. Both of these approaches are capable of describing and controlling interactions among fine particles leading to well-dispersed or agglomerated particles from the nanoscale (>1nm diameter) to macroscales (diameters larger than 1 um to flat surfaces) (1,2,3). However, surface energetics, while useful for macroscopic prediction of adhesion or dispersion among fine particles, is not specifically linked to the surface chemistry manipulation of fine particles. In contrast, DLVO approaches that intimately depend upon control of the surface chemistry, that does not predict whether surface energetics are present that wetting occurs, a necessary but insufficient for thermodynamically stable suspensions. One of the

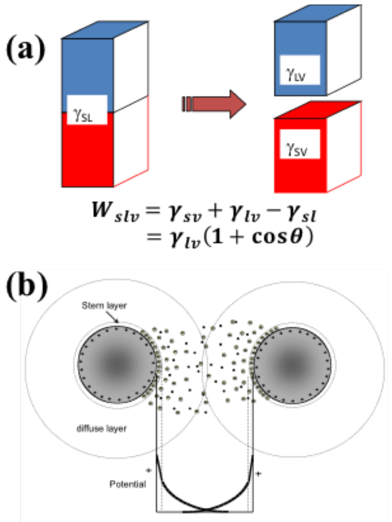

Figure 1. Bases for dispersion of soft material particles based on (a) surface energetics and (b) DLVO surface chemical and van der Waals models generally referred to as DLVO theory. "DLVO" refers to the specific double layer interactions shown in figure (b) but will be used as a general description of models for dispersion that depend upon manipulation of the surface species on soft particle surfaces.

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[1] J.H. Adair, R. Kumar, N. Antolino, C.J. Szepesi, R.A. Kimel, and S.M. Rouse, "Colloidal Lessons Learned for Dispersion of Nanosize Particulate Suspensions," Lessons in Nanotechnology from Traditional and Advanced Ceramics, Proceedings of the World Academy of Ceramics, J.F. Baumard (ed.), Techna Group SrI, Faenza, Italy, pp. 93-145, 2005.

[2] J.H. Adair, E. Suvaci, and J. Sindel, "Surface and Colloid Chemistry of Advanced Ceramics," Encyclopedia of Materials: Science and Technology, Elsevier Publishing, The Netherlands, 2001, 8996-9006.

[3] T.M. Morgan, T.M.Goff and J.H. Adair, "The Colloidal Stability of Fluorescent Calcium Phosphosilicate Nanoparticles: The Effects of Evaporation on Particle Size Distribution," Nanoscale, 3, 2044-2053, 2011.

overarching objectives of this work is to reconcile the two approaches to disperse soft fine particles with surface energetics that ensures good wetting and DLVO approaches leading to surface functional groups that promote thermodynamically stable suspensions.

New science is rapidly emerging in fine particle dispersion. Until fairly recently it was assumed that fine particles in higher ionic strength solutions were only dependent on surface energetic forces mostly associated with either hydrophobic or hydrophilic surface chemical interactions (4a). Surface potential on soft fine particles including cell membranes and polysaccharide macromolecules and oligomers were assumed to be insignificant because of electrostatic shielding by the elevated salt concentrations. Recent experimental data suggests that this assumption is no longer valid. For example, Garg et al. (5a) have recently demonstrated that surface potential determined with a modified optical microscopy approach on five micron diameter, sulfonated polystyrene spheres gives values as large as 40mV in solution ionic strength up to 3 molal NaCl. With a passive approach based on streaming potential, Hoggard et al. (5b) have shown that zeta potential in solutions up to ~0.1M can be determined. Adair and Adair have measured zeta potential on amorphous silica with and without IgA adsorbed up to 100 mV in phosphate saline (10mM phosphate buffered to pH 7.4 with 0.14M NaCl and 0.01MKCl at 0.17 M ionic strength) in recent unpublished data. Goff and Adair, in unpublished work, have also demonstrated that a positively charged protein, lysozyme, in cell culture medium with 10 volume percent fetal bovine serum causes the flocculation of negatively charged 20 nm diameter, citrate – calcium phosphosilicate nanoparticles (CPSNPs). Morgan et al. (3) have shown that 30 to 60 nm diameter CPSNPs with a soft material surface (methoxy-pegylation) completely dried spontaneously redispersed in the solvent system ethanol-water. Thus, given this recent data the assumption that surface potential and charge can be ignored as insignificant in any solution conditions are likely incorrect.

We aim to reconcile the surface energetics approach with DLVO theories via the Lippman equation, in one form given by (4),

$$\frac{\delta \gamma_{sl}}{\delta \psi_s} = \sigma_s \qquad \textbf{[1]}$$

where γ_{sl} is the surface energy at the solid-liquid interface, and ψ_s and σ_s are the surface potential (referred to as experimentally determined zeta potential) and charge at the solid solution interface, respectively. Thus, equation [1], first described by Lippman in 1875 (4c), reconciles the surface energetic DLVO approaches permitting us to utilize all of the relevant tools for dispersion. My lab has recently used the Lippman equation with a new derivation of Gibbs-Wulff particle morphology criteria to predict particle shape as a function of process conditions for α-aluminum

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[4] (a) A.W. Adamson, *Physical Chemistry of Surfaces, Fifth Ed.* New York: John Wiley & Sons, Inc., 1990. (b) D.C. Grahame, "The Electric Double Layer and the Theory of Electrocapillarity," *Chemical Reviews* 41 (1947): 441-501. (c) G. Lippmann, "Relations entre les Phénomènes Électriques et Capillaries," *Ann. Chim. Phys.,* **1875**, *5*, 494-549.

[5] (a) Astha Garg, Charles A. Cartier, Kyle J. M. Bishop, and Darrell Velegol, "Particle Zeta Potentials Remain Finite in Saturated Salt Solutions," Langmuir, 32, 11837−11844, 2016. (b) James D. Hoggard, Paul J. Sides, and Dennis C. Prieve, "Measurement of the Streaming Potential and Streaming Current near a Rotating Disk to Determine Its Zeta Potential," Langmuir, 21, 7433-7438, 2005.

oxide particles. (6). The use of the Lippman equation has attracted recent interest (7) particularly since Ducker et al. (8) demonstrated that γ_{sl} can be determined based on the work of adhesion (W_{slv} in Figure 1a) with force-distance atomic force microscopy. It is also important to recognize the work of Fowkes (9) who used surface energetics to estimate attractive, generally hydrophobic interactions, used in attractive energy calculations for DLVO approaches.

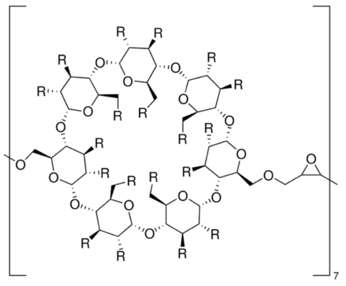
Objective

The objective of the proposed studies is to disperse sparingly soluble polysaccharide fine particles from the nanoscale for macromolecular saccharides to the macroscale for oligomeric polysaccharides. There are three elements to achieve the objective: 1. Develop a fundamental understanding of the colloidal characteristics and dispersion pathway shown in Figure 2 of one model polysaccharide (polymeric β-cyclodextrin is suggested for the preliminary studies) in year 1; 2. Broaden the development to other polysaccharides that are of interest to member companies in IFPRI; and 3. Develop the general paradigm for soft material dispersion with fundamental experimental protocols and calculations that foster and lead to the dispersion of soft fine particles in general.

Approach

Polysaccharides offer an exciting variety of nanoscale macromolecules that permit the development of a comprehensive understanding of the colloidal stability of macromolecules in general. In addition to the evaluation of surface energetics using traditional approaches such as pendant and sessile drop, work of adhesion approaches can be used for more or less direct determination of W_{slv} (8) as shown by Ducker et al. Surface energetic approaches can be combined with DLVO approaches via the determination and quantification of surface charge characteristics using commercially available well characterized and well understood polysaccharides in the cyclodextrin family. Our collaborative group at Penn State has been working to encapsulate various drugs (10) in recent, as yet unpublished studies. In particular, polymeric β-cyclodextrin (pbCD), available commercially from 2kDa to 300kDa, is an attractive model system to develop the theoretical foundations and good engineering practices for the polysaccharides and similar soft materials. The monomeric form of β-cyclodextrin does not have charge based on our zeta potential determinations and the structure, but there are several hydroxy groups and an epoxide that permit modifications with many modified forms commercially

Polymer of β-Cyclodextrin*



* C2485 SIGMA

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[6] J.H. Adair, N.S. Bell, R. Kumar, and R.E. DeHoff, "Recent Developments in Morphological Control of alpha-Al_2O_3 Particles Synthesized in 1,4-Butanediol Solution," to be submitted to *Materials Science Reviews* as a compilation of our publications on the synthesis, morphology control, and surface energetics, early 2018.

[7] (a) J.C. Berg, An Introduction to Surfaces and Colloids: The Bridge to Nanoscience, New Jersey, World Scientific, 2010. (b) D. Tabor, Gases, Liquids, and Solids: and Other States of Matter, 3rd Ed., Cambridge University Press, 1991.

[8] W.A. Ducker, et al. "Forces Between Alumina Surfaces in Salt Solutions: Non-DLVO Forces and the Implications for Colloidal Processing." Journal of American Ceramic Society 77(2): 437-443, 1994.

[9] F.M. Fowkes, "Attractive Forces at Interfaces," Industrial and Engineering Chemistry, 56[12] 40-52, 1964.

[10] D. Zhao, et al., "Synthesis and Properties of Water-Soluble b-Cyclodextrin Polymer Cross-Linked by Citrate with PEG-400 as Modifier," *Carbohydrate Polymers*, 78, 125-130, 3009. R. Namgung, et al., "Poly-Cyclodextrin and Poly-Paclitaxel Nano-Assembly for Anticancer Therapy," *Nature Comm.*, 5, 3702-3714, 2014.

available. Furthermore, many polymeric forms of cyclodextrin are sparingly soluble in water, depending on the functionality of the R group shown in the schematic of the hepta-monomer form. Thus, polymeric β-cyclodextrin is a good model system to develop approaches to establish boundary conditions for colloidal stability in water and possibly other solvents of interest to the members of IFPRI.

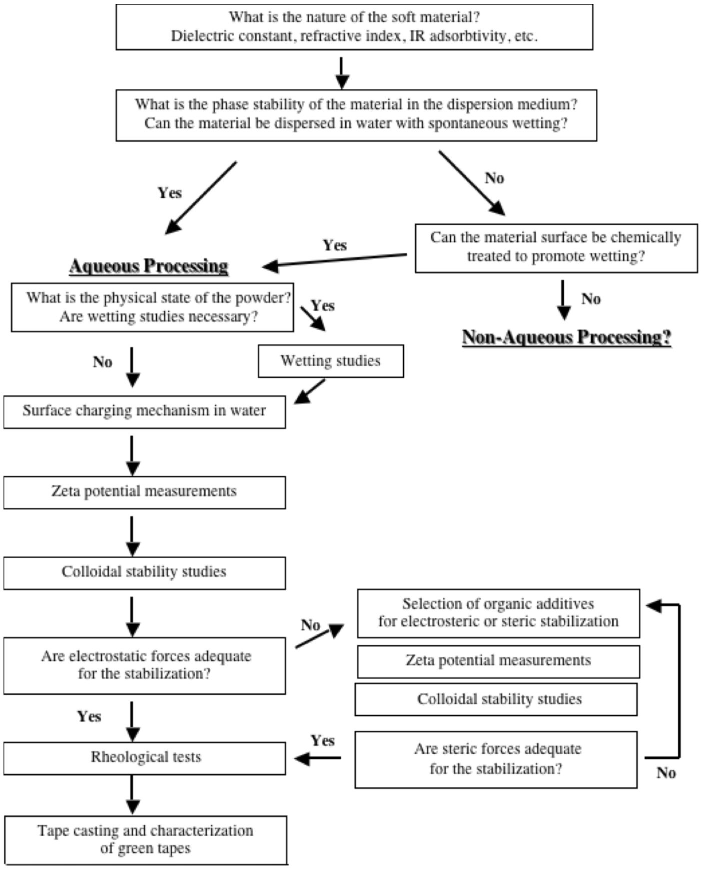

Figure 2. Dispersion approach for good engineering practices in developing well-disperse hard fine particle systems in prior reports will be adapted to soft fine particle dispersion (2). The nature of the material addresses the electronic properties (refractive index, infra-red absorptivity, static dielectric constant, etc. to calculate the van der Waals attractive interactions that dominate attractive interactions using the Bergström approach (11). We will also develop surface energetic approaches developed by Fowkes (9) to calculate attractive interactions among the polysaccharide fine particles to promote wetting of surface groups in the solvent. While rheological properties at high solution concentration are of equal importance to assess dispersion for hard or soft materials, rather than phase separation, wetting behavior is a key feature for soft materials. Hard fine particles processes such as milling and slip casting are replaced by wetting behavior and tape casting with evaluation of the optical properties of the polysaccharide tapes being a key property for well-dispersed soft fine particles as is the ability to dry and redispersed the soft particles. Evaluation of electrostatic, steric or electrosteric dispersion strategies are similar for both hard and soft fine particles.

The dispersion strategy developed in reference 2 will be used to develop the theoretical foundations and pragmatic good engineering practices for dispersion of insoluble polymeric cyclodextrin in water and other selected solvents. The approach developed by Adair et al. (2) for hard sphere dispersion has been modified in Figure 2 for the soft fine particles. The approach is mapped as a pathway paradigm that depends on the specific properties of each soft material. For example, similar to hard fine particle dispersion, the first step is to evaluate the nature of the material related to electronic properties that can be used to calculate the overall van der Waals attractive energies among the polysaccharide fine particles. Also, a polysaccharide with carboxylate groups will have both different zeta potential and γ_{sl} than a polysaccharide with methoxy groups. Our approach accommodates differences among different fine particle materials, characterizes those differences and incorporates the differences to achieve thermodynamically stable suspensions of fine particles (1-3,12). The critical properties include the relative dielectric constant, refractive index, and infra-red adsorption spectra to calculate the attractive van der Waals contributions to the attractive interactions summarized in the value of a constant known as the

Hamaker constant using the Bergstrom calculational approaches (11) developed for hard fine particles. In the Bergström approach, the IR spectra contributions especially accommodate the dipole-dipole (Keeson interactions) and dipole–induced dipole (Debye interactions) attractive van der Waals interactions critical to soft fine particles. Likewise, while milling *per se* is not appropriate for soft fine particles, wetting phenomena determined via the surface energetics is the avenue to promote dispersion of otherwise aggregated, as-received fine particles. Wetting is not predicted in DLVO theories. Thus, the Fowkes approach (9) to evaluate the Hamaker constant via surface energetics will be used at to promote the work of wetting to achieve initial dispersion and reconcile the two approaches. Where needed, manipulation of the surface energetics and surface chemical groups will be accomplished by both bioconjugation techniques and specific adsorbates such as citrate that have been used to modify both hard and soft surfaces in our current work on nanoscale drug delivery platforms (3,12).

Activities

There are three activities delineated by year of this 3-year proposal and by outcomes.

Year 1: Critically assessing the approach proposed in Figure 2 based on the dispersion of Polymeric β-cyclodextrin with both hydrophilic and hydrophobic, positively and negatively charged functional groups will be the focus of the first year. There are a wide variety of polymeric β-cyclodextrins commercially available that will be procured and evaluated during this first year. While some functional groups such as succinates, and amine-containing groups will provide negative and positively charged groups to evaluate, with uncharged groups including –OH, esters, ether, and others will be evaluated as well using the polymeric β-cyclodextrin molecule as the basic platform. Initial wetting/state of dispersion evaluations will utilize the Microtrac Nanotrac Wave II dynamic light scattering system to assess particle size distribution from 1 nm to 6000nm as a function of solution pH and ionic strength. We will also evaluate specific surface modification schemes including metal ligand formation, surfactant, and sparingly soluble metal salts to increase wetting behavior.

Well-laundered amorphous silica with optimal coverage of silanol functional groups verified by FTIR will be used as the substrate materials for some surface energetic determinations (AFM and sessile drop). Surface energetics will be evaluated via dynamic tensiometry (Sensa-Dyne 9000 Dynamic Tensiometer) to determine γ_{lv} and diffusion coefficient of the specific polymeric cyclodextrin with sessile drop used to evaluate contact angle that combined with force-distance atomic force microscopy can provide γ_{sl} and, in principle, γ_{sv}.

Zeta potential will be determined on several different instruments depending on the physical state of the samples. For flat samples such as tape cast films on amorphous silica substrates, the Zetametrix Zeta Spin system developed by Sides (5b) will be used to evaluate zeta potential from pH 4 to pH 8.5. For soft fine particles the Microtrac Nano Wave II (from 1 to 6,000nm diameters) and the Brookhaven Zeta PALS) system (3nm to 30um) can determine zeta potential. Zeta potential values as a function of solution pH and ionic strength will be modeled by the multisite

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[11] L. Bergstrom, “Hamaker Constants of Inorganic Materials,” *Advances in Colloid and Interface Science*, 70, 125-169. 1997.

[12] (a) B.M. Barth, et al., “Bioconjugation of Calcium Phosphosilicate Composite Nanoparticles for Selective Targeting of Human Breast and Pancreatic Cancers *in vivo*,” ACS Nano, 4[3] 1279-1287, 2010. (a) B.M. Barth, et al., “Targeted Indocyanine Green-Loaded Calcium Phosphosilicate Nanoparticles for *in vivo* Photodynamic Therapy of Leukemia.,” ACS Nano. 5[7] 5325–5337, 2011.

complexation model (MUSIC) developed by Hiemstra et al. (13). The Hiemstra model uses specific surface sites and chemical reactions combined with surface mass-action equations for the various sites to predict zeta potential. It is proposed that the specific surface chemistry associated with the polymeric β-cyclodextrin molecules will be a near perfect application of the model. Thus, one of the developments for year 1 is beginning a comprehensive data base for surface energetics and surface charge development (and the related electrosteric dispersion) of the pbCD. The MUSIC model also permits direct determination of γ_{sl} via the Lippman equation [1] based on the zeta potential – surface potential relationships for the surface site models that connect zeta potential to surface charge in equation 1.

Year 2: The soft fine particles provided by IFPRI members will be used to expand the database and develop a broader sense for the reconciled surface energetics and DLVO approaches. We will also expand to more modestly altered model systems by evaluating selected members of α-cyclodextrin and γ-cyclodextrin. The broader database can be used to test the hypothesis *if the role of the extrinsic functional groups associated with a polymer cyclodextrin relative both the incremental surface energetics and the incremental changes to surface potential and charge can be established, then a priori predictions of dispersion can be made and used in the processing of soft fine particles*. Thus, year 2 activities will continue the development of the good engineering practices presented in Figure 2, but with modifications and caveats encountered based on the experience for the broader set of materials evaluated in year 2.

Year 3: Additional materials will be added to the database around the control of dispersion, surface chemistry, surface energetics, surface models for specific systems, and reconciliation between surface energetics and DLVO approaches. The development of the database will continue to expand and test around the validity of the hypothesis articulated in year 2.

Outcomes

Year 1: Development of good engineering practices and theoretical underpinnings to disperse soft nanoparticles based on one model system recommended to be polymeric β-cyclodextrin. A hypothesis will begin to be articulated around the general requirements and good engineering practices to be followed for dispersion of soft fine particles in liquids, mostly directed toward aqueous dispersion.

Year 2: Dispersion of soft nanoparticles provided by IFPRI members to broaden database. The fine soft particles provided by industrial members will be evaluated via the dispersion approach outlined above and placed into the database documenting the specific pathway required for each soft material type. The database for the cyclodextrins will continue to be expanded. Calculational strategies will be sent to member companies to evaluate the beta data set available at the end of year 2.

Year 3: Calculational modules that permit prediction of dispersion strategies for general soft and hard materials will be produced as more comprehensive modules for industrial members to evaluate both general and specific utility of the dispersion approaches developed for soft particles.

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[13] T. Hiemstra, et al., "Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: A new approach: I. Model description and evaluation of intrinsic reaction constants." *Journal of Colloid and Interface Science* 133(1): 91-104, 1989. (b) *Ibid.* "Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: A new approach: II. Application to various important (hydr)oxides." *Journal of Colloid and Interface Science* 133(1): 105-117, 1989. (c) *Ibid.* (1996). "Intrinsic Proton Affinity of Reactive Surface Groups of Metal (Hydr)oxides: The Bond Valence Principle." *Journal of Colloid and Interface Science* 184: 680-692, 1996.

IFPRI Research Project Brief

Atomization Under Industrially-Relevant Conditions

The International Fine Particle Research Institute (IFPRI) wishes to fund a project to investigate the atomization of fluids and slurries under conditions relevant to spray drying. The approach to spray drying varies broadly by industrial application, using several different spray nozzle types and a wide range of operating parameters (mass flow, velocity and pressure), spraying fluids with myriad rheological properties in different chamber conditions (temperature and pressure). Although, there is a large body of literature on spray characteristics, little is focused on comparing sprays at conditions relevant to spray drying industry. The purpose of this research is to map the breadth of spray characteristics for a broad range of industrially relevant fluid systems and operating conditions to enable the selection of a set of nozzles and conditions for a given application. The best choice of nozzle for an application depends in most cases strongly on specifics of the application. For example, it may be critical to limit oversize particles in some application or undersize particles in other. Just focusing on an average particle size, as most of the current correlations do, is rarely sufficient.

More specifically, the project should focus on the spatial variation of droplet size distribution for a variety of nozzle types under a range of operating parameters and fluid rheology. Results should be used to develop a "comparison map" of the different nozzles, identifying their operating range and limitations in terms of quality of atomization, i.e. droplet size distribution, spray pattern, and spray stability.

While the scope of the project should be defined by the PI, IFPRI members come from many industry sectors and therefore utilize a broad range of atomizers and fluids. For this reason, at least two nozzle types and 2-3 different scales should be investigated. Fluids should be selected to span the range fluid rheologies used in spray drying, including Newtonian and non-Newtonian solutions and suspensions over a range of solid fractions.

Characterization of Spray Drying Nozzles at Industrially Relevant Conditions

Nasser Ashgriz
Department of Mechanical and Industrial Engineering
University of Toronto, ON, Canada M5S-3G8
ashgriz@mie.utoronto.ca

Proposal to
IFPRI

Summary

This proposal is aimed at developing a set of benchmark experimental data and better models for the droplet size distributions of sprays formed by nozzles relevant to spray drying technology. Despite decades of research on the atomization process, the current models still fail to properly predict droplet sizes at industrially relevant conditions. The present study intends to characterize near-nozzle atomization process. Fluids with different rheological properties will be tested to determine ligament sizes and shapes close to the nozzle and also further downstream of the nozzle. Droplet size distributions as well as correlations for the mean droplet sizes will be developed for industrially relevant fluids. In addition, effect of chamber temperature on the ligament formation and final droplet sizes will be considered.

1 Introduction

In the spray drying process, active ingredients are dissolved in solvents and the solution is atomized into small droplets, which are dried in a heated gas stream to form particles [1]. The morphology of the particles is intimately related to the droplet size distribution of the spray. The droplet size distribution, in turn, depends on the choice of the nozzle, fluid properties, the operating conditions, such as liquid and gas mass flow rates, velocities, pressures and temperatures, as well as the ambient conditions.

In order to determine the proper operating conditions, the desired fluid is tested at a pilot scale system, the results of which are then extrapolated to the production scale. Because of lack of having proper scaling parameters, such extrapolations require several trials before satisfactory conditions are determined. This is a time consuming and costly process. A better understanding of the atomization process for industry relevant fluids would allow development of better scaling models, which can significantly reduce time and cost from pilot to production scale sprays.

There are numerous spray nozzles, the choice of which depend on the liquid properties and the application area. The more commonly used nozzles for spray drying have been pressure swirl nozzles for the production scale and twin-fluid nozzles for the pilot scale tests. And the most important property that influences the atomization process is the rheological properties of the fluid. Generally, it is more difficult to atomize viscoelastic liquids than viscoinelastic liquids [2]. The breakup pattern of viscoinelastic liquids are similar to those of low viscosity fluids, like water. However, viscoelastic liquids generate ligaments that undergo large stretching motion before they breakup into droplets. It is shown [2] that the extensional viscosity is the most significant rheological property that inhibits breakup. For shear thinning fluids the quality of atomization closely relates to the apparent viscosity of the fluid in the limit of infinite shear rate. The Sauter Mean Diameter (SMD) is found to increase with this viscosity (μ_∞) according to [2]:

$$SMD \propto \mu_\infty^{0.42} \tag{1}$$

However, such relations for pharmaceutically relevant fluids are lacking.

There are several correlations for the average droplet sizes generated by complex fluids. We have selected two of them, which have used complex fluids as provided in Table 1, for comparison in this study. One is by Mansour and Chigier for power law liquids [2]:

$$SMD = d_o\left(1+\frac{\dot{m}_g}{\dot{m}_l}\right)\left\{0.0707We_g^{-0.39} + 0.275Oh_l^{0.78}\right\} \tag{2}$$

and the other is by Aliseda et al. for complex liquids, including polymers [3]:

$$SMD = d_o C_1\left(1+\frac{\dot{m}_g}{\dot{m}_l}\right)\left(\frac{b_g}{d_o}\right)^{1/2}\left(\frac{\rho_l}{\rho_g Re_g}\right)^{1/4}\frac{1}{\sqrt{We_g}}\left\{1 + C_2\left(\frac{b_g}{d_o}\right)^{-1/6}\left(\frac{\rho_l}{\rho_g Re_g}\right)^{-1/12} We_g^{1/6} Oh_l^{2/3}\right\} \tag{3}$$

where, d_o is the nozzle diameter, $\dot{m}_g$ and $\dot{m}_l$ are the gas and liquid mass flow rates, respectively, and Weber, Ohnesorge, and Reynolds numbers are defined as: $We_g = \rho_g\left(u_g - u_l\right)^2 d_o/\sigma$, $Oh_l = \mu_l/\sqrt{\rho_l \sigma d_o}$, and $Re_g = b_g \rho_g u_g/\mu_g$, where $b_g$is the thickness of the gas layer that impinges on the liquid. These correlations are selected since they have some theoretical base. In particular, equation (3) uses jet instability models to come up with form given. The correlation constants are then determined based on experimental results.

None of the spray nozzles can provide satisfactory atomization outcome for the full range of desired viscosities and operating conditions [4]. Therefore, it is important to determine the operating range of each nozzle that results in the desired atomization. For instance, an internally mixed nozzle may result in more ligaments than externally mixed nozzles, which may not be good for drying conditions. Long ligaments may dry quickly before they breakup into droplets.

Many high viscosity liquids also have solid suspensions. Solid particles not only change the effective viscosity of the liquid, but also have added atomization complexity [5]. For instance, larger solid particles may separate from the liquid after atomization resulting in a bimodal droplet size distribution. A correlation for fluids with suspension is given by Mulhem et al. [6] (an IFPRI supported project):

$$SMD = 0.21 d_o Oh_l^{0.0622}\left(\frac{\dot{m}_g}{\dot{m}_l}We_g\right)^{-0.4} \tag{4}$$

And another by Dooher [7]:

$$SMD = \frac{10^4 d_o \sqrt{Oh_g} We_g^{-1.09}}{\sqrt{A_s},} \tag{5}$$

where A_s is the cross sectional area of the spray at the measurement distance from the nozzle.

Inspection of correlations given in equations (2-5) shows a large variation in the exponents of the scaling parameters, We_g, Re_g, and Oh_l. For instance, the coefficients of the We_g are 0.39, 0.4, 0.5, and 1.09, and those of Oh_l are 0.06, 0.5, 0.6, 0.78. This limits the validity of each correlation beyond the conditions and fluid that they are developed for.

There are many more studies and correlations for high viscosity liquids using twin fluid nozzles [8-15]. Although they all indicate that high viscosity liquids generate ligaments that take longer time to breakup or even do not breakup, in the case of polymeric fluids, none have characterized such ligaments. This is the main objective of the present research. We intend to map different sprays based on ligament sizes (length and diameter).

Table 1-Fluid properties tested

Fluid	Viscosity (mPa.s)	Viscosity at the upper shear rate (mPa.s)	Ref.
Xanthan gum + water	30-14,761	1.58-2.82	[2]
Polyacrilamide E10 Polymer +water	2.1-9342	1.2-12.1	[2]
Glycerol+water	1-78	62	[3]
CA-PEG	146	152	[3]
Opadry-HPMC 15% solids	192	133	[3]
Opadry-PVA 20% solid	235	66	[3]
Maltodextrin + water	60-308		[4]

2 Issues and Objectives

Issue I: The literature provides correlations for the average droplet diameter (e.g., SMD) at relatively long distances from the nozzle. The distance has to be long enough that all ligaments and fibers are broken into relatively spherical droplets, so that they can be measured. The literature also shows that high viscosity fluids do not turn into droplets immediately after breakup. The higher the fluid viscosity, the longer it takes for ligaments to breakup, if they breakup at all. This becomes an important issue in spray drying, when the ligaments are exposed to high gas temperature and dried. In such conditions, the ligament and fibers may not have enough time to breakup and the atomization is not completed. **Currently there are no quantitative spray characteristics on the ligaments and fibers generated close to the nozzle.**

Issue II: Although the prior studies measure the droplet size distributions, they mainly report the average size and not the distribution itself. **The information on the droplet size distribution for the atomization of high viscosity liquids is very limited.** Although, correlations for the average droplet size in the spray are useful for design and scaling, they do not provide the width of the size distribution. The larger droplets play a significant role in the final particle quality.

Issue III: The available correlations are mainly obtained by using a narrow range of nozzles sizes but a wide range of operating conditions. Therefore, they cannot reliably be used for large scale production nozzles and conditions. **Correlations that provide droplet size information for a large range of nozzle scales are needed.**

Issue IV: The currently available literature on the droplet size distributions are obtained at normal ambient conditions. **Effect of the hot ambient conditions, as in the spray dryers, on the evolutionary process of primary and secondary atomization is not available.** This information is needed since ligaments may quickly dry before secondary atomization, completely changing the final spray size distribution.

Objectives:

I. **Develop a benchmark data set for the near nozzle spray characteristics for high viscosity fluids.** Sprays will be characterized based on the size and shape of the ligaments at different distances from the nozzle. Such data would provide information on the evolution of the droplet size distribution and the influence of the secondary atomization on the final droplet sizes. We will

- develop a comparison map for different nozzles identifying their operating range and limitations in terms of the quality of the atomization, including, near-field droplet and ligament shape and length distributions, and far field droplet size distribution, and
- determine the time and distance it takes for ligaments with certain initial characteristics (length, thickness, and fluid properties) to breakup into droplets.

II. **Determine correlations for the nozzle scaling.** We will perform spray characterization at several different scales to identify the governing parameters for proper scaling of the nozzles. We will determine how the nozzle and flow parameters need to be changed for a production scale nozzle to generate the desired droplet size distribution as obtained from the pilot scale nozzle.

III. **Determine correlations for the effect of ambient temperature,** on the droplet size distribution.

Scope: In order to limit the range of parameters, it is proposed to characterize sprays at the following conditions: Twin-fluid and pressure swirl nozzles with three different scales and several different fluid types with varying rheological properties. These may include water-glycerin mixtures, water–maltodextrin solutions, complex fluid with varying shear and extensional viscosities, fluid with suspensions, and organic polymer solution (Pharmaceuticals). The final choice of the solutions will be based on recommendations by the industry partners.

3 Proposed Research

3.1 Near Nozzle Spray Characterization

The atomization process of high viscosity fluids is different than those of low viscosity liquids mainly because of two important factors. One that it takes more energy to atomize a high viscosity fluid and the other that it takes a much longer time for the atomized ligaments to become somewhat spherical droplets. These effects are loosely referred to as the primary atomization (for the initial atomization process) and the secondary atomization (for the later breakup of ligaments). For low viscosity liquids, there is basically no secondary atomization, and the ligaments formed are small enough that they quickly become spherical. However, for high viscosity liquids, the ligaments can be very long, and they may stretch to become even longer once they are separated from the core flow. This effect is exasperated for fluids containing polymers.

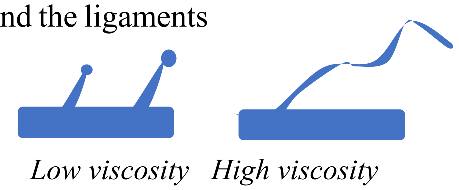

Figure 1 [4] shows images of a spray close to two different types of twin-fluid nozzles, and for inlet air pressures of 0.14 and 0.28MPa and gas to liquid ratios of 10% and 20%. The solution is water-maltodextrin-50% at room temperature, resulting in a 308mPa.s. It is observed that the atomization process generates long filaments close to the nozzle. Such filaments were observed for solutions as low as 40% maltodextrin with viscosity of 60 mPa.s, however, the filaments were thinner [4]. Another observation is that the atomization behavior of the ligaments depends on the nozzle type.

Although, spray images, such as those in Fig. 1 [4] are sporadically available in the literature, none have quantitatively characterized them. One of the objectives of the present research, which distinguishes it from other studies, is that we intend to characterize the primary atomization, or the spray close to the nozzle. Filament sizes (e.g., length, diameter, and shape) will be characterized for different nozzles and operating conditions, and for changes in the elongational and shear viscosities.

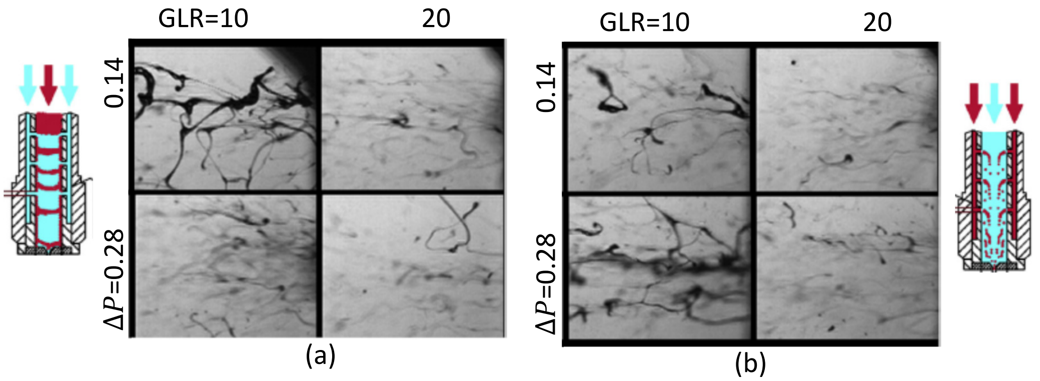

Figure 1- Near-nozzle spray pattern for two different nozzles and for $\mu_l = 308\ mPa.s$ and for different injection pressures (ΔP) and gas to liquid ratios (GLR) [4].

3.2 *Droplet Size Distribution*

Although most studies that measure and provide correlations for the average droplet size in the spray actual have data for the droplet size distribution, they do not report them. For low viscosity fluids the droplet size distributions curves are mainly similar and authors do not report them to limit redundancy. However, for high viscosity fluids, the size distribution can significantly change from one condition to another.

Figure 2 shows the droplet size distributions for three different water/glycerin mixtures (120, 30, 1.3mPa.s) and at three different distances from the nozzle ($x^* = x/d_o$) [16]. An internal mix twin-fluid nozzle was used in this study. The figure shows bimodal distributions for high viscosity cases. The results also show that close to the nozzle, x^*=17, the large droplet volume fraction is large for the high viscosity solution. This difference shows that the primary atomization for the high viscosity solution is worse than low viscosity solution. As atomization proceeds, fragments break up further and small drops begin to merge. The distribution changes to unimodal when x^*= 50 for two lower viscosities. With a further increase in distance, x^*= 133, right shifts of the peaks are observed, probably due to droplet coalescence. At this distance, the distributions for the two lower viscosities becomes almost unimodal.

Clearly, reporting only the SMD does not provide any of the significant changes that is observed in the spray. Therefore, we intend to measure and report all droplet size distributions across the spray and at different distances from the nozzle.

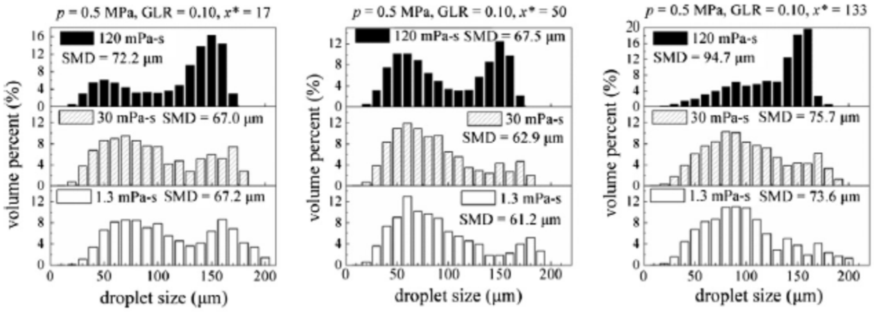

Figure 2- Droplet size distribution for different liquid viscosities and different distances form the nozzle [16].

Such data would allow the user to determine whether there are size segregations and significant secondary atomization along the spray axes or if there are many large droplet sizes.

3.3 Droplet Size Correlations

Correlations for droplet sizes for pharmaceutically relevant fluids are very limited. Currently, correlations similar to those given in equations (2-5) are used to scale different nozzles. We intend to develop similar correlations for pharmaceutically relevant fluids. Our correlations will most likely be in the following form:

$$SMD = d_o\left(1+\frac{\dot{m}_g}{\dot{m}_l}\right)\left\{C_1 We_g^{-a} + C_2 Oh_l^b\right\} \tag{6}$$

which is shown to include all relevant scaling parameters. Except that we need to provide Oh in terms of relevant viscosity of the solutions. This requires a knowledge of the shear rate at the nozzle so that the fluid viscosity can be estimated. The liquid viscosity (shear and elongational viscosities) will be fully characterized in this study and will be incorporated in the correlations to determined the relationship between the size and viscosity: $SMD \propto \mu_l^n$.

By exploring a broad selection of fluids and operating conditions, we can determine the effects of key non-dimensional parameters (We, Oh, and Re numbers) on the atomization phenomena. In addition, studies with two-fluid nozzles have shown that the spray characteristics depend on the atomization gas to liquid flow rate. This study would help us elucidate the atomization mechanism with changes in the gas to liquid ratios.

3.4 Scaling of a Nozzle

Studies on the utilization of spray drop size correlations in the production scale [e.g., 17] have shown that the correlations do not work for high viscosity fluids, even though they were developed for such fluids at the pilot scale. One explanation for this is that the correlations have not used a wide enough nozzle scales to extrapolate the results to the production scale.

One of the important variables involved in the control of droplet size for a two-fluid nozzle is the mass ratio of atomization gas flow rate to liquid flow rate (GLR). An increase in this ratio should cause a decrease in droplet size. At a critical GLR value the atomization gas reaches its maximum velocity, which is the speed of sound for a convergent nozzle, and subsequent increases in the atomization gas flow rate only increases the atomization gas pressure (density). This will have a much smaller effect on atomization than the atomization gas velocity (i.e., the SMD is constant).

At the lower atomization gas flow rates, the SMD is found to increase with faster liquid flow. At the higher operating gas flows, no difference in SMD is found among the investigated liquid flows. The degree of atomization is determined by the velocity difference between the atomization gas and the liquid. Therefore, the liquid flow rate has lower importance when operating at higher atomization gas flow rates.

The above information is currently used to scale up a nozzle. However, scaling studies [17] have shown that GLR leading to the same droplet size distribution is substantially lower for the production scale nozzle than the pilot scale nozzle. This is attributed to higher atomization gas velocities for the production scale nozzle when compared to the pilot scale nozzle resulting in smaller droplets for identical atomization gas to liquid flow ratio. Therefore, scaling up just using the GLR is not correct.

We intend to increase the nozzle size until the changes in the GLR can be properly quantified, before reaching the critical conditions for the pilot scale. Then, the knowledge of the droplet size distribution for the pilot scale nozzle in combination with a model can be used to predict nozzle operation conditions resulting in same droplet sizes for a larger nozzle of similar design.

3.5 Effect of Ambient Conditions

If long ligaments and filaments are introduced inside a hot gaseous environment, they may dry before they breakup, resulting in long dried filaments. Therefore, the secondary atomization is needed to breakup these ligaments into small droplets, otherwise, they will remain as such in the flow. One of the main issues with scaling pilot scale tests to production scale is the time requirement for the secondary atomization of the filaments, which may be incorrectly scaled.

We will test different sprays inside a temperature controlled chamber to determine the effect of ambient temperature on the droplet and ligament size distribution. An environmentally controlled chamber, as shown here, already exists in our labs, which can be used for this study.

3.6 Measurement Technique

The prior studies have mainly used light scattering techniques to measure the droplet sizes. The commonly used instruments are the Spraytec system by Malvern and PDPA systems by TSI, Dantec, and Artium. These systems cannot properly work if the liquid is the form of long ligaments. An imaging system is a better choice for characterizing such sprays.

We will use an inhouse imaging instrument as shown in Fig. 2. This system can generate high intensity flash lights of 15 nanoseconds duration. And it can resolve sizes down to 2 microns. An image processing software analyzes the images at a fast rate to determine the particle shape factors. The particle shapes, in terns of their length and thickness will then be used to map different types of sprays.

Figure 2- The spray sizer based on imaging.

4 A detailed outline of the proposed program

1) Testing of twin fluid and swirl nozzles to identify and map the dominant atomization mechanisms for different solutions, and to provide guidance on the selection of nozzles based on nozzle dimensions and operating conditions (Year One).
2) Development of droplet size distribution and mean droplet size correlations for industrially relevant conditions, including the environmental conditions, to identify conditions that provide tight monomodal droplet size distributions, and quick droplet formation for fast drying (Year Two).
3) Measurement of the variation of the sizes of droplets and ligaments along the axis of the sprays at elevated ambient temperatures to develop models for the secondary atomization of relevant fluids (Year Three).

5 Critical unknowns that may influence the direction/outcome of the project.

Determining a correlation for drop size distribution in terms of rheological properties of the fluid requires a detailed understanding of atomization process that occur near the nozzle. For low viscosity liquids droplets are instantly separated from the liquid core, however, for high viscosity and non-Newtonian liquids fibers and ligaments are formed that later will break into droplets. Therefore, a unified correlation that defines all fluids may not be possible. It may be necessary to identify, categorize and map the spray based on atomization mode and rheological properties.

In addition, the filaments may be too convoluted to be able to measure their lengths. It may be necessary to only categorize the filaments, as long, medium or short, in order to map different types of sprays.

Many spray size distributions follow log-normal distribution pattern. In such cases, it is possible to identify the distribution based on two parameters, mainly mean and standard distribution. However, based on the type of atomization there might be flow conditions that do not necessarily follow a log-normal behavior, namely, multi-mode atomization, where different sizes are produced due to different type of atomization.

6 What will be accomplished: Accomplishments Tasks and goals.

- Selection of the nozzles and identification of the operating conditions.
- Capturing near-field and far-field images of the spray for a range of fluids.
- Identify the atomization regimes for various mixtures and nozzles.
- Provide droplet size distributions for all operating conditions.
- Compare size distribution of fluids with varying rheological properties.
- Obtain SMD correlations for all the tested conditions with emphasis on the fluid properties and nozzle scaling.

7 How this project could leverage into existing programs in which your research team is engaged

This project can be leveraged to obtain government funds from Canadian research organizations, including NSERC, MITACS, and OCE. These organizations provide 2 to 1 support for any industrial cash grant. In many cases, if the scope of the project is expanded, it is possible to receive funds from two of the above three organizations, making the leverage 4 to 1. Therefore, $38,000 USD annual grant from IFPRI, which is equivalent to $48,640 Canadian dollars, can be increased to $145,920 or possibly to $243,200.

The spray labs at the university of Toronto is equipped with Spraytec instrument by Malvern, PDPA system by TSI, and IPI (interferometric particle imaging) by Dantec, as well as our own particle imaging system. Therefore, all spray characterization system are already available and there in no requirement to acquire new systems.

Out lab is also equipped with an environmental chamber to control the ambient temperature and pressure. The chamber is equipped with a set of windows for using instruments from the outside of the chamber, and it is large enough to put instruments inside the chamber for closeup imaging.

8 Indications where IFPRI members could support the program through provision e.g. of model test materials, test methods, industrial experience.

This project will be in close collaboration with the IFPRI members with regular conference calls. We will test fluids of interest to the industry and the operating conditions for their pilot scale and if possible the production scale.

9 References

[1] Masters, K., “Part V. Applications of spray drying in industry”, in Spray Drying Handbook, 5th Ed.; Longman Scientific & Technical U.K.: Harlow Essex, England, 1991; 491–680.

[2] Mansour, A. and Chigier, N., “Air blast atomization of non-Newtonian liquids,” *Journal of non-Newtonian Fluid Mechanics,* 58, 1995, pp:161-194.

[3] Aliseda, A., E.J. Hopfinger, J.C. Lasheras, D.M. Kremer, A. Berchielli, E.K. Connolly, “Atomization of viscous and non-Newtonian liquids by a coaxial, high-speed gas jet. Experiments and droplet size modeling”, International Journal of Multiphase Flow, Volume 34, Issue 2, February 2008, Pages 161-175.

[4] Mlkvik, M., Stähle, P., Schuchmann, H.P., Gaukel, V., Jedelsky, J., Jicha, M., “Twin-fluid atomization of viscous liquids: The effect of atomizer construction on breakup process, spray stability and droplet size,” International Journal of Multiphase Flow Volume 77, December 2015, Pages 19-31.

[5] S.Y. Son, K. K. (1998). Effect of coal particle size on coal water slurry atomization. *Atomization and Sprays*, 503-519.

[6] Mulhem, B., Gunther Schulte, Udo Fritsching, “Solid-liquid separation in suspension atomization”, Chemical Engineering Science, Volume 61, Issue 8, April 2006, Pages 2582-2589

[7] Dooher, J. P. (2005). Fundamental Considerations for coal slurry atomization . *Atomization and sprays*, 585-602.

[8] U. Fritsching, B. M. (2009). Influence os suspended solid particles on suspension atomization process.

[9] Semiao, V., Pedro Andrade, Maria da Graca Carvalho, Spray characterization: Numerical prediction of Sauter mean diameter and droplet size distribution, Fuel, Volume 75, Issue 15, November 1996, Pages 1707-1714

[10] M. Sacchetti, and M. M. Van Oort. Spray-drying and supercritical fluid particle generation techniques. In A. J. Hickey (ed.), Inhalation Aerosols, Physical and Biological Basis for Therapy, Vol. 94, Lung Biology in Health and Disease, Marcel Dekker, New York, 1996, pp. 337–384.

[11] Bittner, and T. Kissel. Ultrasonic atomization for spray drying a versatile technique for the preparation of protein loaded biodegradable microspheres. J. Microencapsul. 16:325–341 (1999).

[12] B. S. Freitas, H. P. Merkle, and B. Gander. Ultrasonic atomisation into reduced pressure atmosphere—envisaging aseptic spray-drying for microencapsulation. J. Control. Release 95:185–195 (2004).

[13] S.C. Tsai, B. Viers, Airblast atomization of viscous liquids, Fuel 69 (1990) 1412–1419.

[14] S.C. Tsai, K. G. (1991). Air blast atomization of micronized coal slurries using a twin fluid jet atomizer . *Fuel*, 483-490.

[15] L. Zhouhang, W. Yuxin, Y. Hairui, C. Chunrong, Z. Hai, H. Kazuaki, T. Keiji, L. Junfu, Effect of liquid viscosity on atomization in an internal-mixing twin atomizer, Fuel 103 (2013) 486–494.

[16] Li, Z., Wua, Y., Yang, H., Cai, C., Zhang, H., Hashiguchi, K., Takeno, K., Lu, J., “Effect of liquid viscosity on atomization in an internal-mixing twin-fluid atomizer,” Fuel 103 (2013) 486–494.

[17] Thybo, P., Hovgaard, L., Anderson, S.K., and Lindelov, J.S., “Droplet size measurement for spray dryer scale-up,” Pharmaceutical Development and Technology, 13, 2008, pp: 93-104.

Research Proposal for IFPRI Project 2018-2020

Mapping the spray characteristic within atomization of non-Newtonian liquids for spray drying applications

Dr.-Ing. Lydia Achelis and Prof. Dr.-Ing. habil. Udo Fritsching
Particles and Process Engineering, University of Bremen, Bremen, Germany
Institute of Materials Science, Bremen

Introduction

The most suitable or ideal spray for spray drying operation contains monodispersed (equally sized) droplets homogeneously spreading at constant concentration (resp. mass flux distribution), a condition that can practically not be achieved. The atomization process of the liquid feed in spray drying delivers a spray of liquid droplets that is characterized by its **spray quality** in terms of drop size distribution (DSD, typically given in terms of some overall mean or characteristic drop size of the distribution) and the **spray homogeneity** (spray shape and / or morphology, spray angle, or more precisely the spatial mass flux distribution). Practical spray drying operations and spray dried products need to address problems of oversized particles (e.g. causing process problems due to sticking within the dryer, or afterwards in the product e.g. the need to be comminuted / milled or grinded in post processing) or undersized particles (dust removal from product or agglomeration necessity for instance by fines return into the dryer atomization zone). Therefore, in order to characterize the atomizer characteristics and process performance in spray drying correctly it is necessary to describe the **shape and the width of the specific drop size distribution** (in terms of distribution moments or characteristic span values) and its spatial variation together with the spray homogeneity.

Spray drying atomization fundamentals regarding nozzle design and operations with respect to the specific fluids to be atomized are important for proper layout of the drying process for specific feed streams [Maj14, Mas02]. The liquid feed in spray drying is to be characterized in terms of its specific **rheological behavior**. Typical fluids to be operated in spray drying are melts or solutions (typically at higher viscosities) with Newtonian or non-Newtonian viscosity behavior and slurries or emulsions with non-Newtonian behavior [Mew12, Wil13]. The rheological liquid behavior impacts the disintegration behavior of the feed and thus the spray quality.

Atomizer or nozzle types in spray drying applications are utilizing either potential (pressure), kinetic or centrifugal energy (in rotary atomizers, twin-fluid nozzles, or pressure swirl atomization devices). Thus either jet or sheet fragmentation is found. Choosing the most appropriate nozzle for a specific spray drying task is always challenging. However, typical operation conditions and relations of spray quality and homogeneity can be found in literature and from manufacturers.

Though myriads of investigations can be found in literature that are known to describe the spray quality of specific atomizer configurations (see summaries in: [Lef17, Wal05] a **lag of knowledge** and data needs to be postulated especially when it comes to:

- industrial scale atomizers (at relevant throughputs)
- spatial (or temporal) variations in the spray characteristics
- inhomogeneous liquids (suspensions, emulsions, ...) and non-Newtonian liquids.

Challenges in experimental spray characterization and spray analysis at these industrially-relevant conditions arise especially from the highly dynamic processes (impeding the identification of disintegration mechanisms) and the high spatial drop densities (dense sprays) that may lead to measurement problems and inaccuracies.

Aims

This proposal and investigation of spray drying atomizers operating with non-Newtonian liquids aims the **derivation of scaling maps and correlations for the basic spray parameters spray quality (DSD) and spray homogeneity (flux)** for the

- Droplet-size-distribution DSD (not just mean size, but also distribution width - in terms of e.g. characteristic deviation, span value, or RRSB parameter)
- local (or spatial) variations in the DSD,
- local spray homogeneity (spray angle and mass flux distribution).

The parameters to be investigated are reflecting typical conditions in spray drying operations in terms of:

- atomizer or nozzle type (jet or sheet, centrifugal, ...)
- process parameters (throughput, ...)
- liquid parameters (rheology, ...)

The project aims at derivation of scaling and / or comparison maps describing the spray quality and spray homogeneity for typical spray drying nozzle types and operation conditions especially for non-Newtonian liquid feed rhelogy. The correlations should enable scaling possibilities for different operational conditions and principles of atomizer devices.

Critical unknowns / State of the art in atomizer design for spray drying

Characteristics of industrial scale atomizer systems within spray drying applications principally are based on:

- correlations on basic atomizer setups from scientific or technical application literature, typically derived at **labscale devices**
- operational charts and diagrams from atomizer device manufacturers, typically derived for **water as operating liquid**.

The most appropriate nozzle for a specific spray drying task and operation is not easily found. Scaling typically is not possible as mechanism limits are not indicated. Typical operation conditions and spray information can be found in literature and from manufacturers for "simple" fluids only.

Atomization of a liquid stream depends on inherent liquid instabilities and the interaction of the fluid stream with the surrounding gas (at the interface). As a result, liquid fragmentation occurs in different modes depending on liquid and process parameters. Engineering derivations typically summarize these specific modes in mode charts and correlations depending on dimensionless influencing numbers (as Reynolds, Weber, Ohnesorge, Bond, Froude, ...). It is important that specific correlations are only valid within the device and process window and atomization mode where these have been derived for (or the experiments have been done).

Research program for initial three years

Characterization of non-Newtonian liquid atomization behavior for spray drying applications needs a fundamental approach. Thus the initial phase of the project is devoted to **generic atomization experiments**. In the first instance, the disintegration of (laminar) liquid jets and sheets (from rotary as well as pressure nozzles) is analyzed. Here, individual threads and planar sheets will be investigated and analyzed in basic studies. It is postulated in this context that conventional disintegration charts, scaling laws and drop size correlations need to be extended by one (at minimum) additional parameter (repectively dimensionless number) characterizing the **non-Newtonian behavior**. Starting from a description of the rhelogical behaviour in a pseudoplastic approach with shear thinning behavior based on the Ostwald/deWaele equation (power law), the exponential factor of shear thinning will be taken as base of the correlation. However, further approaches need to be taken into account. The models to be derived will be transferred to **spray dryer scaled atomization systems** that will be specified and investigated in the course of the project.

Schedule and Milestones

The tentative working program and the intended milestones/deliveries within the first period (years 1 - 3) are as follows:

<u>Year 1</u>

Subject: Setup of experimental facility (spray rig) for pressure and centrifugal atomization in lab and industrial scale
Installation of measurement devices for **local** measurements: laser diffraction, light sheet, patternator, high-speed video, ...
Spray and breakup characterization for water based (water/glycerol) liquids
Milestones: Proof of principle for the experimental and measurement systems
Setting up of an evaluation procedure for description of:
- local DSD (mean and width)
- spray homogeneity (mass flux)
- breakup mode

<u>Year 2</u>

Subject: Generic studies of laminar Newtonian and non-Newtonian jets and sheets
Installation and testing large scale atomization systems
Milestones: Disintegration chart for non-Newtonian jets and sheets (pressure and rotary),
Initial formulation of local DSD correlations
Identification of relevant dimensionless parameters for non-Newtonian fragmentation behavior
Creation of break-up mode charts for non-Newtonian liquids

Year 3

Subject: Investigating the role of turbulence on jet and sheet breakup in non-Newtonian liquids
Analyzing (some) commercial or equivalent based atomization nozzle systems (at least in 2 different scales)

Milestones: correlations and scaling laws for pressure and centrifugal atomization of non-Newtonian liquid jets and sheets in commercial spray drying application nozzle systems

Outlook onto second period (years 4 to 6):

Topics to be addressed in the second period of the project are mainly on extension of the program to other nozzle systems and other rheological feed parameters. The close-up of the investigation to commercial nozzle systems is to be checked. The exact definition of the research program and its parameter to be evaluated is to be defined (in cooperation with IFPRI industrial members) after the first period. Some possible topics for the second period are:

- Other atomization principle: Atomization of non-Newtonian liquids in twin-fluid (gas assisted) nozzle configurations.
- Other feed systems: Evaluating relevant suspension liquids in terms of: particle concentration (Bachelor) and particle shape (thus including Krieger/Doherty and shear hardening behavior)
- Other nozzle system: The relation and relevance of commercial nozzles in spray drying (e.g. GEA/Niro, Spraying Systems, Delavan, BETE, ...) will be screened.
- Other nozzle systems: Evaluating the potential of hybrid atomization systems (e.g. gas assisted pressure swirl) in spray drying applications [Fri12]

Fitting into the PI research portfolio / Preliminary investigations

The research group at the University Bremen investigates multiphase flows and atomization processes of complex liquids with demanding rheological properties within the past 30 years. Here e.g. metal melts (high surface tension) [Fri06, Ach08, Hen17], high-viscosity liquids and melts [Loh02, Czi08], suspensions [Lix11, Mul03, Mul06] and emulsions [San17] among others have been studied. In this context the development of tailored atomization systems has been performed that are described in [Czi08, Fri12]. The atomization process in spray drying and its impact on spray quality and agglomeration processes has been studied [Lit12, Ver04].

Several general overview articles and handbook contributions on atomization and spray systems have been published [Fri06, Fri16, Hen17, Lix17].

The Particles and Process Engineering group at the University Bremen is one of the promoting and inventing institutions for laser diagnostics in sprays and multiphase processes, namely for Phase-Doppler-Anemometry (PDA) [Men03], and in-process spectroscopy [Gil01, Gla15].

IFPRI support with project

This research proposal intends cooperation and proper support of IFPRI member institutions and industrial partners, especially by:

- identification of relevant operational conditions in spray drying
- identification and delivery of typical feed materials for spray drying purposes: suspension particles, commercial and technical liquids, ….
- identification and characterization/description of rheological properties of spray drying relevant liquids
- identification of commercial relevant atomization systems and suppliers

References

General

[Maj14] Majumdar, A.S.: Handbook of Industrial Drying, CRC Press 4th Edition 2014

[Mas02] Masters, K.: Spray Drying in Practice, SprayDryConsult Int. ApS Denmark 2002

[Mew12] Mewis, J.; Wagner, N.: Colloidal Suspension Rheology, Cambridge Univ. Press 2012

[Lef17] Lefebvre, A.; McDonnel, V.: Atomization and Sprays, CRC Press, 2nd Edition 2017

[Wal05] Walzel, P.: Spraying and Atomizing of Liquids, Ullmann´s Encyclopedia of Industrial Chemistry, 2005

[Wil13] Willenbacher, N.; Georgieva, K.: Rheology of Disperse Systems, in: Bröckel, U.; Meier, W.; Wagner, G. (Eds): Product Design and Engineering, Wiley-VCH Verlag GmbH, Weinheim, pp. 7-49 (2013)

Bremen contributions

[Ach08] Achelis, L., Uhlenwinkel, V. "Characterisation of metal powders generated by a pressure-gas-atomizer.", MSE A 477, Volume 477 (Issues 1-2) 15-20 (2008)

[Czi08] Czisch, C; Fritsching, U.: Atomizer design for viscous-melt atomization; Mat. Sci. Engng. A 477 (2008) 1-2, 21-25

[Fri06] Fritsching, U.; Bauckhage, K.: Sprayforming of Metals in: Ullmann´s Encyclopedia of Industrial Chemistry, 7th Edition, 2006 Electronic Release, Wiley VCH, Weinheim 2006

[Fri12] Fritsching, U.; Uhlenwinkel, V.: Hybrid Gas Atomization for Powder Production; In: Kondoh, K. (Ed.): Powder Metallurgy, InTech Publ., March 2012, pp. 99-124

[Fri16] Fritsching, U. (Ed.): Process-Spray: Functional Particles Produced in Spray Processes; Springer Int. Publ. Switzerland (2016)

[Gil01] Gillandt, I.; Fritsching, U.; Bauckhage, K.: Measurement of Phase Interaction in Dispersed Gas / Particle Two Phase Flow; Int. J. Multiphase Flow 27 (2001), 1313 – 1332

[Gla15] Glasse, B.; Riefler, N.; Fritsching, U.: Intercomparison of Numerical Inversion Algorithms for Particle Size Determination of Polystyrene Suspensions Using Spectral Turbidimetry; Journal of Spectroscopy Volume 2015, Article ID 645879

[Hen17] Henein, H.; Uhlenwinkel, V.; Fritsching. U. (Eds.): Metal Spray and Spray Deposition; Springer International Publishing, Switzerland (2017)

[Lit12] Littringer, E.M., Mescher, A., Schroettner, H., Achelis, L., Walzel, P., Urbanetz, N.A. "Spray dried mannitol carrier particles with tailored surface properties - The influence of carrier surface roughness and shape", European Journal of Pharmaceutics and Biopharmaceutics, 82 (1) 194-204 (2012).

[Lix11] Li, X.G.; Heisterüber, L.; Achelis, L.; Uhlenwinkel, V.; Fritsching, U.: Spray Process Modelling in Metal Matrix Composites Powder Production; Atomization and Sprays 21 (2011) 11, 933–948

[Lix17] Li, X.; Fritsching, U.: Spray Systems, In: Multiphase Flow Handbook Second Edition (Eds: Michaelides, E.E.; Crowe, C.T.; Schwarzkopf J.D.); CRC Press - Taylor & Francis Boca Raton 2017, pp. 1091-1250

[Loh02] Lohner, H.; Fritsching, U.; Bauckhage, K.: Melt Atomization by Heated Gases; ILASS-Europe 2002, Zaragoza, Spanien, 9-11 September 2002, Proceedings

[Men03] Menn, P.; Schulte, G.; Fritsching, U.: Phasen-Doppler-Anemometrie bei Zerstäubung von Prozessfluiden in der Sprühtrocknung, GALA Laser Anemometry 2003

[Mul03] Mulhem, B.; Fritsching, U.; Schulte, G.; Bauckhage, K.: Effect of Solid Particle Characteristics on Suspension Atomization; Atomization and Sprays 13 (2003) 2&3, pp. 321-343

[Mul 06] Mulhem, B.; Schulte, G.; Fritsching, U.: Solid-liquid separation in suspension atomization, Chem. Eng. Sci. 61 (2006) 8, 2582-2589

[San17] Sander, S.; Tischler, C.; Achelis, L.; Henein, H.; Fritsching, U.: Production of Polymer Microparticles by Electrospray Atomization; Atomization and Sprays, 27(5): 457–464 (2017)

[Ver04] Verdurmen, R.E.M.; Menn, P.; Ritzert, J.; Blei, S.; Nhumaio, G.C.S.; Sonne Sørensen, T.; Gunsing, M.; Straatsma, J.; Verschueren, M.; Sibeijn, M.; Schulte, G.; Fritsching, U.; Bauckhage, K.; Tropea, C.; Sommerfeld, M.; Watkins, A.P.; Yule, A.J.; Schønfeldt, H.: Simulation of Agglomeration in Spray Drying Installations: The EDECAD Project; Drying Technology 22 (2004) 6, S. 1403-1461

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IFPRI Research Project Brief

Adhesion of Powders to Metal Surfaces During Compaction

The International Fine Particle Research Institute (IFPRI) wishes to fund a research project to develop fundamental understanding and predictive relationships between a powder's physical and chemical properties and its propensity to adhere to metal surfaces of compaction tooling. The project should include the following elements:

- Identification of appropriate test powders and characterization of their relevant physical and chemical properties. Note that IFPRI is comprised of member companies from many industry sectors, so the choice of powder should not be constrained to those of pharmaceutical interest. Powders of interest range in mean particle size from 5 to 500 microns.

- Establishment of a test method to quantify material adhesion on compaction tooling over an industrially relevant range of process and environmental conditions

- Identification of key factors affecting the amount and/or rate of powder adhesion on compaction tooling such as:
    - molecular, crystal, surface, and mechanical properties of the powder
    - surface finish and chemistry (including coated surfaces)
    - process conditions (e.g. pressure/stress)
    - environmental conditions (temperature, relative humidity)

- Establish predictive criteria for the propensity of adhesion given a set of molecular/crystal properties and process/environmental conditions

Adhesion of Powders to Metal Surfaces during Compaction

IFPRI Research Project Proposal

Dr. Csaba Sinka
Department of Engineering, University of Leicester, UK
ics4@le.ac.uk

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Adhesion of powders to metal surfaces during compaction (referred to succinctly as "sticking") is a significant problem in powder pressing sectors including pharmaceuticals, food, detergents, batteries etc. Sticking is difficult to predict in early stage of product formulation and process development and usually manifests during full production scale where high productivity machines such as rotary tablet presses are used. The remedy consists of stopping production, remove, clean, reassemble tooling and continue processing until the material builds up on the tooling surfaces again. In pharmaceuticals it is believed that 25% of solid dosage forms are affected by sticking.

Review of state of the art research on sticking

Empirical research on sticking reported in the literature include observations and mitigating procedures based mostly on lubrication of the powder and/or change of surface finish of the tooling. Toyoshima et al. (1988) correlated sticking tendency with the surface roughness of the tablets and alleviated sticking by lubrication. Bakar et al. (2007) characterised sticking by measuring the damaged area on the surface of the tablet and used granulation to mitigate the problem. Reed et al. (2015) used different tools on a rotary press at the same time and evaluated the sticking tendency visually. Mullarney et al. (2012) assessed tablet-sticking propensity by weighing the powder accumulated on a removable punch tip. They observed that increasing internal lubrication increased sticking for ibuprofen but decreased sticking for mannitol. Roberts et al. (2014) confirmed that increasing lubrication increased sticking of ibuprofen but noted stearic acid didn't. McDermott et al. (2011) examined sticking using electron microscopy and X-ray diffraction mapping and observed that increased solid fraction and increased lubricant concentration led to decreased sticking tendency. Waimer et al. (1999) developed an instrumented upper punch to measure the adhesion force to the top of the tablet. Hamid and Betz (2012) associated sticking with high radial stress transmitted to the die wall. Simmons and Gierer (2012) reported empirical observations using a number of punches, Wang et al. (2015) related sticking to surface roughness while Uchimoto et al. (2013) related sticking to punch surface roughness.

Research on sticking, however, is not limited to empirical observations. Wang et al. (2003) used molecular simulations and atomic force microscopy to determine the work of adhesion and linked this information with bulk scale compaction experiments (Wang et al. 2004). A project 'Tabletting Science Anti-stick Research' project (TSAR) involving a UK pharmaceutical punch manufacturer and academic partners used punch profilometry, contact angle, atomic force microscopy (to determine surface energy and adhesion force), scanning electron microscopy and spectrospy to develop a model to help choose punch material and coating for a given formulation. Markarian (2013) describes an adhesion map which included input from discrete element modelling. In summary, the research above identified the following potential factors affecting sticking: Van der Waals forces, capillary action, morphology (surface roughness), deformation mechanics of the granule, environment (humidity), chemistry. Sticking is related to competing mechanisms between interparticle bonding and particle-wall adhesion.

Research on sticking published in 2017 continues along the same lines, and some basic ideas linked to mechanistic models emerge, which are consistent with our hypotheses developed independently (described later). Paul et al. (2017) measured the mass of powder adhering to a punch during successive compaction events and fitted the data with a classic chemical reaction rate equation leading to a conceptual model for sticking while still requires linking parameters to underlying sticking mechanism. Tsosie et al. (2017) used electron microscopy observations and identified that material not only sticks to tool surfaces but can also be removed during compaction. They proposed a mechanism for sticking which includes fragmentation at the interface of the tooling. Jasevičius and Kruggel-Emden (2017) applied discrete element modelling and an adhesive contact law to analyse the sticking of bacteria to glass; this framework is also relevant to this proposal. Samiei et al. (2017) links sticking to electrostatic properties of the powders, which can be considered as a special case of contact law. Empirically, Al-Karawi et al. (2017) looked at powder lubrication and tool coating while Swaminathan et al. (2017) reported on the use of an instrumented punch to evaluate sticking.

An engineering analysis relevant to sticking

Before a suitable research methodology for sticking could be constructed it is instructive to reduce the problem to the bare essentials and consider a mechanical engineering analysis to identify potential mechanisms.

At 10 mm (tablet) scale: the contact between two bodies is generally described by considering normal and tangential interactions. Normal interaction involves contact pressure and adhesion forces. These are influenced by the constitutive behaviour of the bulk powder (including elasticity, plasticity and densification), while adhesion can be considered using classical cohesive zone models. Tangential interaction (e.g. friction) can be described by the coefficient of friction (which may depend on contact pressure, sliding velocity and surface properties such as roughness, contamination treatment etc.). The build-up of material on the tool faces during successive compaction events will result in an evolution of the interface properties (friction and adhesion).

At 1 mm (embossing) scale: sticking can be triggered in regions where features (grooves for letters and symbols) are present on the punch faces. Mechanisms of adhesion and friction aided interlocking are present at this scale also but the geometric details became important for the compaction stage as well as unloading. A model at this scale should include the mechanical deformation of the steel punch. This mechanical interlocking can be present at tablet scale too (e.g. deep punch curvatures).

At 0.1 mm (granule) scale: contact laws developed in the field of contact mechanics provide a detailed description of the complex mechanical pressure distributions and adhesive forces acting between two particles in contact or a particle and a metal surface (adhesive models such as JKR, DMT etc. are extensively used). This is further complicated by the breakage of granules during compaction; important for sticking are the processes at granule - tool interface. Lubricants affect local friction and adhesion. The granule breakage results in new surfaces which behave according to the lubricant admixing method (intra-granular or during granulation vs. extra-granular, where a thin coating is thought to be forming on the outer surface of the granule during lubrication just before compression).

At angstrom (10^{-10} m), or atomic scale: The interaction between atoms is governed by force fields (e.g. Lennard-Jones type potentials). This is complicated by the anisotropy of the crystal and presence of functional groups attached to the surface.

Sticking hypotheses and critical unknowns

1. Sticking can be understood as a coupled thermo-mechanical problem which involves mechanisms such as particle rearrangement, elastic deformation, plastic deformation and/or breakage, which in turn lead to further rearrangement. Relevant to sticking are the detailed processes occurring at the interface between particles and tooling, usually made of stainless steel. The interaction between particles and tooling requires consideration of friction and adhesion. Powder compaction involves dissipative processes that generate heat. At the tool interface heat is also generated due to friction. As sticking (gradual deposition of the material to surfaces) progresses the properties of the materials and surfaces evolve:
    a. Stress, strain rates, and temperature causes phase transformations, particularly in materials with low melting points.
    b. Contact areas of deforming particles increase, exposing new pristine surfaces
    c. Particle breakage exposes new pristine surfaces with high surface energy

Unknowns: what are these properties and how do they evolve?

2. Sticking can be understood as a balance between material deposition on the surface and material removal (similar to wear as the powder itself continues to slide along the surface during compaction). The formulation can include abrasive components.

Unknowns: what are the rates and how are the parameters are related to mechanisms?

3. Sticking often initiates at small geometric features (embossing) of the tooling, which requires consideration of the elastic deformation of the punch subject to pressure from powder during compaction.

Unknowns: none – all covered under hypothesis 1. Finite element analysis is required.

4. There may exist high energy hot-spots on the surface of the metal tooling and on the surface of particles.

Unknowns: origin and activation of these sites.

5. Sticking is linked to segregation during die fill, resulting in a non-homogeneous powder blend before compaction.

Unknowns: segregation patterns during die fill.

Project planning

Year 1

WP1: Identification of test materials and characterisation procedures following consultation with IFPRI members covering the industries of interest. These measurements will provide input into testing hypothesis 1 in WP2. The testing methods will be standard and available at Leicester and industrial partners, leveraging existing programmes and capabilities (6 months).

WP2: Thermo-mechanical analysis of the powder-tool interface during compaction. Sticking is a problem inherent to compaction, thus detailed knowledge of stress and deformation is necessary between tooling and particles as well as bulk level. Finite element analysis of the interactions between the formulation and tool surface pertinent to sticking will be carried out to verify hypothesis 1 and analyse isolated and combined contributions from different mechanisms. The multi-particle finite element method will be used to resolve not only deformation but also rearrangement of particles during compaction.

Compaction involves a thermo-mechanical process, whereby powder particles rearrange, deform, and break under the applied stress. Heat is generated by densification work and friction. In order to represent multi-component formulations, a method based on multi-particle finite element analysis will be applied to identify potential mechanisms where particles adhere to the punch face. Such mechanisms will include rearrangement (leading to changing contact areas – and contact stress - between particles and tooling), deformation (flattening of features of irregular particles subject to high contact stresses), exposing of fresh, high energy surfaces by fracture. In the process the material properties, friction and adhesion change with temperature. The combinations favourable for material sticking will be identified in terms of 1) material properties (elastic, plastic, fracture), 2) particle-surface interactions laws (adhesion in normal direction and friction in tangential direction) and 3) processing conditions (stress, strain rate) prevailing at the interface between powder bed and surface. The multi-particle finite element analysis requires inputs from the detailed loading conditions on the particles which arise from the compression of the bulk powder. These conditions are non-homogeneous and can only be estimated numerically for punches with complex geometry containing embossing details which provide preferential sites where sticking manifests. The analysis of bulk compaction will use state of the art (continuum) finite element models with constitutive equations that incorporate density and temperature dependent material behaviour, with parameters obtained experimentally.

The analysis at particle level will cover the design space. Functional relationships will be developed for the individual mechanisms identified, which will be assembled into a general constitutive law for sticking. The sticking law will be implemented in the continuum model which will be used to 1) support hypothesis 1 and analyse individual and combined contributions from different sticking mechanisms and 2) create a predictive tool to evaluate material deposition on the punch face under stress and strain rate conditions characteristic to practical tabletting operations in WP6.

Deliverable: sticking mechanisms, influencing factors and sticking law. (24 months)

Year 2

WP3: Development of an apparatus to characterise sticking, to verify the sticking mechanisms and determine sticking rates (hypotheses 1 and 2). The apparatus will discern effects from: molecular, crystal, surface, and mechanical properties of the powder; surface finish and chemistry (including coated surfaces); and will apply representative stress at the interface between powder and tooling at macroscopic (compact) and microscopic (particle) level. The rig will include temperature measurement (18 months).

WP4: Finite element analysis to verify the mechanical interlocking hypothesis 3. Using input generated from WP1-3 finite element analysis will be carried out using procedures embedded at Leicester to model compaction and capping.

WP5: Experimental characterisation of surface energy of tooling and powders to verify hypothesis 4 (existence of hot spots).

Year 3

WP6: Establish predictive criteria for sticking propensity and develop a software tool with a hierarchical input structure to predict sticking from 1) molecular information, 2) particle characteristics and 3) bulk powder characteristics. (12 months). The deliverable are: 1) predictive tool for use in industry; 2) requirement specification for multi-scale and multi-physics model to be developed in years 4-6 which will consider other environmental conditions, including humidity and eliminates the need for bulk level characterisation (sticking will be predicted from particle properties and molecular structure only).

Hypothesis 5 will be verified using methods already embedded at Leicester (linear and rotary shoe die system, coupled CFD-DEM analysis etc.) if required by the IFPRI membership or leveraged from other programmes.

Leveraging into existing programmes

The work packages outlines above will be carried out by a dedicated full time PhD student funded 50% funded from this project and 50% from Leicester. Materials and consumables will be covered from this project. The PhD student will be embedded in my group. I currently supervise (first supervisor) 5 PhD students working on:

- Understanding densification and crack propagation in pharmaceutical tablet manufacturing
- Modelling of solid-solid and air-solid interactions for particulate handling and processing
- Influence of contact strength between particles on the constitutive law for powder compaction
- Swelling and disintegration of multi-component polymeric structures
- A numerical investigation into particle interactions and transformations using coupled DEM-CFD modelling

The group owns bespoke facilities to characterise compaction, powder flow, and mechanical behaviour in general at all length scales described above and we have free access to the University's high performance computing cluster for numerically intensive work.

Specific to sticking I have supervised final year undergraduate and Masters level projects which produced feasibility work leading to some of the hypotheses proposed above.

The experiments will be performed in the Mechanics of Materials Laboratory (Department of Engineering) and the Advanced Electron Microscopy Centre (College of Science and Engineering), both free at point of use (excluding consumables). We anticipate that IFPRI partners will contribute their publically available data and share their industrial experience to guide the programme. We have strong collaboration with the Departments of Chemistry and Physics at Leicester and other institutions to cover characterisation needed in WP5.

The project will be leveraged with the EPSRC (UK research council) project EP/N025261/1 "Virtual Formulation Laboratory (VFL) for prediction and optimisation of manufacturability of advanced solids based formulations", a £1.5m project which I coordinate. The project runs until 2020 and involves 2 post-doctoral research associates at Leicester and 3 based in Chemical Engineering Departments at Leeds, Imperial and Greenwich. VFL is low TRL project addressing flow, segregation, compaction and caking.

It is important to note that sticking, although very important, was omitted in the design of VFL, as is was felt it necessitated a separate and substantial effort. The IPFRI project will make substantial steps towards elucidating sticking and will establish a platform leading to a major collaborative research grant proposal involving key academics and industries interested in sticking in the next 2 years.

References

Abdel-Hamid S. and Betz G. 2012. A novel tool for the prediction of tablet sticking during high speed compaction. *Pharmaceutical Development and Technology*, 17 (6), 747–754.

Abu Bakar N.F., Mujumdar A., Urabe S., Takano K., Nishii K., Horio M. 2007. Improvement of sticking tendency of granules during tabletting process by pressure swing granulation. *Powder Technology*, 176, 137-147.

Al-Karawi C., Lukášová I., Sakmann A., Leopold C.S. 2017. Novel aspects on the direct compaction of ibuprofen with special focus on sticking. *Powder Technology*, 317, 370-380.

Bunker M., Zhang J., Blanchard R., and Roberts C.J. 2011. Characterising the surface adhesive behavior of tablet tooling components by atomic force microscopy. *Drug Development and Industrial Pharmacy*, 1–11.

I Holland Limited. 2014. Solving Tablet-Sticking Problems with I Holland's Predictive Model. P*harmatech*.

Jasevičius R., Kruggel-Emden H. 2017. Numerical modelling of the sticking process of a S. aureus bacterium. *International Journal of Adhesion and Adhesives*, 77, 15-28.

Markarian J. 2013. Tablet-Sticking Solutions. Screening methods and predictive models address tenacious tablet-sticking problems. *Pharmaceutical Technology,* 37 (10).

McDermott T.S., Farrenkopf J., Hlinak A., Neilly J.P., Sauer D. 2011. A material sparing method for quantitatively measuring tablet sticking. *Powder Technology*, 212 (1), 240-252.

Mullarney M.P., MacDonald B.C., Hutchins A. 2012. Assessing tablet-sticking propensity, by weighing accumulated powder on a removable punch tip. *Pharmaceutical Technology*. 36 (1), 57-62.

Paul S., Taylor L.J., Murphy B., Krzyzaniak J.F., Dawson N., Mullarney M.P., Meenan P., C.C. Sun C.C. 2017. Powder properties and compaction parameters that influence punch sticking propensity of pharmaceuticals, *International Journal of Pharmaceutics*, 521 (1–2), 374-383.

Reed K., Davies C., Kelly K. 2015. Tablet sticking: Using a ‘compression toolbox’ to assess multiple tooling coatings options. *Powder Technology*, 285, 103-109.

Roberts M., Ford J.L., MacLeod G.S., Fell J.T., Smith G.W., Rowe P.H., Days A.M. 2004. Effect of lubricant type and concentration on the punch tip adherence of model ibuprofen formulations. *Journal of Pharmacy and Pharmacology*, 56 (3), 299-305.

Samiei L., Kelly K., Taylor L., Forbes B., Collins E., Rowland M. 2017. The influence of electrostatic properties on the punch sticking propensity of pharmaceutical blends. *Powder Technology*, 305, 509-517.

Simmons D.M. and Gierer D.S. 2012. A material sparing test to predict punch sticking during formulation development. *Drug Development and Industrial Pharmacy*, 38 (9), 1054–1060.

Swaminathan S., Ramey B., Hilden J., Wassgren C., 2017 Characterizing the powder punch-face adhesive interaction during the unloading phase of powder compaction. *Powder Technology*, 315, 410-421.

Toyoshima K., Yasumura M., Ohnishi N. and Ueda Y. 1988. Quantitative evaluation of tablet sticking by surface roughness. *International Journal of Pharmaceutics*, 46, 211-215.

Tsosie H., Thomas J., Strong J. et al. 2017. Scanning Electron Microscope Observations of Powder Sticking on Punches during a Limited Number (N < 5) of Compactions of Acetylsalicylic Acid. *Pharm Res* 34, 2012.

Uchimoto T., Iwao Y., Yamamoto T., Sawaguchi K., Moriuchic T., Noguchi S., Itai S. 2013. Newly developed surface modification punches treated with alloying techniques reduce sticking during the manufacture of ibuprofen tablets. *International Journal of Pharmaceutics,* 441, 128– 134.

Waimer F., Krumme M., Danz P., Tenter U., Schmidt P.C. 1999. A novel method for the detection of sticking of tablets. *Pharmaceutical Development and Technology*, 4 (3), 359-367.

Wang J.J., Guillot M.A. T, Bateman S.D., Morris K.R. 2004. Modeling of Adhesion in Tablet Compression. II. Compaction Studies Using a Compaction Simulator and an Instrumented Tablet Press. *Journal of Pharmaceutical Sciences*, 93, 407–417.

Wang J.J., Li T., Bateman S.D., Erck R., Morris K.R. 2003. Modeling of Adhesion in Tablet Compression—I. Atomic Force Microscopy and Molecular Simulation. *Journal of Pharmaceutical Sciences*, 92, 798–814.

Wang Z., Shah U.V., Olusanmi D., Narang A.S., Hussain M.A., Gamble J.F., Tobyn M.J., Heng J.Y.Y. 2015. Measuring the sticking of mefenamic acid powders on stainless steel surface. *International Journal of Pharmaceutics*, 496, 407–413.

A Proposal to IFPRI

Adhesion of Powders to Metal Surfaces During Compaction

Changquan Calvin Sun, Ph.D.

Pharmaceutical Materials Science and Engineering Laboratory

Department of Pharmaceutics, University of Minnesota

October 30, 2017

308 Harvard Street S.E., 9-127B WDH, Minneapolis, MN 55455, USA

Email: sunx0053@umn.edu; Tel: 612-624-3722; Fax: 612-626-2125

Introduction and Background

Powder adhesion onto tooling, known as punch sticking, is a common problem in cold welding processes to manufacture compacts from powders of pharmaceutical, metallurgy, and energy materials. Without being properly addressed, it can result in significant problems in manufacturing. Punch sticking requires intermittent stoppage of the tableting process to clean the punch sets, which grossly reduces production efficiency. In addition to poor aesthetic quality, inconsistent weight will lead to rejection of an entire batch of compacts in severe cases. Tooling can also be damaged leading to costly down time. The punch sticking phenomenon is a complex problem, known to be affected by process conditions (compaction pressure, dwell time)[1-3], particle properties (size, shape, surface roughness, deformability) [4-7], environmental factors (humidity, temperature) [8, 9], formulation composition [10], and punch tip properties (coating, surface asperity and roughness) [11, 12]. Punch sticking has been investigated using several techniques, including atomic force microscopy to quantify adhesion [13, 14], measuring tablet detachment force [7], scanning electron microscopy [15], HPLC analysis of quantitatively extracted adhering mass [10, 16, 17], and monitoring weight of sticking mass using a punch with a removable punch tip [18].

The removable punch tip method is a material-sparing method capable of generating quantitative punch sticking kinetics. In this experimental approach, the material of interest is blended with a non-sticking matrix material, e.g., microcrystalline cellulose. The mixture is then compressed under a controlled pressure and speed. The amount of material adhering to the punch tip is measured periodically to obtain the adhering mass – number of compression data, which quantifies punch sticking kinetics. It is suitable for rank ordering sticking propensity of compounds as well as different batches of the same compound. For example, the generated data can be used to characterize different batches of a drug, which helps flag potential sticking problems during manufacturing due to batch-to-batch variations.

Using the removable punch tip technique, we have quantified the punch sticking propensity of a large number of pharmaceutical materials by tracking the kinetics of mass accumulation during compression [19]. The role of various factors on punch sticking, such as compaction force, drug surface area, drug mechanical properties have also been investigated [4, 6, 20]. Our studies led to a punch sticking model (Figure 1) [19].

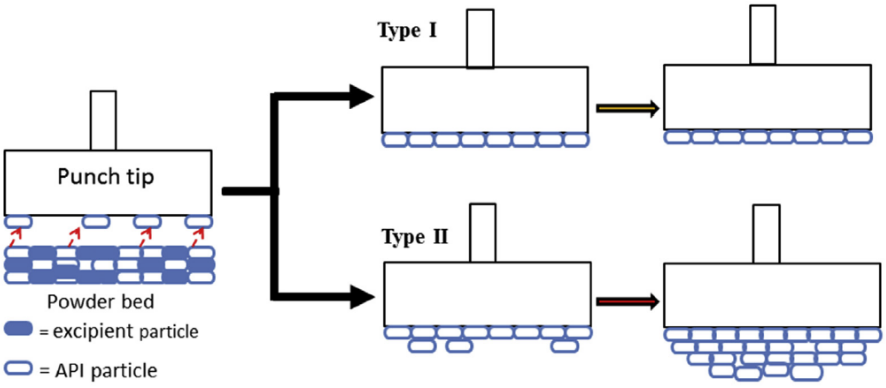


Figure 1. Schematic representation of the punch sticking kinetics based on interactive forces.

To apply this model, the formulated powder is considered to be a mixture between a main component (such as a drug or fine iron ore), **A**, and a matrix. This model predicts punch sticking outcome based on the interplay among three competing forces, i.e., F1 (**A**-punch adhesion), F2 (**A**-**A** cohesion), and F3 (**A**-matrix adhesion). Punch sticking is avoided if F1 is lower than F2 and F3, but sticking occurs when F1 is greater than F2 and F3. When a monolayer of sticking mass is present on punch surface, F1 has no further role in controlling the sticking kinetics. Instead, the relative magnitude of F2 and F3 determines the kinetics of subsequent mass build-up. Only a monolayer of sticking mass (or filming) is expected when F2 < F3, but continued build-up of material is expected when F2 ≥ F3.

This model is consistent with several known features of punch sticking, including a) APIs are enriched in the punch adhered mass [19]; b) mechanical properties and particle size impact sticking propensity [6]; and c) tooling construction materials can influence punch sticking by the same powder [21]. This model suggests the possibility of modulating sticking propensity by controlling the magnitude of F2 and F3. While F2 is constant for a given batch of **A**, punch sticking propensity can be minimized by elevating F3 through appropriate selection of excipients in a formulation. For example, simply choosing a binder that exhibits higher F3 should reduce sticking severity. The model was supported by our recent work where two model drugs, Celecoxib and ibuprofen, were studied in four excipient matrices (Microcrystalline cellulose Avicel PH102 and Avicel PH105, hypromellose, and starch). Punch sticking indeed decreased with increasing F3 for both drugs and at both compaction pressures investigated (Figure 2).

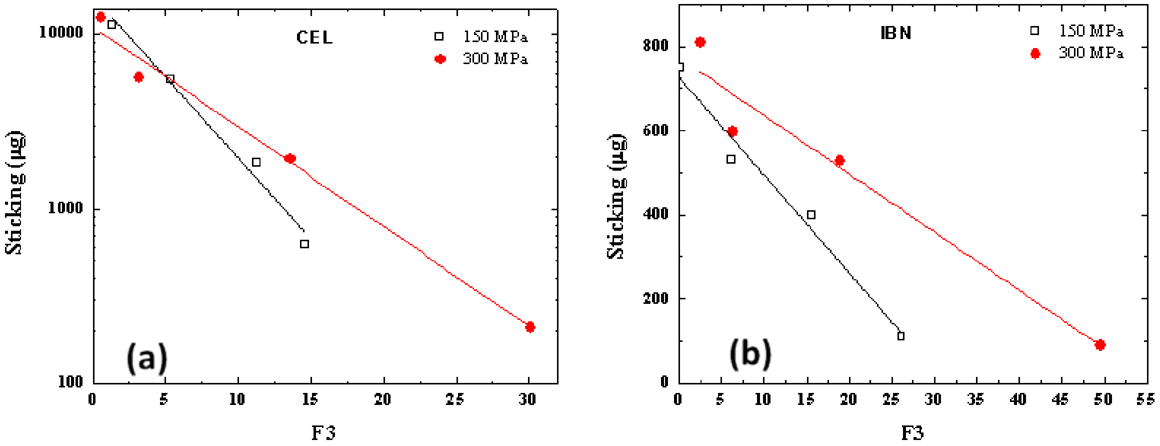


Figure 2. Dependence of sticking on F3 for (a) celecoxib and (b) ibuprofen. Tableting was performed at two pressures, 150 MPa and 300 MPa.

Despite the extensive earlier efforts, a mechanistic understanding of punch sticking phenomenon remains elusive. Systematic further investigation of this phenomenon is required to elucidate the punch sticking mechanism, which is critical for effective formulation design or process engineering. The goal of following research is to ultimately eliminate punch sticking problems during manufacturing.

Research Plan

Although useful in rank ordering sticking propensity among different powders, the removable punch tip method faces two problems for broad adoption for reliably predicting sticking behavior during manufacturing: 1) only flat punch surface has been used, which is different from real punch tips having curvature and embossed letters and numbers. 2) an absence of correlation between data from the removable punch tip study and sticking propensity during actual manufacturing. Therefore, the first stage of this research is to develop an improved removal tip method for reliable prediction of punch sticking that can be applied over any desired compaction pressure and environment conditions using a compaction simulator. In the following experiments, a total of 100 tablets will be compressed and the weight of adhered mass will be measured every 20 compression.

Goal #1. Optimize the design of removable punch tip for conducting laboratory punch sticking assessment. In this part of the research, punch tips with different curvatures and embossed with selected letters and numbers will be compared. The hypothesis is that such tips are more sensitive in detecting punch sticking. Using such tips, future punch sticking assessments can be performed more quickly and reliably using less material. Punch tips will be prepared using standard tool steel, with and without embossed letters and numbers (O, A, R, 0, 6, 8, 9). Along with monitoring the amount of adhering mass, the locations of punch sticking will be documented by microscopic images. Three powders (exhibiting low, medium, and severe punch sticking propensity) will be used. Based on the results, tips with different curvatures will be made and evaluated to identify the most sensitive tip design for use in subsequent studies.

Goal #2. Establish a calibrated scale that allows reliable predictions of punch sticking during manufacturing from the laboratory assessments using the optimized tip. Meeting this goal requires the use of 6 - 10 powders with known punch sticking propensity during manufacturing. The comparison of laboratory punch sticking data to the known sticking propensity will lead to a calibrated scale, which can be used to reliably predict sticking propensity during commercial manufacturing based on laboratory assessment using the removable punch tip method. A critical unknown is the availability of sufficient quantity of powders (estimated 500 g) with well documented punch sticking propensity during commercial manufacturing and details on punch design and construction material. If such desired powders or information are not available, we will prepare different model formulations in sufficient quantity and assess their punch sticking propensity using a standard concave tooling on a laboratory rotary press (Piccola). We will assess their punch sticking propensity in parallel using the optimized tooling identified in Goal #1.

Goal #3. Examine effects of tooling material and coating on punch sticking propensity. When punch sticking problems are discovered in a late stage of development, modifying formulation is rarely an option due to the high costs. In those cases, a common solution is to reduce punch adhesion using different tooling steels or coating. Here, we will compare sticking propensity of three model formulations (low, intermediate, and high sticking propensity) on three types of steel and three coatings as summarized in the table below.

Variable	**Options**		
Steel type	S7	D2	M340
Coating	Hard chrome	chromium nitride (CrN)	titanium nitride (TiN)

The PI has secured full commitment from Natoli Engineering to support this project by providing all needed tooling (punch and tips) manufactured with different materials and coating types. An engineer from Natoli will also be dedicated as a consultant on all tooling related issues or problems. There are no foreseeable critical unknowns that may influence the outcome of the project.

Goal #4. Determine effects of particle size on punch sticking. Particle size is a property that is relatively easy to control for modulating punch sticking propensity. The conventional wisdom suggests that smaller particles always correspond to more severe sticking. However, our preliminary work suggested this notion is not always correct. Here, we will study the effect of size using four model drugs, exhibiting a range of mechanical properties (brittle to ductile) and sticking propensity (medium to high). Each model drug will be obtained in four different size fractions through recrystallization, milling, and sieving. Different sizes of hematite (0.005 – 1 mm), obtained commercially, will also be evaluated. Punch sticking propensity will be assessed for each of the sizes and correlated to particle size to develop a general rule. If needed, more model compounds will be investigated to ensure robustness of the proposed rule.

Research beyond year 3. The long term goal of this research is to develop a classification scheme of powders punch sticking propensity based on easily accessed information, such as particle size, surface energy, and mechanical properties. For each class of materials, sticking-free formulation space will be identified and appropriate strategies for avoid punch sticking by each class of material will be recommended. Strategies for developing sticking-free formulations will involve crystal engineering (e.g., spherical crystallization, alternate solid form), particle engineering (e.g., granulation, particle coating, and use of appropriate excipients), and process optimization (e.g., speed, pressure, tooling material and design). Effects of tooling design on punch sticking will also be elucidated.

Model compounds

1) Organic powders: Several active pharmaceutical ingredients exhibiting widely different physicochemical properties and sticking propensity will be selected based on our previous work on 24 compounds [19]. Two compounds will be obtained with different sizes by recrystallization and milling (e.g., jet milling and cryomilling). This allows the study of effects of particle size or impact of processing on punch sticking. **2) Inorganic powders:** Alpha alumina, Gamma alumina, and Hematite (0.005-1 mm).

Other model compounds may be included in accordance to suggestions by IFPRI members.

Summary of the key objectives and expected outcomes from the proposed research

	Key objectives	Expected outcomes
Year 1	Design and evaluate punch tip design on sticking assessment	1) Identify an optimal tip design 2) Annual report to IFPRI
Year 2	Establish a calibrated scale for predicting punch sticking during manufacturing based on laboratory assessment	1) Development of a calibrated scale capable of predicting sticking during manufacturing 2) Journal publication 3) Annual report to IFPRI
Year 3	1) Effects of tooling material and coating on sticking 2) Effects of particle size and mechanical properties on sticking	1) Clear understanding of effects of tooling material and coating on punch sticking 2) Development of a rule for predicting particle size effect on sticking 3) Journal publication 4) Annual report to IFPRI

Leverage into existing programs

The Minnesota lab is dedicated to solving problems related to solids formulation and powder processing. My research emphasizes on fundamental understanding of problems from which solutions are identified through appropriate crystal and particle engineering. The same approach will be applied in this research. This lab has worked on the problem of punch sticking since 2014. We have accumulated a wealth of knowledge on the problem and expertise in conducting punch sticking using the removable punch tip method. The punch sticking model developed by us (Figure 1) will be a foundation for investigating the role of punch material, coating, and design on sticking. We have ready access to many state-of-the-art powder and particle characterization instruments that are required to fully characterize model materials in this research. The proposed work can be efficiently conducted because the fully instrumented compaction simulator, a central piece of instrument to this research, resides in my lab. In summary, this proposed research is an important extension of ongoing work in my lab, for which we are well equipped to carry out. Also importantly, Natoli Engineering, a leading tablet tooling manufacturer, is fully committed to design and provide all required tooling as well as expert consultancy throughout this project.

IFPRI member support

IFPRI members' support are sought in four ways: 1) Suggest suitable model compounds for this research. The current list of model compound is based on advice from one of the IFPRI members (William Ketterhagen). 2) Provide model formulations with known sticking propensity during tablet manufacturing for testing in our lab using the removable punch technique. Such results are essential for developing a calibrated scale for predicting sticking propensity during industrial manufacturing based on laboratory assessment. 3) Support on characterizing samples using instruments not available through existing resources. 4) Perform periodic review of our research and provide constructive comments to assure the success of this project.

Risks and contingency plan

1. The proposed research heavily relies on the compaction simulator. There is the chance that the simulator has mechanical or electrical parts failure due to aging or misuse. The problem of misuses can be minimized through rigorous user training and frequent refreshers. The simulator is now marketed and served by our collaborator, Natoli Engineering. In the case of problems occurring with the compaction simulator, there will be down time but we expect speedy repair by Natoli Engineering. In the worst case scenario, we can arrange having work done at Natoli Engineering's facility if repair of our simulator will take an unexpectedly long time.
2. There is also a slight risk that some of the materials characterization cannot be done at University of Minnesota due to a lack of instrument, e.g., inverse gas chromatography. In that case, help from IFPRI members will be sought first. If no IFPRI members could provide timely assistance needed for this project, we will seek help from other academic laboratories. In the worst case scenario, we will use commercial service companies for samples characterization. In all these cases, careful planning and close communication will ensure the quality of data.

References

1. Abdel-Hamid, S. and G. Betz, *A novel tool for the prediction of tablet sticking during high speed compaction.* Pharm Dev Technol, 2012. **17**(6): p. 747-54.
2. Otsuka, A., *Adhesive properties and related phenomena for powdered pharmaceuticals. .* Yakugaku Zasshi, 1998. **118**(4): p. 127-42.
3. Kakimi, K., T. Niwa, and K. Danjo, *Influence of Compression Pressure and Velocity on Tablet Sticking.* Chemical and Pharmaceutical Bulletin, 2010. **58**(12): p. 1565-1568.
4. Paul, S., et al., *Powder properties and compaction parameters that influence punch sticking propensity of pharmaceuticals.* International Journal of Pharmaceutics, 2017. **521**(1–2): p. 374-383.
5. Waknis, V., et al., *Molecular Basis of Crystal Morphology-Dependent Adhesion Behavior of Mefenamic Acid During Tableting.* Pharmaceutical Research, 2014. **31**(1): p. 160-172.
6. Paul, S., et al., *Dependence of punch sticking on compaction pressure – roles of particle deformability and tablet tensile strength.* J. Pharm. Sci., 2017: p. In review.
7. Hooper, D., et al., *Effects of crystal habit on the sticking propensity of ibuprofen—A case study.* International Journal of Pharmaceutics, 2017. **531**(1): p. 266-275.
8. Corn, M., *The adhesion of solid particles to solid surfaces. II.* Journal of the Air Pollution Control Association, 1961. **11**(12): p. 566-84.
9. Corn, M., *The Adhesion of Solid Particles to Solid Surfaces, I. a Review.* Journal of the Air Pollution Control Association, 1961. **11**(11): p. 523-28.
10. Roberts, M., et al., *Effect of lubricant type and concentration on the punch tip adherence of model ibuprofen formulations.* Journal of Pharmacy and Pharmacology, 2004. **56**(3): p. 299-305.
11. Roberts, M., et al., *Effects of surface roughness and chrome plating of punch tips on the sticking tendencies of model ibuprofen formulations.* J. Pharm. Pharmacol., 2003. **55**(9): p. 1223-8.

12. Roberts, M., et al., *Effect of punch tip geometry and embossment on the punch tip adherence of a model ibuprofen formulation.* J. Pharm. Pharmacol., 2004. **56**(7): p. 947-50.
13. Bunker, M., et al., *Characterising the surface adhesive behavior of tablet tooling components by atomic force microscopy.* Drug Development and Industrial Pharmacy, 2011. **37**(8): p. 875-885.
14. Wang, J.J., et al., *Modeling of adhesion in tablet compression—I. atomic force microscopy and molecular simulation.* Journal of Pharmaceutical Sciences, 2003. **92**(4): p. 798-814.
15. Tsosie, H., et al., *Scanning Electron Microscope Observations of Powder Sticking on Punches during a Limited Number (N < 5) of Compactions of Acetylsalicylic Acid.* Pharmaceutical Research, 2017. **34**(10): p. 2012-2024.
16. Al-Karawi, C., et al., *Novel aspects on the direct compaction of ibuprofen with special focus on sticking.* Powder Technology, 2017. **317**(Supplement C): p. 370-380.
17. McDermott, T.S., et al., *A material sparing method for quantitatively measuring tablet sticking.* Powder Technology, 2011. **212**(1): p. 240-252.
18. Hutchins, A., B.C. MacDonald, and M.P. Mullarney, *Assessing tablet-sticking propensity.* Pharm. Technol. , 2012. **36**: p. 57–62.
19. Paul, S., et al., *Mechanism and Kinetics of Punch Sticking of Pharmaceuticals.* J Pharm Sci, 2017. **106**(1): p. 151-158.
20. Paul, S., et al., *Mechanism and Kinetics of Punch Sticking of Pharmaceuticals.* Journal of Pharmaceutical Sciences, 2017. **106**(1): p. 151-158.
21. Paul, S., et al., *Dependence of Punch Sticking on Compaction Pressure-Roles of Particle Deformability and Tablet Tensile Strength.* J Pharm Sci, 2017. **106**(8): p. 2060-2067.

IFPRI Research Project Brief

Powder Flow Near Boundaries

The International Fine Particle Research Institute (IFPRI) wishes to fund a project to develop extensions for dry-flowing powder rheology that describes flow, stress, and packing densities at boundaries including a free surface. Given IFPRI's industrial focus, the project should include industrially-relevant powder flow characterization techniques that are appropriate for studying flows at boundaries.

The flow of powders under low consolidation stress and with a free surface is relevant to a range of industrial processes and emerging technologies. Conditions of low consolidation stress are encountered in many applications: fluidized bed, small silos, capsule filling, additive manufacturing, etc. In these applications, cohesion may induce flow intermittences, waves and complex density fluctuations [1]. These phenomena are relevant in processing, for example in powder-bed-based additive manufacturing where the creation of successive thin and homogenous powder layer is needed [2]. To select the best powder properties and to optimize the process, we need modeling and characterization methods relevant to flows that are dominated by boundary-layer physics. Ideally, measurement methods should reflect the flow, stress and packing fields of powders in thin-layer flows.

Validation should include a practical range of boundary conditions on the thin-layer substrate (e.g., previous free surface, belt, etc.) and underflow boundary (e.g., weir or roller) used to control layer thickness. Experimental and computational techniques should be able to capture a range of particle size, shape and density distribution, as well as variations in bulk cohesion and particle mechanical properties (e.g. modulus, roughness).

More specifically, we are interested in flows relevant to thin layers of particles, where layer thickness (H) is no more than 10X the median particle size (D), spread over a width (W) that is relatively large: $H/D < 10$; $W/H > 100$. The flow regime should include quasi-static and intermediate flows, where the regime is defined at the point of metering the powder into the layer.

References:

[1] M. Wojtkowski, O. I. Imole, M. Ramaioli, E. Chávez Montes and S. Luding, Behavior of cohesive powder in rotating drums, AIP Conference Proceedings 1542 (2013)

[2] G. Yablokova, M. Speirs, J. Van Humbeeck, J.-P. Kruth, J. Schrooten, R. Cloots, F. Boschini, G. Lumay, J. Luyten, Rheological behavior of β-Ti and NiTi powders produced by atomization for SLM production of open porous orthopedic implants, Powder Technology 283, 199–209 (2015)

1. Introduction

Granular and powder flows are the core components of many industries, including additive manufacturing, pharmaceuticals, solids and food processing, biotechnology, and energy technology. The International Fine Particle Research Institute (IFPRI) recently supported a collaborative study in dense granular flows [1]. It did not address the more complex tribological-rheological particle-surface interactions at the boundaries and so the planned effort seeks to do this. The three-year overall objective of the planned work involves researching, developing, and experimentally validating fundamental powder dynamics model so that it can form the nucleus of a predictive framework that intelligently guides and improves performance in various applications, such as additive manufacturing (i.e., powder bed 3D printing/spreading, powder-weir/blade flow interactions, silo/hopper flows-wall interact spreading processes. A couple of these relevant applications are expanded upon below.

Additive Manufacturing. Powder bed 3D printing involves numerous modes of powder dynamics that are of concern to powder companies. For example, there is unconfined gravity-driven powder flow out of a hopper to dispense the powder on to the build plate. Next, there is a thin film spread (by a recoater) or rolled during the powder spreading process just prior to the printing step. During spreading, there are interactions of the powder with the interfacial surfaces, which in the field tribology are known as the 'tribosurfaces'. In a system involving powder media in relative motion between surfaces, the topography and micro-scale surface features in concert with the powder rheology dictate the performance of the powder. However, the powder spreading step is far from ideal [2,3] and a lack of fundamental understanding of the powder rheology and particle-boundary surface effects is often the central cause to two powder layer defects: varying heights (or high roughness) and high porosity.

Hopper/Silo Powder Flows. Some of the most common shear flow geometries seen in industrial applications are hoppers and silos, which are containers of varying shapes used in the aforementioned solid processing industries. The geometry of hopper and silo designs is dependent on the materials being used and particle-surface interaction parameters, namely the coefficients of friction (COF) and restitution (COR), surface roughness, size of the materials, and other parameters [5]. Understanding particle-boundary surface interactions can result in high mass flow (discharge) rates without jamming [7]. Another design issue is "inadequate emptying" that occurs in silos when the container cone or exit angles are too low, resulting in an undesirable remnant of un-discharged bulk material [4].

Free surface mixer/blender flows. Powder flows over weirs (or single blades) must be understood to ensure predictable performance in applications such as mixers and blenders [6].These granular material devices abound in pharmaceutical and solid processing industries. However, the mixing of granular material are not well understood because of the lack of constitutive relation descriptions, but also because of the lack of understanding of the particle-boundary interactions especially when the particles are on the order of the dimensions of the surface asperities. This is often the case when using fine powders. Similar to mixers or weirs where powder moves over single blades, the Freeman FT4 rheometer has a rotating blade which descends into a powder-filled cylinder.

Summary of overall strategy. In this work, *Rice University* (Rice) will pursue research to elucidate the behavior of powder near boundaries. The strategy is that by introducing rheometry measurables plus tribology-level fidelity (which involves intensive mechanical and surface characterization of the particle media and the surfaces involved), the most sensitive parameters in the 'near boundary' region can be identified. Methods for measuring and mathematically representing these parameters (e.g., surface roughness, friction coefficient, cohesion/adhesion) in DEM models will be established. Beyond the current effort, the outcomes of this work can be used to inform continuum model boundary conditions [7, 8].

Preview of 3-year research plan. Figure 1 shows how the PI's lab plans to achieve the aforementioned strategy. They will be pursuing a 3-year research plan that consists of three independent yet overlapping phases. **Phase 1** will focus on full characterization of the powders' rheological and tribological properties using a powder rheometer (measures the energy and resistance required to spread powders under different states), powder tribometer (measures the friction between thin powder films and prescribed surfaces). **Phase 2** focuses on the research and development of a computational modeling framework for elucidating the rheology of powder in the rheometer and then extended to various applications such as additive manufacturing. Once the powder rheology is obtained from an experimentally-validated model of the powder rheometer, the accurate rheology can then be combined with the advanced surface parameter descriptions to form the basis for predicting the behavior of the powder in industrial applications. For example the spreading process variables (e.g., spreading speed, spreading flowrate, and layer thickness) can be related to the spreading process output variables (e.g., powder layer roughness and porosity). The **Phase 3** work will be comprised of model validation, where experiments with a powder rheometer and a 3D printer's spreader package are conducted.

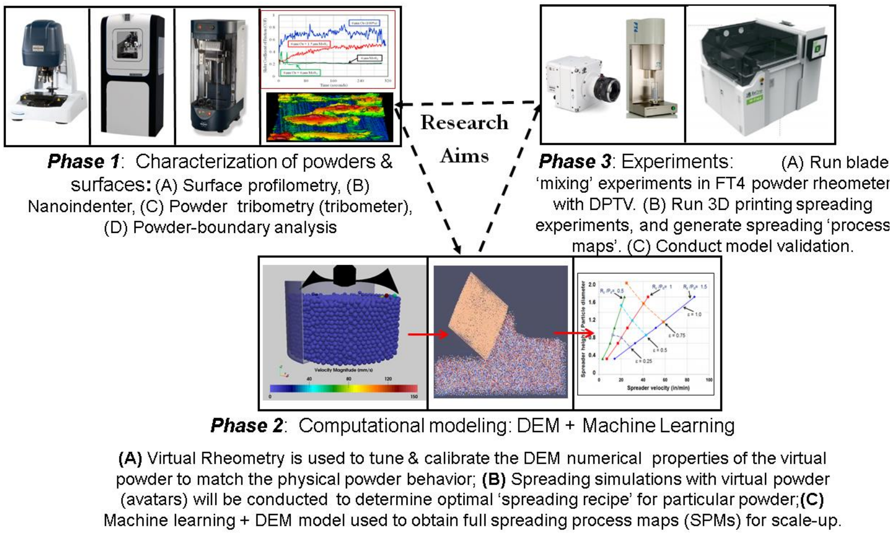


Fig. 1: Overall Three Phase Research Plan: (1) Characterization of the powder behavior. (A) Surfaces to be analyzed with profilometry tools; (B) Nanoindenter can measure mechanical properties (modulus) of particles; (C) the tribometer will be employed to measure powder-boundary frictional interactions. (D) Image of powder coverage at the surface asperity scale. Characterization studies used to measure and calibrate properties for models. **(2)** Computational modeling: (i) DEM modeling simulations of the powder rheometer will be advanced to determine the numerical values which enable the virtual powder to exhibit the real powder's behavior. (ii) DEM modeling simulations of powder spreading process will be employed to determine the best spread parameters (i.e., optimal spreading speed V, layer thickness H) to obtain a quality powder layer. (iii) Combine DEM modeling with machine learning to generate 'spreading process maps' that relate 3D printer spreading process input variables (roller/spreader speed and layer thickness) to the process outputs (layer roughness, layer porosity) will be completed. (**3**) Experimental validation of the models. (i) Model the powder rheometer including the complex particle-surface interactions near the boundaries; (ii) Compare spread layer of experiments to those from models; (iii) Assess spreading process maps' (in 3D printing) accuracy.

IFPRI collaboration. Beyond unrestricted financial support, IFPRI members can support this work with in-kind contributions of powder materials, free surface experimental rigs (e.g., chutes, small silos), and feedback on results. Summer internships of relevance to this effort and testing of the PI's models will also be welcomed.

How this planned research will impact PI's existing program. The PI wants to impact two key sectors: solid processing and additive manufacturing. He is developing a suite of experimentally-validated models and scale-up methods (e.g., machine learning) to make these models tractable and available to industry. This work will help make strides towards these goals.

2. Historical Review

History of AM powder spreading modeling.

The history of AM powder spreading modeling is brief. Only a handful of studies [9-12] have attempted to answer the influence of spreading step in the entire 3D printing process. None of them work in real size simulation domains with massive particle numbers as the proposed work will.

A major goal for powder-bed AM end-user companies, such as Arconic and P&G, is to spread any powder anytime, or less ambitiously, to spread more than a few powder systems. In other words, 3D printing companies and researchers would be greatly aided if a model or perhaps a 'spreading process map' (derived from the model) existed, where such as model or map could link the main spreader inputs, layer height H and spreader velocity V to the spread process outputs of layer roughness and porosity. The planned research will contribute to the R&D of an experimental and modeling platform to study the mechanics of powders in the powder-bed AM spreading process. A key scientific deliverable is to uncover the relationship between the spreading process inputs and the spread powder layer quality and defects.

2.2 Spreadability of powder films in AM processes.

Most powder industries are transporting powders through aeration process or through hopper and silo discharge nozzles, which means that 'powder flowability' is of the appropriate governing parameter to evaluate various powders [13]. A hall flow meter, which is a gravity driven device where the time it takes to discharge different powders are record, is the common instrument. A powder's flowability, which is intrinsic to the powder, is assumed to directly correlate with its 'spreadability' in the context of direct metal AM processes and it does not. Spreadability relates to the ability of a powder candidate to spread a powder layer with uniform thickness, density, and coverage for a prescribed AM process environment.

Relation of powder properties to spreadability in AM

'Spreadability' refers to the ease with which a powder will **spread** under a specified set of conditions. Normally, powders are 'spread' within a sliding contact (i.e., relatively moving surfaces). In order to quantify the spreadability of a powder film, one must measure the properties of the discrete and bulk properties of the powder. The properties help describe the potential of a spread powder film to be uniform.

The cohesion or friction between the particles (i.e., the internal friction), would greatly affect the final configuration of the particles; the surface roughness on the particles would likely have a similar effect. Smaller particles might not have enough weight to overcome the short-range cohesive (e.g., Van der Waals, capillary) or repulsive (e.g., electrostatic, tribo-electrification) surface forces. These surface forces would impact the particle packing and the energy required to spread the powder film. As opposed to cohesion which occurs between particles, adhesion involves the interaction between the powder media and the boundaries; tools such as powder rheometry and tribometry can provide quantitative insight here.The interplay of the large number of variables that effects powder flowability is severe.

3. Preliminary work conducted by the PI

The preliminary work is broken into 2 segments: (1) Powder tribology (friction in the interface, including the interfacial media and surface features) work conducted by the PI's group and (2) Powder rheology conducted by his group. Figure 2 shows an image from the PI's white light interferometer (optical profilometer) which captures powder coverage on a surface

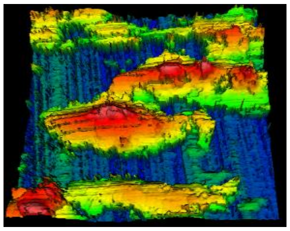


Fig. 2: Spread powder layer is fractionally covering a substrate (blue)

3.1 Preliminary work by the PI: Measuring the tribology when spreading powder layers

Higgs and Wornyoh [14-17] conducted powder film experiments on a pellet-on disk with slider pad tribometer (instrument for measuring friction, wear, and interfacial conditions).

3.2 Preliminary work by PI: Analyzing AM Materials through Powder Rheometry

The PI has also conducted investigations into the spreadability of candidate AM materials using powder rheometry. In utilizing one of the state-of-the-art powder FT4 rheometers, this technique focuses on the elucidation of key parameters involved in a powders ability to flow. Sample measurables include the Bulk Flow Energy (BFE), is a measurement for the energy to spread over confined powder such as the powder in the binded powder sub-layer (BSL); it represents the average energy during this downward motion. The Specific Energy (SE) represents the energy to spread over loose unbinded powder. The *bulk density* is also captured which represents the packing state of the loose powder. ***One key outcome of this work will be a detailed use and elucidation of the FT4 powder rheometer for broad applicability to any industry that needs a tool to predict the behavior of powder media in their applications.***

3.3. Preliminary work in DEM simulations of powder flows

A discrete element method (DEM) solver was developed in PI Higgs's research group to study complex granular flows. The solver possesses capabilities to model the physics which dominate granular flows such as particle-particle heat transfer and particle-fluid coupling [18-22]. Material properties become important for quantitative comparison to experiments conducted in the PI's laboratory [23]. The work culminated in our in-house multi-physics code called as the **Particle-Surface Tribology Analysis Code (P-STAC)**. The code has computational modules for modeling the fluid dynamics, particle mechanics, solid/contact mechanics, thermal physics, and material wear [*26*]. Cohesion and adhesion modules have also been incorporated.

3.4 Preliminary work on virtual powder rheometry

Preliminary modeling work for the RAPID 2015 conference [*28*] was carried out to study rheometry of a benchmark granular media- 2mm glass beads. A DEM solver is faced with two competing effects: accurate modeling of the bulk behavior of the discrete medium and computational efficiency. The choice of the interaction model, from now on referred to as the contact model, is a difficult one considering the absence of a constitutive law for DEM solvers. There is no single holistic contact model capable of replicating the bulk behavior of the medium without applying some sort of calibration procedure. Therefore, a simple, first-order contact model is chosen for this study.

A calibration process has been employed wherein the parameters of the contact model are iteratively changed till the bulk behavior of virtual glass beads matches that of the real glass beads seen in the published experimental results. Sample P-STAC simulation snapshot is shown in Fig. 3 (a) with a tuning of micro-parameters or contact model parameters to obtain a good match with the published experimental and numerical results is shown in Fig. 3 (b) for the force experienced by the rheometer blade as it penetrates through the glass beads.

(a) (b)

Fig. 3: (a**)** Simulation snapshot for confined-compressive loading inside 48mm virtual rheometer with 2mm glass beads. The particles are colored by the magnitude of their velocity. (b) P-STAC tuning the micro-parameters to match the experimental results.

4. The planned technical approach:

The planned research consists of three independent yet overlapping phases aimed at elucidating powder mechanics, with a focus on characterizing the particle-boundary surface interactions in order to understand industrial processes, namely powder spreading (in additive manufacturing) and powders in a FT4 rheometer which is a mixing type of device albeit primarily used for characterization of homogenous powders. **Phase 1 (characterization)** will involve characterization of the powder rheological, mechanical, and tribological properties and also the boundary surface properties as well. **Phase 2 (modeling)** consists of computational modeling DEM framework which will be developed as an *in silico (virtual)* tool for relating the FT4 powder rheometry variables to the AM powder spreading variables. **Phase 3 (experiments)** will focus on running FT4 experiments to characterize the behavior of powder samples in the FT4 rheometer; 3D printing (i.e., layer spreading) experiments of varying parameters will also be conducted.

Phase 1: Characterization of the powder's rheology and spreading behavior

Task 1.1 characterizing the powder flow behavior via powder **rheometry**

The powders being tested and printed must first be characterized. Powders exhibit many properties, but the key is to determine which variable are most sensitive to good 'spreadability', namely for powders that are moving under low consolidation stress and with a free surface (e.g., in AM spreading). Similar low consolidation, free surface conditions exist in small silo flow. The variables that will be measured in the FT4 rheometer (see facilities attachment) are numerous.

Task 1.2 In situ characterizing the powder spreading behavior of powder materials via powder **tribometry**

The powders from the rheometer will be tested in a pin (i.e., roller, sphere, flat slider, etc.) on disk tribometer experiments (see diagram in Fig. 4). The slider can be fabricated to resemble a smaller version of the spreader in the 3D printer. The friction when spreading the slider over the powder of various states can be measured. The pin/slider can also be made with the same materials of a small silo to directly measure the friction at the powder media-to-boundary interfaces. The tribometer allows the layer height H and sliding speed V, which will be linear and reciprocating to be varied. The slider on the tribometer will be run over the different substrates which match those of interest in the targeted industrial applications.

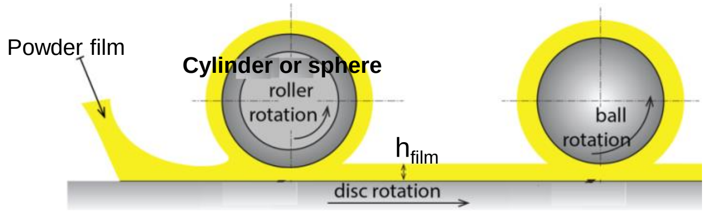


Fig 4: Pin-on-disk powder tribometery. Thin powder film on disk moves under a 'pin' (i.e., a fixed or rotational roller, sphere, or slider flat (not shown) which can be used interchangeably). A load can be applied to, or disengaged from, the pin. The coefficient of friction (COF) between the powder and relevant surfaces can be measured as a function of the surface topographies. The tribological behavior during spreading can also be obtained. This will yield detailed transient tribological (friction and wear/attrition) data for powder samples.

Task 1.3 characterizing the powder spreading behavior of powder materials via 3D printer spreading

The powders will be put in the 3D printer and spreading tests will be conducted. Spread powder layers and the underlying substrate will be characterized to examine the spread layer quality and to measure for powder layer roughness (layer height varying with position) and powder layer holes (porosity).

Other characterization measurements. Nanoindentation of the powder particles and films will be conducted to measure the mechanical properties (i.e., hardness, elastic modulus, and yield strength) of the powders. Optical microscopy will be used to ascertain fractional coverage, particle sizes, and other types of segregation measurable.

Phase 2: Computational Modeling of Powder Spreading

In Phase 2 of the planned research, the discrete element method (DEM) will be used to construct a computational modeling framework capable of accurately simulating the behavior of the different powder media during spreading and the resulting frictional response.

Task 2.1: Develop DEM simulation of FT4 powder rheometer

The PI's group will use numerical tuning to match key parameters in DEM simulation of the FT4 rheometer to the output from physical rheometer experiments. The PI calls this forming 'virtual avatars' of the powder media. The particle sizes of such micro-powders vary from 10's to a few 100's of microns. Large particle number simulations can be handles as the PI's in-house code P-STAC employs GPU (Graphics Processing Unit) processing. For a powder in a DEM framework to match a physical powder, the appropriate DEM micro-parameters, such as stiffness **K**, damping **β** and sliding friction coefficient **μ,** must be tuned. This process will involve a two-step validation where the qualitative behavior of the virtual powder is validated by performing virtual angle of repose tests and the quantitative behavior of the virtual powder is validated by performing a confined compressive test in a virtual rheometer.

For particle-particle properties, the FT4 powder rheometer will be used for each candidate powder to find the internal friction angle (AIF), which can be correlated to the normal (n) and tangential (t) DEM powder stiffness **K**, sliding friction coefficient **μ**, and damping **β**; damping is determined from the coefficient of restitution (COR). COR values for micro-powders must be extrapolated from COR curves generated from FEM simulations (see PI's prior work [24]). Information on the PI's DEM approach can be found, here [25-27]. The virtual powder bulk thus obtained can be extended to in simulations of other industrial applications, such as powder spreading or small silo flow.

Task 2.2: Develop DEM simulation of spreading. This task will try to address the issue of spreadability by performing virtual spreading experiments. A deliverable for this task will be a powder-and-application specific 'spreading recipe'. Thus, the model will ultimately enable one to know the proper spreading inputs needed to achieve a uniform spread. This spreading recipe is related to the powder's rheological and tribological traits as discussed in the preceding sections.

Future extension of this work. This also has implications for the pharmaceutical industry as well. For example, with the correct powder rheology known from this framework, a simulation can be developed to optimize capsule filling or small silo flow. Figure 5 shows how such an approach might be used to design better spreaders for a particular type of powder. This approach can help powder manufactures know what type of spreader best spreads its powder for AM applications.

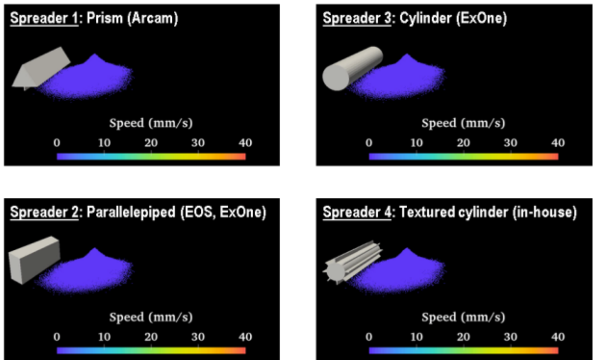


Fig. 5: DEM calibration process: The virtual powders can be calibrated to behave similarly to the real powder by tuning the DEM stiffness and damping micro-parameters.

Task 2.3: Scale-up with machine learning: Deriving a 'Spreading Process Map' from the DEM simulations

One often wonders how DEM modeling can be used to inform industrial processes. Here is one way the PI postulates for an application such as powder spreading. Imagine a 'spreading process map' is developed. The spreading process map will have the key process input variables of spreader height H and spreader velocity. The output response parameters will be the powder layer roughness and the powder layer porosity ε ($0 < \varepsilon < 1$). In addition to lines of constant porosity, lines of constant max roughness to particle diameter ratios (Rz/Pd) might be plotted to maximize the number of representative spread process parameters. For simplicity, a representative (albeit fictitious at this point) 'spreading process map' may look similar to Fig. 6.

Since these models are cost prohibitive, the PI has been employing machine learning to uncover the trends in the behavior [28, 29]. We now review the overall process needed to get a powder process map like this one shown. First, one characterizes the powder using powder rheometry (Phase 1). One, then matches physical rheometry with DEM-based virtual rheometry to produce a 'virtual avatar' representation of the powder. Third, the virtual powder can be used in the application (in this case AM powder spreading). The DEM is employed to generate numerous points of the process map. Finally, machine learning can be used to run the DEM code and generate training data to produce advanced interpolated points. Instead of taking months to generate spreading process maps for a particular powder, machine learning can construct interpolations to build the entire process map in a week on a GPU cluster. Note, that the machine learning is dependent on the physics from the DEM to be accurate before it begins extending the number of process map data points to construct a full process map.

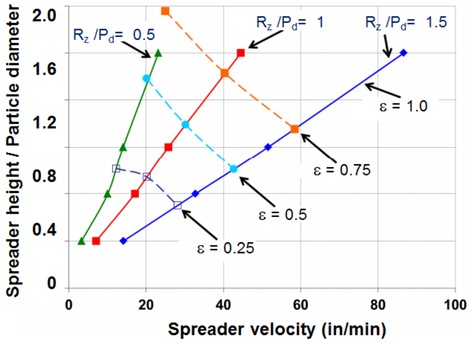


Fig. 6: Proposed 'spreading process map' which would be derived from the model. The solid symbols would be values validated by experiments.

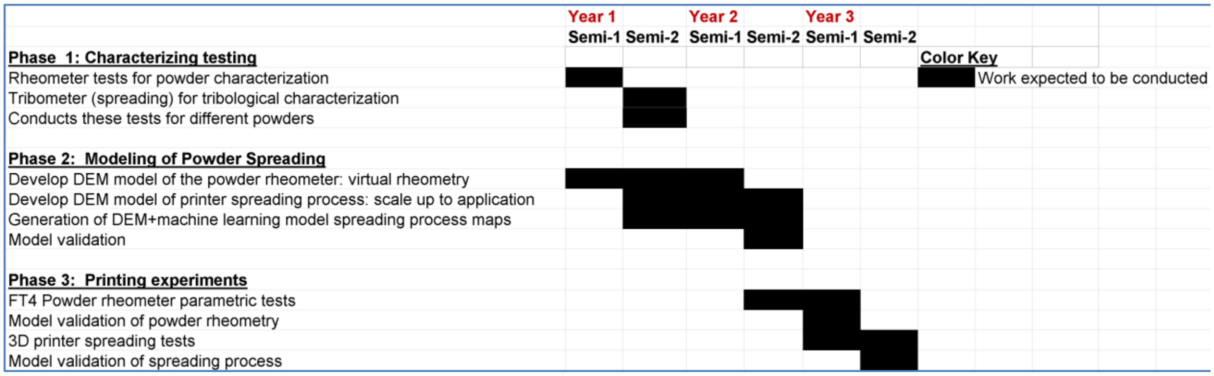
Phase 3: Experiments

The goal here in Phase 3 is to validate the Phase 2 model with experiments. *First*, experiments will be conducted with the Freeman FT4 powder rheometer. The authors express no bias for this instrument but have found that it provides a large number of measurements for different conditions. This work inherently aims to add knowledge to the field and powder industry about the applicability and appropriate use of this instrument. *Second*, spreading experiments will be conducted with the PI's ExOne 3D printer.

The PI's group will spread powder layers with model guidance from the PI's models in Phase 2, and also spread layers for assessment un-guided by the model (i.e., via trial and error), as is the convention. The roughness and porosity will be evaluated for the two cases, in addition to the time taken to start the appropriate spreading conditions for the final printed part. Insight from the post-measurements will help determine if there is efficacy to physics-based modeling being introduced into industrial processes, in this case 3D printing.

Management and Timeline

The PI will advise research assistants to conduct the proposed research. Additionally, they will continue to work with undergraduate researchers, who will assist with lab experiments, and parametric studies. Each four-month period is shown as "*Tri*" in **Table 2** below. The black bars indicate the proposed work period.



	Year 1		Year 2		Year 3	
	Semi-1	Semi-2	Semi-1	Semi-2	Semi-1	Semi-2
Phase 1: Characterizing testing						
Rheometer tests for powder characterization	■					
Tribometer (spreading) for tribological characterization		■				
Conducts these tests for different powders		■				
Phase 2: Modeling of Powder Spreading						
Develop DEM model of the powder rheometer: virtual rheometry	■	■	■			
Develop DEM model of printer spreading process: scale up to application		■	■	■		
Generation of DEM+machine learning model spreading process maps		■	■	■		
Model validation				■		
Phase 3: Printing experiments						
FT4 Powder rheometer parametric tests				■	■	
Model validation of powder rheometry					■	
3D printer spreading tests					■	■
Model validation of spreading process						■

Color Key
■ Work expected to be conducted

Table 2: Gantt chart with the milestones/tasks for the three research phases

References

1. Mort, P., Michaels, J. N., Behringer, R. P., Campbell, C. S., Kondic, L., Langroudi, M. K., ... & Wassgren, C. (2015). Dense granular flow—A collaborative study. Powder Technology, 284, 571-584.
2. Bertrand, P.H., F. Bayle, C. Combe, P. Goeuriot, and I. Smurov, Ceramic Components Manufacturing by Selective Laser Sintering. Applied Surface Science, 2007.
3. Gu, D.D., W. Meiners, K. Wissenbach, and R. Proprawe, Laser Additive Manufacturing of Metallic Components: Materials, Processes, and Mechanisms. International Materials Reviews, 2012. 57(3): p. 133-164.
4. Pereira, M. and U. Thombansen. Contributions for the next generation of 3D metal printing machines. in SPIE LASE. 2015. International Society for Optics and Photonics.
5. Frazier, W.E., Metal additive manufacturing: a review. Journal of Materials Engineering and Performance, 2014. 23(6): p. 1917-1928.
6. Radl, S., Brandl, D., Heimburg, H., Glasser, B. J., & Khinast, J. G. (2012). Flow and mixing of granular material over a single blade. Powder technology, 226, 199-212.
7. Higgs, C. F., & Tichy, J. (2008). Effect of particle and surface properties on granular lubrication flow. Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 222(6), 703-713.
8. Higgs, C. F., & Tichy, J. (2004). Granular flow lubrication: continuum modeling of shear behavior. TRANSACTIONS-AMERICAN SOCIETY OF MECHANICAL ENGINEERS JOURNAL OF TRIBOLOGY, 126(3), 499-510.
9. Haeri, S., Wang, Y., Ghita, O. and Sun, J., 2017. Discrete element simulation and experimental study of powder spreading process in additive manufacturing. Powder Technology, 306, pp.45-54.
10. Herbold, E.B., Walton, O. and Homel, M.A., 2015. Simulation of Powder Layer Deposition in Additive Manufacturing Processes Using the Discrete Element Method (No. LLNL--TR-678550). Lawrence Livermore National Lab.(LLNL), Livermore, CA (United States).
11. Mindt, H.W., Megahed, M., Lavery, N.P., Holmes, M.A. and Brown, S.G.R., 2016. Powder bed layer characteristics: the overseen first-order process input. Metallurgical and Materials Transactions A, 47(8), pp.3811-3822.
12. Parteli, E.J. and Pöschel, T., 2016. Particle-based simulation of powder application in additive manufacturing. Powder Technology, 288, pp.96-102.
13. Sun, C.C., Setting the bar for powder flow properties in successful high speed tableting. Powder technology, 2010. 201(1): p. 106-108.
14. Higgs III, C.F. and E. Wornyoh, An In Situ Mechanism for Self-replenishing Powder Transfer Films: Experiments and Modeling. Wear, 2008. 264(1-2): p. 131.
15. Wornyoh, E.Y.A. and C.F. Higgs III, An asperity-based fractional coverage model for transfer films on a tribological surface. Wear, 2011. 270(3-4): p. 127-139.
16. Higgs, C.F. and E.Y.A. Wornyoh, An in situ mechanism for self-replenishing powder transfer films: Experiments and modeling. Wear, 2008. 264(1-2): p. 131-138.
17. Wornyoh, E.Y.A. and C.F. Higgs III. Self-replenishing, self-repairing solid lubrication: Modeling and experimentation. 2005. Washington, D.C., United States: American Society of Mechanical Engineers, New York, NY 10016-5990, United States.
18. Terrell, E.J. and C.F. Higgs, A particle-augmented mixed lubrication modeling approach to predicting chemical mechanical polishing. Journal of Tribology, 2009. 131(1): p. 012201.
19. Mpagazehe, J.N., G.A. Thukalil, and C.F.H. III. A Study to Estimate the Number of Active Particles in CMP. in Materials Research Society Spring Meeting. 2009. San Francisco, CA.
20. Mpagazehe, J.N., G.A. Thukalil, and C.F.H. III. A Multi-Physics Computational Framework to Predict Dishing and Erosion in Patterned Wafers. in ASME/STLE 2009 International Joint Tribology Conference (IJTC2009) 2009. Memphis, Tennessee, USA

21. Mpagazehe, J.N., A.F. Queiruga, and C.F.H. III, Towards an Understanding of the Drilling Process for Fossil Fuel Energy: A Continuum-Discrete Approach. Tribology International, 2012, submitted.
22. Marinack Jr., M.C., J.N. Mpagazehe, and C.F. Higgs III, An Eulerian, Lattice-based Cellular Automata Approach for Modeling Multiphase Flows. Powder Technology, 2012. 221: p. 47-56.
23. McCarthy, J.J., V. Jasti, M. Marinack, and C.F. Higgs, Quantitative validation of the discrete element method using an annular shear cell. Powder Technology, 2010. 203(1): p. 70-77.
24. Marinack Jr, M.C., B.G. Gaudio, R.E. Musgrave, C.E. Rizzo, M. Lovell, and C.F. Higgs Iii. Coefficient of restitution testing: Explicit finite element modeling and experiments. in STLE/ASME 2010 International Joint Tribology Conference, IJTC2010, October 17, 2010 - October 20, 2010. 2010. San Francisco, CA, United states: American Society of Mechanical Engineers.
25. Marinack, M.C., J.N. Mpagazehe, and C.F. Higgs, An Eulerian, lattice-based cellular automata approach for modeling multiphase flows. Powder Technology, 2011.
26. Mpagazehe, J.N., A Physics-Based, Eulerian-Lagrangian Computational Modeling Framework to Predict Particle Flow and Tribological Phenomena, in Mechanical Engineering2013, Carnegie Mellon University.
27. Mpagazehe, J.N., A.F. Queiruga, and C.F. Higgs Iii, Towards an understanding of the drilling process for fossil fuel energy: A continuum-discrete approach. Tribology International, 2013. 59: p. 273-283.
28. Desai P., Dougherty P. and Higgs III C. F., Towards an understanding of the spreadability of metal additive manufacturing (AM) powders, RAPID Conference, 2016.
29. Zhang, W., Mehta, A., Desai, P., Higgs, C. F., “Machine Learning-enabled Powder Spreading Process Maps for Metal Additive Manufacturing (AM)”, 2017 Solid Freeform Fabrication Symposium Proceedings, 2017.

RHEOLOGY AND INSTABILITIES OF FLOWING COHESIVE GRAINS AND POWDERS

Pr. Nicolas Taberlet
University of Lyon, France
Physics Laboratory ENSL

In this project, I propose to study the rheological properties of cohesive powders and grains flowing on an inclined plane through experiments and discrete elements simulations. A great deal of experimental, theoretical and numerical effort was made in recent years to propose an empirical constitutive law for flowing dry granular material but the universality of these results still remains debatable. I propose to extend this effort to cohesive material flowing in thin layers. I will use both a numerical and an experimental approach, in order to measure the stress within the material as well that acting directly on the boundaries of the flow. Moreover, I will study the roll waves and traffic waves instabilities in thin flowing layers of powders and granular material. Such instabilities are of great fundamental interest but can also be the cause of malfunctioning in industrial processes.

IFPRI Call for Proposals 2017

I. State of the art and Scientific goals

At the frontier between physics and mechanics, the flow of powders and granular materials has become a very active research domain [1-4]. The behavior of assemblies of particles can be very complex. Indeed, even in the simple case of dry cohesionless particles, where the mechanical properties of the material are only controlled by the momentum transfer during collision or frictional contacts between grains, a universal constitutive law is still lacking. Moreover, capillary forces, van der Waals forces or viscous interactions render the mechanical behavior of cohesive powders even more complex and difficult to model [5].

In 2008, a group lead by O. Pouliquen [6] proposed a constitutive law for flows of dry granular material. Based on the study of a variety of flow configurations (confined flows in channels, free surface flows on piles, chute flows to flow in a rotating tumbler… see Figure 1) the authors propose that the flow is governed by the inertia number *I*:

$$I = \frac{\dot{\gamma}\mathrm{d}}{\sqrt{P/\rho}}$$

where $\dot{\gamma}$ is the shear rate, d is the average particle size, P is the confining pressure and ρ is the density of the material (taking its porosity into account). Compiling the experimental and numerical data in all geometries, the authors propose that the effective friction coefficient at the base of the flow, μ_{eff}, (defined is the ratio of the shear stress over the normal stress) is only a function of the inertial number, *I*, and follows a general behavior (see Figure 1).

Later, Jop et al. [7] proposed to extend this rheological law to the bulk of 3D flows by assuming the following constitutive law:

$$\sigma_{ijk} = \mu_{eff}(I)\frac{\dot{\gamma}_{ijk}}{|\dot{\gamma}|}$$

where σ_{ijk} are the components of the stress tensor. This simply assumes that the amplitude of the shear stress is given by $\mu_{eff}(I)$ and that its main direction is that of the shear rate. These authors showed that this 3D extension of the empirical law can capture the features of the flow of granular material over an erodible bed, and confined between frictional walls.

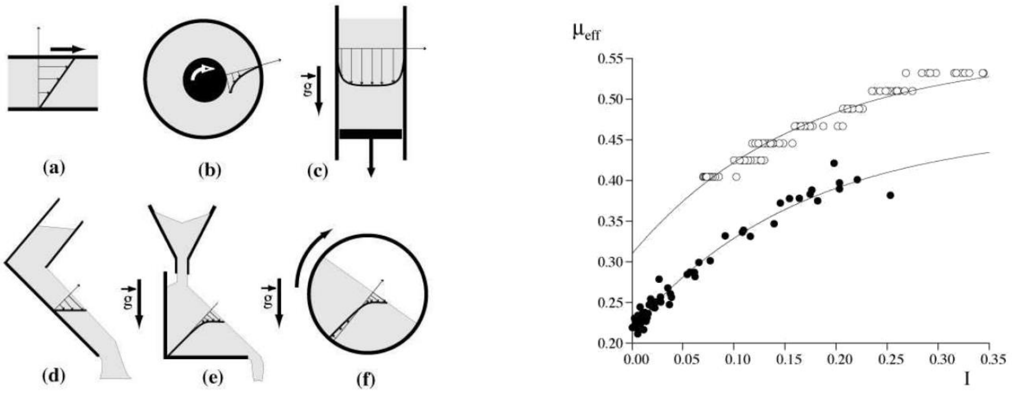


Figure 1. Left: The six configurations of granular flows studied in [6]: (a) plane shear, (b) annular shear, (c) vertical chute flows, (d) Inclined plane, (e) heap flow, (f) rotating drum.. Right: Comparison of the effective friction function of I in the plane shear (•) and the inclined plane (◦) configurations.

Although the proposed $\mu_{eff}(I)$ rheology has risen great interest and shown unquestionable success, the span of its applicability appears to be limited. For instance, the effect of the packing fraction is to date not well captured in this model. But most importantly, the relevance of this constitutive equation to industrial processes (in the pharmaceutical, mining or food industries) remains questionable since it only applies to large (d>250µm), dry and cohesionless particles.

In this project, I propose to revisit the constitutive equations and to extend its scope to cohesive powders and grains. Through numerical simulations and laboratory-scale experiments, I will measure the flow properties of thin-layer flows of benchmarked cohesive material on inclined planes as well as in rotating tumblers. More specifically, I will study how the stress tensor within the flow and at the boundaries is related to all other relevant quantities (shear rate, porosity, internal cohesive stress…).

A second aspect of the project I would like to develop consists in studying the instabilities that exist in shallow granular flows. Flow instabilities are of fundamental interest but are also of great importance for industrial processes as they create large fluctuations in the flow rate (or discharge rate) and may cause clogging and jamming.

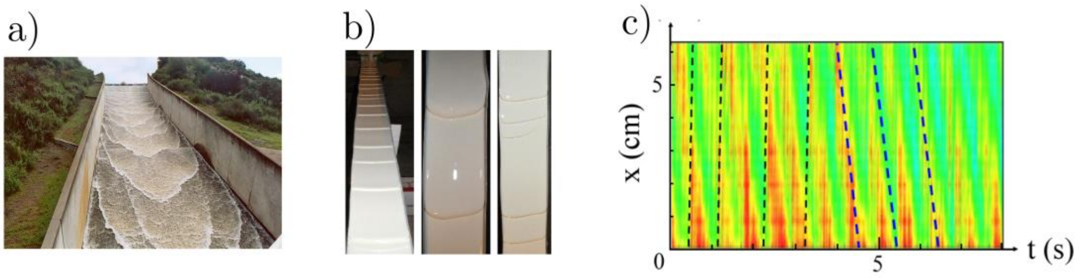


Figure 2. a: Roll waves in a shallow flow of water [10]. b: Roll waves in flow of cornstarch mixtures [11]. c: Traffic waves in granular flows (N. Taberlet).

Roll waves are a classical instability of shallow liquid flows. When a thin layer of water flows down an inclined plane, the surface may become unstable and surge waves, which travel faster than the average speed of the flow can develop (see Figure 2a). This phenomenon is known to exist in viscous and complex fluid (Figure 2b shows roll waves in flowing mixtures of cornstarch) as well as in dry granular material (see references [8,9]). I propose to bridge the gap between the complex fluids and the dry cohesionless granular material by studying the conditions under which roll waves appear in thin flowing layers of cohesive powders and grains. The phenomenon will be investigated through numerical simulations as well a laboratory experiments.

A second type of instability can occur in shallow granular flows. Recently, I observed waves at the surface of an inclined plane flow traveling against the direct of the flow (see Figure 2c). In this figure, *x* is the position along the direction of the flow and the colors encode the thickness of the flowing layer. Periodic oscillations of the thickness are clearly visible but the most striking feature is that these waves travel upstream (the oblique lines indeed indicate that the propagation is against the direction of the flow). Such upstream waves are reminiscent of traffic waves which occurs on congested roads [12]. Again, I will investigated both experimentally and numerically the conditions under which such granular traffic flow appear and fully characterize their physical properties (amplitude, velocity, dispersion…).

II. Experimental and numerical tools

a. Experimental techniques

I will study the mechanical properties of cohesive powders and grains flowing over an inclined flat surface (smooth and/or rough). This configuration has proven to be a reliable tool for probing the rheological properties of flowing granular matter [6]. It allows one to easily vary quantities such as the flow rate, the thickness and density of the flowing layer of material. Figure 3 shows a variety of experimental setups I have built and used in the laboratory in recent years.

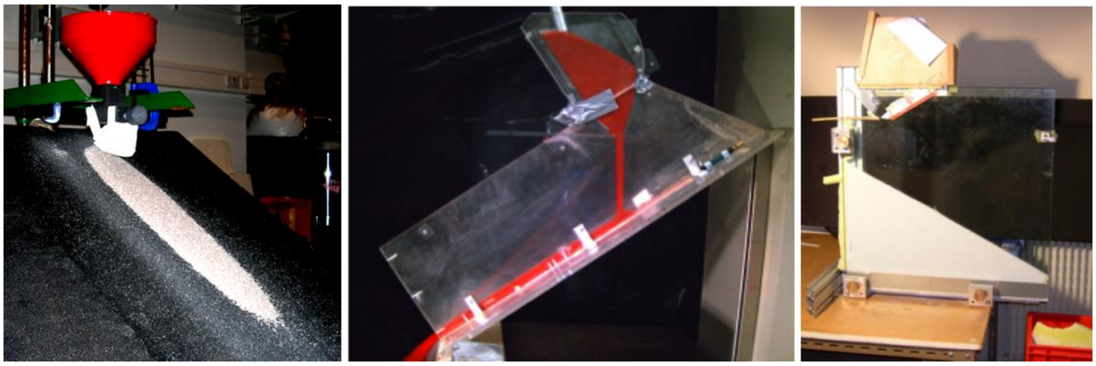


Figure 3. Variety of experimental setups developed by the author of this proposal for the study of granular and powder flows. From left to right: unconfined flows over a rough surface, shallow flow over an incline, flow over an erodible sand-bed.

The velocity profiles will be obtained through Particle Imaging Velocimetry (PIV) using a fast camera (such as the Phantom VEO4K 590L), monitoring the flow both directly from above and from the side through transparent side-walls. Measurements of the thickness of the flow (which is expected to fluctuate quickly when roll waves have developed) will be achieved using a laser scanner such as the Micro-Epsilon scanCONTROL 2900-100, which allows one to measure the profile at a rate of 300 Hz and with an accuracy of 12 µm. The boundary bottom plane will be equipped with force sensors (Honeywell FSG15N1A and Omega LCMKD-2KN) which can simultaneously measure the normal and tangential stress applied by the flowing material onto the base.

The cohesion of the material at rest can be determined through classical bi-axial or tri-axial compression but my research group is equipped with two rheometers (Anton Paar MCR 102 and TA Instruments AR 2000) which can also be used to measure the internal cohesive stress of material under an applied shear stress. Recently, while studying the Washboard Road instability [13], I have used a simpler method for measuring the cohesive stress of a powder. A variable normal stress is applied onto a plane resting on the material and the tangential force required to create a slippage is measured. The results are in excellent agreement with more complex experimental methods.

b. Discrete Element Method for numerical simulations

In this project, I will use the soft-sphere molecular dynamics method, one of the Discrete Elements Methods (DEM). This method deals with deformable frictional grains colliding with one another. Although not flawless, it has been widely used in the past two decades and has proven to be very reliable [14-15].

The DEM method aims at simulating granular assemblies using physical laws, rather than ad hoc rules (as opposed to cellular automata for instance). When two grains collide, they experience a repulsive elastic normal force, given by Hertz' law, and a dissipative term is added in order to model the inelasticity of the collisions. Grains also experience a tangential force (based on the Cundall and Strack model [16]) which models a history-dependent solid friction and which allows residual stress to be maintained within the simulated material. The method is time-driven and the position, velocity and rotation speed of all grains are simultaneously (unlike in Monte-Carlo simulations) calculated using Newton's law of mechanics at the next time step using the forces and torques acting on each individual grain.

I have been using this method actively in the past decade and the numerical results I have obtained are essential elements to 25 of my 50 publications in peer-reviewed journals. Figure 4 shows a few examples of physical phenomena that I have simulated using the DEM method (gravity driven flows, flow in a rotating tumbler, fluidized beds).

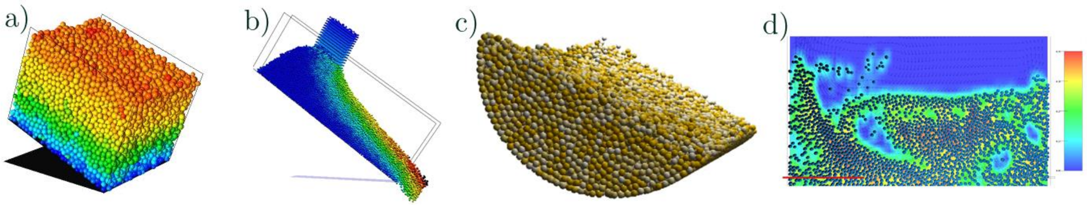


Figure 4: Examples of DEM simulations by the author of this proposal. a) and b): gravity-driven flows, c): flow in a rotating tumbler and d): fluidized bed (granular suspension)

One of the great advantages of DEM simulations is that all parameters can be varied easily. One can choose the size distribution over a wide range, a variety of shapes can be simulated by "gluing" particles together and the mechanical properties of the material (friction, elastic modulus, inelasticity, cohesion…) can be chosen independently. Most importantly, since all the positions, velocities and forces are known at all time, one can easily compute (or measure) any relevant quantity. More particularly, the stress tensor can be defined from individual particle-particle interactions, f, and the distance between two grains in contact, r, and averaged over a control volume V [17]:

$$\sigma_{ij} = \frac{1}{V} \sum_{contacts} r_j \cdot f_i$$

DEM simulations have been widely used to simulate dry grains but cohesive forces can be easily implemented in order to simulate powders and attractive suspensions (due to capillary forces for instance). Recently, in another project, I have simulated cohesive powders by adding an attractive force between two contacting grains. Figure 5 shows the result of preliminary tests, showing the angle of repose of simulated powders with increasing internal cohesive stress. I will apply this method to simulations of flowing powders and study the effect of cohesion on the characteristics of the flow (thickness, basal stress, flow rate, instabilities…).

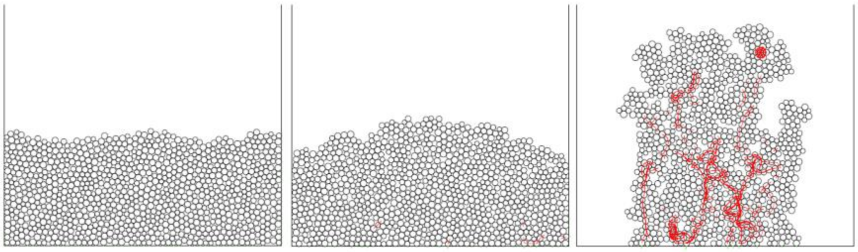
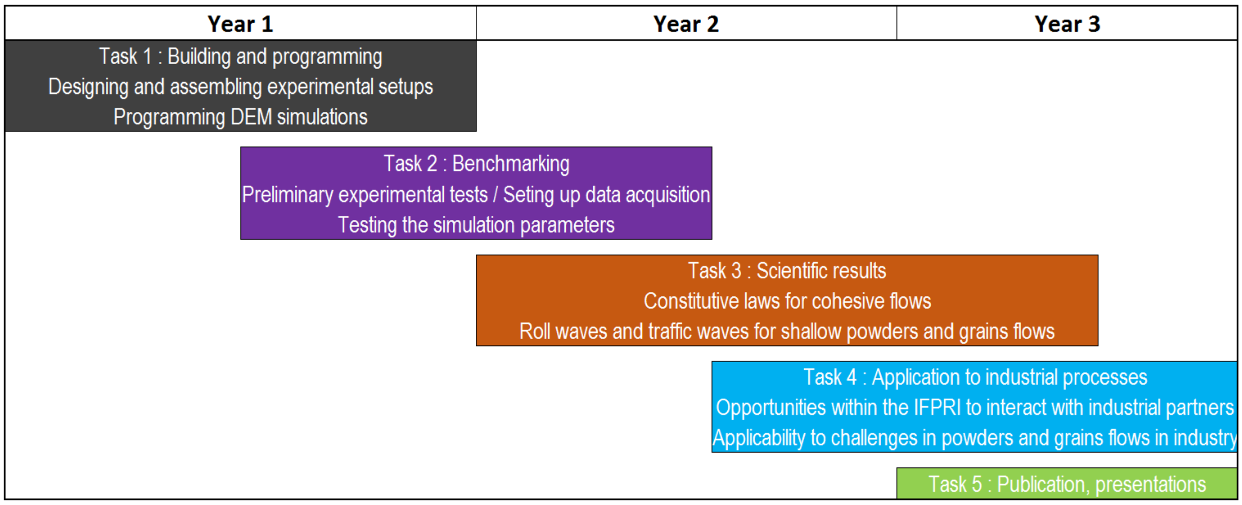


Figure 5: Simulated powder at rest (released from a hopper) with increasing internal cohesive stress (from left to right). The red lines indicate the intensity of inter-particle attractive forces.

III. Project timeline



Task 1 : Building and programming
Designing and assembling experimental setups
Programming DEM simulations

Task 2 : Benchmarking
Preliminary experimental tests / Seting up data acquisition
Testing the simulation parameters

Task 3 : Scientific results
Constitutive laws for cohesive flows
Roll waves and traffic waves for shallow powders and grains flows

Task 4 : Application to industrial processes
Opportunities within the IFPRI to interact with industrial partners
Applicability to challenges in powders and grains flows in industry

Task 5 : Publication, presentations

IV. Budget

Equipement			USD
Linear aluminium rail	Bosch		4000
Fast Camera	Phantom VEO4K 590L		20000
Laser Scanner	Micro-Epsilon scanCONTROL		6000
Force sensors (10 units)	Omega LCMKD-2KN		7000
Data aquisition card	National Instruments DAQ USB		3000
Computer			1500
Other costs			
Travel expenses	annually	3000	9000
Publication Costs	annually	2000	6000
Partial PhD student wage	annually	18000	54000
Total			**110500**

References

[1]. R. L. Brown and J. C. Richards, Principles of Powder Mechanics,
Pergamon, New York, 1970.

[2]. J. Duran. Sand, Powders and Grains,
Springer-Verlag, New-York, 1999.

[3]. H. J. Herrmann, J.-P. Hovi, and S. Luding, editors, Physics of Dry Granular Media.
Kluwer Academic Publishers, Dordrecht, 1998.

[4]. P.G. De Gennes, Reflections on the mechanics of granular matter
Physica A, 261:267–293, 1998.

[5]. M. Wojtkowski, O. I. Imole, M. Ramaioli, E. Chávez Montes and S. Luding, Behavior of cohesive powder in rotating drums
AIP Conference Proceedings 1542, 2013.

[6]. G.D.R Midi, On dense granular flows
Eur. Phys. J. E 14: 341, 2004.

[7]. Pierre Jop, Yoël Forterre and Olivier Pouliquen, A constitutive law for dense granular flows
Nature 441, 727-730, 2006.

[8].Cristiana Di Cristo, Michele Iervolino, Andrea Vacca, Barbara Zanuttigh
Journal of Hydrology, Volume 377 (1) 50-58, 2009.

[9]. Andrew Neal Edwards, Roll waves and erosion-deposition waves in granular flows
PhD Thesis, University of Manchester, 2004.

[10]. San Diego State University, College of Engineering
http://eh.sdsu.edu/chow_froude_and_vedernikov_presentacion.html

[11]. Neil Balmforth, University of British Columbia
https://www.math.ubc.ca/~njb/Research/rollo.htm

[12]. Hayakawa, H., & Nakanishi, K. Universal behavior in granular flows and traffic flows. Progress of Theoretical Physics Supplement, 130, 57-75, 1998.

[13]. B. Percier, Washboard Road Instability
PhD Thesis, University of Lyon, 2013.

[14]. Radjai et al. Journal de Physique I 7(9), 1053-1070, 1997.

[15]. Schafer et al. J. Phys. I France 6, 5 1996.

[16]. Cundall, P. A., & Strack, O. D. A discrete numerical model for granular assemblies.
Geotechnique, 29(1), 47-65., 1979.

[17]. Andreotti, Bruno, Yoël Forterre, and Olivier Pouliquen. *Granular media: between fluid and solid*.
Cambridge University Press, 2013.

Curriculum

Dr. Nicolas Taberlet
UCBL - ENS-Lyon, Laboratoire de Physique, 46, Allée d'Italie F-69007 Lyon, France
Born March 12, 1978, Countries of citizenship: France and Switzerland

Experience

Since 2006	**Professor** at University of Lyon **Université Claude Bernard, École Normale Supérieure de Lyon, France** Research topics: granular flows, granular compaction, complex fluids in complex flows, ultrasound velocimetry, soft glassy materials.
Since 2015	**Elected Vice-chair** of the Physics Department, ENSL
Oct 2005- Sept 2006	**Postdoc at DAMTP, University of Cambridge, UK** **Department of Applied Mathematics and Theoretical Physics**, “Laterally unconfined flows of complex fluids”, under the supervision of Prof. E.J. Hinch
2002-2005	**Ph.D. at Université de Rennes 1, France** & **University of Maryland, USA** “Gravity-driven Granular Flows”: channelised flows, confined flows, segregation and diffusion in a rotating drum, long runout avalanches.

Funding & Contrats

Research projects
Projet Emergent PALSE, 2013-2015, 300 k€, Principal Investigator
ERC USoft, 2010-2015, 1.3 k€, Associate Investigator
National Swiss Fund, 2005-2007, 50 k€, Principal Investigator

International collaborations
CECAM fund (France), with Pr. Sobral, U. Brasilia, 6k€
CAPES fund (Brazil), with Pr. Sobral, U. Brasilia, 20k€
Laboratoire international associé (LIA) – France – Argentine
ECOS program (Chile), 20k€
MIT (USA), 20k€

Miscellaneous

50 peer-reviewed publication & 2 patents

5 graduated PhD students under my supervision

h-index: 20 (Google scholar), 18 (Research Gate), 15 (Isi Web of Science)

Reviewer for scientific journals: ~25 papers / year

Reviewer for research projects
FNS, Fond National Suisse
EPSRC (Engineering and Physical Sciences Research Council), UK
CONICYT (Comisión Nacional de Investigación Científica y Tecnológica), Chile

List of selected publications – on granular flows

1. Grains unchained: local fluidization of a granular packing by focused ultrasound
   P. Lidon, N. Taberlet, S. Manneville
   Soft Matter, Volume: 12, Issue: 8, Pages: 2315-2324 (2016)

2. Insights on the local dynamics induced by thermal cycling in granular matter
   B. Percier, T. Divoux, N. Taberlet
   Euro. Physics Letters 104, 24001(2013)

3. Lift and drag forces on an inclined plow moving over a granular surface
   B. Percier, S. Manneville, J.N. McElwaine, S.W. Morris, N. Taberlet
   Phys. Rev. E 84, 051302 (2011)

4. The effect of side-wall friction on dense granular flows
   N. Taberlet, P. Richard, R. Delannay,
   Computers and Mathematics with Applications 55, 230 (2008).

5. Density inversion in rapid granular flows: the supported regime
   N. Taberlet, P. Richard, E. Henry, R. Delannay,
   European Physical Journal E. 22, 17 (2007).

6. Towards a theoretical picture of dense granular flows down inclines
   R. Delannay, J. T. Jenkins, M. Louge, P. Richard, N. Taberlet, A. Valance,
   Nature Materials 6, 99 (2007).

7. Rock avalanche dynamics: Insights from the granular physics experiments
   J. Friedmann, N. Taberlet, W. Losert,
   International Journal of Earth Sciences 95, 911 (2006).

8. 2D and 3D Confined Granular Flows: Experimental and Numerical Results
   W. Bi, R. Delannay, P. Richard, N. Taberlet, A. Valance,
   Journal of Physics: Condensed Matter 17, S2457 (2005).

9. Super Stable Granular Heap in a Channel
   N. Taberlet, P. Richard, A. Valance, W. Losert, JM. Pasini, J.T. Jenkins, R. Delannay,
   Physical Review Letters 91, 264301 (2003).

10. Two-dimensional inclined chute flows: transverse motion and segregation
    G. Berton, R. Delannay, P. Richard, N. Taberlet, A. Valance,
    Physical Review E 68, 051303 (2003).

11. Leidenfrost granular flows
    N. Taberlet, P. Richard, R. Delannay
    Proceedings of Traffic and Granular Flows 07, Pages: 565-576, Springer (2009).

12. How sidewalls influence granular flows
    N. Taberlet, P. Richard, R. Delannay, M. Louge,
    in Powders & Grains 2005, Balkema, Rotterdam, 873 (2005).

13. Volume fraction profile in channelled granular flows down an erodible incline
    M. Louge, A. Valance, N. Taberlet, P. Richard, R. Delannay,
    in Powders & Grains 2005, Balkema, Rotterdam, 885 (2005).

IFPRI Research Project Brief

Predicting and Characterizing Crystal Surface Modification in Milling

The International Fine Particle Research Institute (IFPRI) wishes to fund a project in the broad area of crystalline structure modification during milling. Milling (size reduction) is often the final step in production of crystalline powders, used to control the particle size distribution of the product. It is not unusual that milling also causes undesirable structural changes, in the bulk and on the surface of crystals. The mechanism of these transformations is not understood, and it is not possible to predict whether a given crystalline phase will be sensitive to milling or not. This project aims to build a mechanistic understanding of mechanically-induced *surface* transformations, with the expectation that this will provide the basis for prediction of, aiding characterization of, and potentially avoiding surface damage in milling.

More specifically, the objective of the project is computational prediction of transformation (energy absorption and potentially fracture, disorder and/or phase change) in a brittle or semi-brittle crystalline structure caused by a mechanical shock at a surface due to a collisional impact that applies stress at rate and extent relevant to impact milling. There is no restriction on the modelling approach used in the project. The project should likely focus on physical phase modification; chemical (damage /reactivity) prediction is presumed to be too challenging to be within initial scope. Both organic and inorganic crystals are in scope; semi-crystalline thermoplastics are out of scope.

Molecular Dynamics Simulations of Aspirin and Sodium Chloride Impact Loading

A Research Proposal
submitted to the
International Fine Particle Research Institute

by

Prof. Doros N. Theodorou

and Dr. Christos Tzoumanekas

Department of Materials Science and Engineering
School of Chemical Engineering
National Technical University of Athens
9 Heroon Polytechniou Street, Zografou Campus
Tel. +30 210-772-3157, Fax +30 210-772-3112
e-mail doros@central.ntua.gr

website http://comse.chemeng.ntua.gr

October 2017

Introduction and Background

The outcome of a milling process depends upon a complex interaction between material properties, mill type, and operational conditions (number of stress events, type of stresses, their intensity, etc.) [1]. Understanding and quantifying this interaction is essential for predictive modeling of the size-reduction process [2]. It has been shown that the primary material properties responsible for the breakage of solid particles are Young's modulus (E), hardness (H), and critical stress intensity factor (K_c), representing the resistance of the material to elastic deformation, plastic deformation, and crack propagation, respectively [3-6]. Microscopic processes related to particle breakage, such as cleavage along slip planes, generation of surface steps, point defects and dislocations, and crack nucleation, are manifested in these properties. In parallel, it is widely accepted that changes in surface/bulk structure, particle shape, and surface energetics are equally important [7,8]. Milling increases the total surface area but also changes the relative exposure of different crystal faces in the powder and therefore the surface chemistry [9,10]. Moreover, the strong heat generation of most dry milling processes can lead to surface melting of small particles. These changes can lead to enhanced agglomeration and affect milling sensitivity and powder processing (e.g., flowability, compactibility, mixing) [1]. In addition, critical product properties can be altered [11]. A prominent example is the modification of the dissolution behavior of active pharmaceutical ingredients (APIs) whose size reduction by milling increases their surface area, hence their dissolution rate (the majority of screened drug candidates have low solubilities). Changes in crystal habit, surface melting, recrystallization, amorphization, and stress-induced transformation to a different crystal polymorph (stable/unstable), can affect wetting, aerosolization, mixing, compaction, thermodynamic stability, and dissolution behavior of the API [11]. Understanding fundamentally the effects of milling on particle surface properties has become even more important with the advent of nanomilling [11-13]. Among other applications, the dispersion of nanocrystalline particles in a host material, leading to reinforcement and tailored mechanical/electrical properties [14], as well as the stabilization of API nanocrystals by polymers or surfactants [15], are of utmost technological importance.

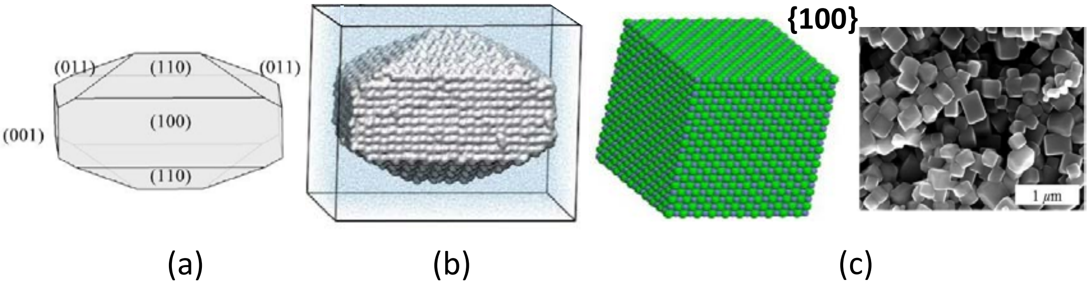
Overview. The mechanical properties of a material measured at low strain rates may be inadequate for describing its breakage and deformation behavior at high strain rates. During milling the particles are subjected to different kinds of loads. Impact testing can conform to strain rates operating in various milling machines and is more relevant than nano-indentation for strain-rate hardening materials. Single particle impact studies have been employed to develop an understanding of failure processes and mechanisms under different loading conditions, as well as to provide useful data that can be used for predictive analysis of milling [3,16-18]. In the proposed work we will undertake molecular dynamics (MD) simulations of acetylsalicylic acid (aspirin) and sodium chloride (NaCl) nanoparticles hitting an impact surface, analyze the resulting changes in the size/shape, crystallinity, defect generation, stress distribution, surface free energy, and surface charge of the particles, and perform an energy balance on the process. Furthermore, we will design a multiscale MD/continuum thermomechanical approach for conducting analogous studies on μm sized particles.

Proposed Work. The particle will approach an immovable wall (impact surface) with prescribed impact angle (orientation) and initial translational and angular velocities. The plan is to simulate the entire collision process and record all changes (energetic, thermal, structural, local stress) taking place in the particle during/after impact, including 'crunching' and particle breakage into fragments. (Distributions of) initial particle velocities and angular velocities should be chosen so as to be representative of the actual milling process (in the range 10-300 m/s, or much larger to simulate jet mill processes). The roughness of the impact surface (height and wavelength of asperities) should also be representative of the process; varying it systematically would give us the opportunity to conduct an interesting parametric study.

To probe surface and bulk crystal structure modifications, the particle and the impact surface (IS) *should be described with atomistic resolution*. If the duration of impact is of the order of one μs, atomistic impact simulations of nanoparticles using MD with molecular mechanics-type force fields, by exploiting parallel computing, are possible. However, milling is an intrinsically multiscale process, and in industrial practice the target size distribution can be centered in the mm, μm, or nm length scale. Therefore, starting from atomistic simulations our intention is to formulate a multiscale modeling approach that would smoothly interface with continuum approaches to large length and time scale phenomena.

Fully Atomistic Simulations. *Particle.* Two compounds whose equilibrium structure are known from X-rays will be studied. Aspirin, an organic molecular crystal, and NaCl, a prototype ionic crystal. The shot particles will be single nanocrystals without defects, as shown in Figure 1. Their habitus will be representative of the compound with typical linear size between 50 and 150 nm. The selected crystals have been simulated with MD in the past [20,24] and used in milling and single particle impact studies [3,6,18,33].

Figure 1: (a) crystal habit of Aspirin, form I [19], (b) Aspirin nanocrystal [19,20], (c) NaCl nanocrystals [21]



Aspirin has two ambient mechanically stable polymorphs, form I and II [22], distinguished by a small lateral shift of layers and very small energy difference, 2.56 kJ/mol (298K) [23]. Sodium chloride exhibits a high pressure transition from the low pressure B1 phase (rocksalt structure) at ambient conditions to the B2 phase (CsCl structure) at 30GPa [24].

Force field. Given the significant computational effort required and our focus mainly on physical and not chemical phenomena, the use of a simple force field is appropriate. Minimum requirements of the force field are that it exhibit a minimum near the correct (X-ray) crystal structure of the particle, that it yield a good estimate of the cohesive energy density (lattice energy), and that the matrix of isothermal elastic coefficients extracted from it be reasonable. It would be nice if, in addition, it can reproduce the equilibrium melting point and heat of fusion, and give a good estimate of the thermal conductivity and of the attachment energies of primary slip planes.

Impact Surface (IS). It will be represented as a semi-infinite medium (Fe atomistic lattice) with lateral dimensions much larger than the particle. No periodic boundary conditions will be applied. Atoms on the impact surface are expected to mainly execute vibrations around their average positions. No significant plastic deformation of the impact surface is expected; most of the damage due to the collision will be experienced by the particle. Asperities can easily be introduced on the IS with prescribed height and wavelength. Rough surfaces have been simulated in the past [25]. Since the particle is much less massive than the impact surface, three to five atomic layers and asperity atoms near the approaching particle will be allowed to move in the MD in order to allow for heat dissipation through the IS, while the rest will be treated as a medium consisting of stationary atoms. A molecular mechanics-type potential corresponding to Fe will be used to describe interactions within the IS and interactions between the IS and particle atoms. The potential due to the stationary atomic layers of the semi-infinite part of the IS can be precomputed and pretabulated in three dimensions [26]. The moving atoms of the IS will be thermostated with Brownian dynamics. Sophisticated thermostating schemes exist which can reproduce the thermal conductivity of Fe [27]. It will probably be satisfactory to assume that the IS has infinite thermal conductivity in relation to the particle. Whatever scheme is adopted, we will be able to calculate the energy that is conducted away as heat through the IS during the collision.

Notes on the selected materials. ▪ Fragmentation occurs through cleavage along preferential slip planes or crack propagation. The primary slip planes of both crystals are well known and characterized [18,32]. Additionally, there is a wealth of published data on the thermophysical and mechanical properties of the materials. ▪ A relative measure of the resistance to fracture and grinding is the brittleness index, BI=H/K_C, where H is the hardness and K_C is the fracture toughness. K_C and BI of aspirin and NaCl crystals are very different: between 0.02 and 0.034 MPa $m^{1/2}$ and $2.9 \times 10^3 - 10.5 \times 10^3$ $m^{1/2}$, respectively, for aspirin (due to fracture anisotropy [6,18]); 0.5 MPa $m^{1/2}$ and 0.4×10^3 $m^{1/2}$ for NaCl [28]. It would be interesting to see how this one order of magnitude difference in BI alters impact behavior. ▪ Single crystals of both aspirin polymorphs have been grown from solution, while it has been shown that the two phases are frequently intergrown [29]. Form I was found to undergo a reversible phase transition to a new polymorph (form III) at 2 GPa (hydrostatic pressure) [30]. Form II did not undergo any phase transition for pressures up to 10 GPa, but exhibited a disordered structure above 7 GPa [30]. It has been reported that it transforms to form I slowly (over several months) at ambient conditions but the transformation is accelerated by shear stress upon mechanical grinding [31]. Shear slip along $\{100\}\langle 001\rangle$ provides a mechanistic rationale for the observed solid-state II/I transformation [30,31]. ▪ The thermal expansion of aspirin is larger by a factor of two perpendicular to the direction [010]. The anisotropy of the longitudinal elastic stiffness is less pronounced; the difference between the minimum and maximum values is approximately 30% [32].

Multiscale simulations. The μm size limit estimated by studies of the brittle to ductile transition [34] (which do not take into account temperature and stress rate effects) has been superseded by current milling technology (wet milling in stirred media mills, jet mills, etc.) [11-13]. The true grinding limit [35] lies in the nm range, which falls within strain rates and length scales treatable with MD. In industrial practice, however, the need for controlled and energetically efficient milling, with target particle size distribution in the μm or mm size, will always exist. Such length scales are many orders of magnitude larger than the systems we can simulate atomistically with MD.

In order to scale up the system, only the domains of the particle and the impact surface which come into close contact during the collision will be represented *with atoms* and simulated with full MD (MD regions). The remaining (largest) domains of the particle and IS will be represented with Finite Element (FE) meshes (i.e., with *mesh nodes*). As far as their motion is concerned, they will be considered as rigid bodies. As far as heat transfer and stress distribution is concerned they will be treated as continua with given boundary conditions (temperature and loading) and known elastic stiffness and thermal conductivity tensor. The thermomechanical problem within the continua will be solved with the Finite Element Method (FEM). No periodic boundary conditions will be applied. An outline of how multiscale simulations can be conducted is given below. The discussion will be restricted to the particle. The extension to the impact surface is fairly obvious. A sketch of the model system, as envisioned before the collision, is also given in Figure 2. The multiscale scheme is based on the Embedded Statistical Coupling Method (ESCM) for coupling MD with FE [36,37]. The method uses statistical averaging over both time and volume of atomistic subdomains at the MD/FE interface to provide nodal displacement boundary conditions to the continuum FE domain. In response to the atomic displacements, the FEM generates interface reaction forces that are uniformly distributed over the interface atoms in the form of constant traction boundary conditions to the MD domain [36].

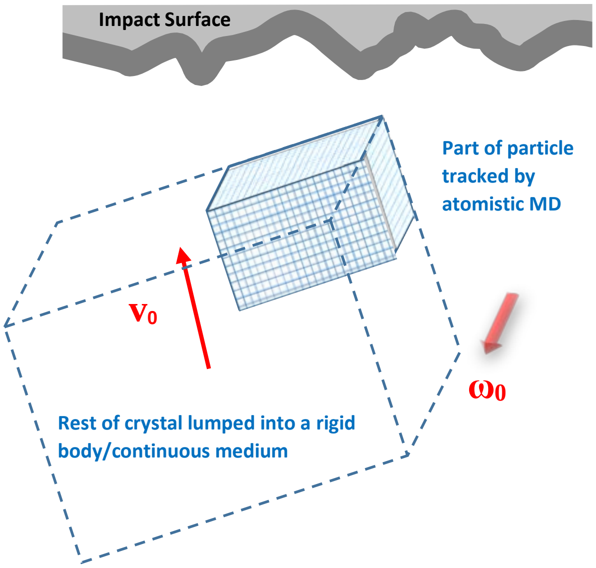


Figure 2: Schematic representation of the multiscale model. The initial linear and angular velocity of the particle are denoted as $\mathbf{v_0}$, $\boldsymbol{\omega_0}$, respectively.

The FE and MD computational systems (describing the particle) are effectively independent and communicate only through an iterative update of the boundary conditions at the MD/FE interface (coupled boundary value problem). The continuity of material properties at the interface, and of the interface itself, is achieved by the immersion of interfacial FE nodes within the MD region. Each one of these nodes is surrounded by certain atoms (specified by geometric criteria) of the local MD region. Thus, the interface becomes a set of interfacial FE nodes surrounded by corresponding MD subdomains. MD subdomains are defined only at the MD/FE interface. The MD simulation is divided in coarse time steps of $\Delta t \simeq 1$ ps or less. During this time the interfacial nodes are kept still and apply constant forces (tractions) to the atoms of MD subdomains, transferring the static FE domain stress field to the MD domain. Because of the collision, each atom at the MD/FEM interface will experience an average net displacement (with reference to the average atom positions in the previous Δt step). These displacements are much smaller for particle atoms in the interior of MD subdomains than for atoms in contact with and near the interface. By averaging the displacements within MD subdomains, a displacement for each interfacial node is calculated. In this way, an iterative update of the coupled boundary conditions at the MD/FEM interface is achieved. The nodal displacements will generate new reaction forces from FEM that will then be applied to MD subdomains. The latter, after time Δt, will generate new FEM nodal displacements, and so on.

Any conventional FEM code, including commercial packages, can be used to solve the continuum mechanical problem. The FEM and MD computational systems are effectively independent, making the multiscale model convenient and extendable to different chemistries. Additionally, the continuum thermal problem, which plays a crucial role in the energy balance of the collision, can be solved with FEM in parallel with the mechanical problem and on the same continuum FE mesh. The mechanical/thermal analogy is the following: displacement becomes temperature, stress becomes heat flux, load (force) becomes heat, and the elastic stiffness matrix becomes the thermal conductivity matrix. From the short-time averaged kinetic energy of molecules in MD subdomains the temperature distribution at all FE nodal points of the interface will be known, and the continuum heat transfer problem will be solved with FE. The heat flux at the MD/FE interface will be fed back to the atomistic MD and used to rescale atomic velocities of MD subdomains. In this way, a seamless representation of heat transfer within the particle will be accomplished. The heat generated from the collision will be transferred from the MD to the FE domain. The thermal problem can be coupled with the mechanical one to take into account the temperature dependence of elastic constants and thermal expansion coefficients of the crystal [32,38]. One can also envision solving the continuum equations of elasticity within the continuum with surface tractions derived from the atomistic part and thereby tracking cleavage along primary slippage planes, or crack propagation [39], in the FE domain.

As can be seen in Figure 2, the MD domain can be considered as an atomistic nanoparticle with some free faces, but also with surface boundary conditions derived from a continuum thermomechanical model representing a larger μm size particle. On impact, the surface changes in free faces will be affected by the aforementioned boundary conditions. Thus, it is possible that surface changes would be different for different size particles, and studies at different length scales have a merit on their own. Technically, the multiscale model poses many difficulties, and it needs to be developed at increasing levels of sophistication. For example, during impact the particle could roll on the IS, bringing into contact the FE domain of the particle with the FE domain of the IS and necessitating a change in focus in the atomistically represented part. In this project we will develop only the multiscale MD/FE thermal model in the 3rd year.

Observables to be tracked

- Movies of the entire collision process with defect accumulation and/or stress scale coloring; Duration of the collision.
- Detection of face, edge or vertex impact, and insight on outcome differences.
- Energetic analysis of the collision: Energy balance. Fraction of the initial kinetic energy that goes to increase the internal energy of the particle. Increase in potential energy and its components (inter- vs intra-molecular, stretching, bending, torsional etc.). Increase in kinetic energy of molecules after subtracting overall translational and rotational motion. Spatial distribution of the increase in internal energy. Fraction of the initial kinetic energy that is dissipated as heat through the impact surface. Overall particle momenta and angular momenta before and after collision. Overall kinetic energies before and after collision. Coefficient of restitution of the collision.
- Structural and specific surface energy changes brought about by the collision and their time evolution. Local density $\rho(\mathbf{r},t)$ as a function of position and time. Crystalline defects (point, dislocations [38], grain boundaries, surface steps), with respect to the initial crystalline structure, their spatial distribution and their evolution with time. Presence of ductility, cleavage plane analysis based on attachment energy of nanocrystal slip planes. Development of voids by analysis of clusters of accessible volume: void shape, orientation, spatial distribution and evolution. Onset and propagation of surface/internal cracks. Detection of surface melting, amorphization, recrystallization. Transition into different polymorphs in the surface/bulk region. Particle structure factor and interpretation of its features based on observed structural changes. Profiling of the

damage region and its time evolution based on the above structural measures. Overall charge developing in NaCl as a result of the collision and distribution of surface charges.

- Stress distribution as a function of time, $\boldsymbol{\sigma}(\mathbf{r},t)$. Both atomic-level stresses and locally averaged stresses will be computed through the virial theorem. Analysis of local stress in the light of continuum criteria for fracture.
- Temperature distribution throughout the particle as a function of time, $T(\mathbf{r},t)$, from short-time averaging of atomic kinetic energies after subtraction of overall particle motion. Detection of surface melting or phase transitions based on the temperature-time history at specific points.

System parameters whose effect will be studied

- Particle size, habit or shape.
- Initial velocity and angular velocity of particle with respect to the impact surface. A distribution of those should be studied. At a later stage, this distribution could be connected to a macroscopic simulation of the actual milling process.
- Frequency and height of asperities on the impact surface.
- Effect of repeated collisions of the same particle. At a later stage, subsequent collision simulations could be conducted on the fragments obtained from an initial particle.
- Effect of temperature [39] (e.g., cryogenic vs ambient milling conditions).
- Initial particle orientation with respect to the impact surface and asperities (for example, the two following cases). Several interesting variations can be envisaged.
- Shear vs compressive stress effects, by comparing impact with zero angular velocity and particle face oriented parallel to a flat impact surface for near-0° and 90° impact angle (promoting development of shear vs compressive stresses on the particle/impact-surface interface, respectively).
- Single (one loading ‘point’) vs double (two loading ‘points’) impact. On double impact the orientation of the particle will be adjusted to hit the surface on two points simultaneously: a point on the flat part of the surface and a point located on a protruding asperity near the flat part.

Future extensions could include the simulation of particles of various chemical constitutions, the simulation of multicrystalline or defective particles, an analysis of particle-particle collision along the same lines (jet mills), simulation in the presence of moisture in the mill, etc.

Critical unknowns, and limitations. ▪ Setup and validation simulations will be performed on the 128 core cluster of our group. To analyze the scaling of required computational resources vs system size we will exploit the use of preparatory access projects (for setting large-scale simulations) granted (after application) by High Performance Computing (HPC) centers. This is the first stage for getting access to powerful large-scale computational platforms to perform production simulations (proof of scaling is a must when applying). Post-processing can be performed in our lab. We will apply for access to at least two HPC organizations, PRACE (European) and ARIS (Greek) [40,41], where we have carried out recent projects. ▪ By searching the literature we found that there is limited work (if any) concerning impact (breakage) simulations of solid particles with real chemistry, though impact problems have been studied with large-scale MD simulations [42,43]. Considering this gap, atomistic impact simulations are considered absolutely necessary before embarking on a multiscale approach ▪ We expect that the nanoparticles will break upon impact (as in nanomilling [35]). Atomistic simulations of NaCl clusters and nanocrystals [44,45] have led to the conclusion that they are brittle (i.e., do not undergo a brittle to ductile transition). Another issue is whether or not continuum mechanics can be used to describe a particle at the nanometer scale [14]. Recent simulations have shown that Hertzian theory of the deformation, due to an external load, of two elastic NaCl nanocrystals in contact can be applied down to sizes of 5 nm [46]. Nevertheless, in case of enhanced ductile behavior, temperature reduction, increase of impact velocity, and introduction of preexisting flaws to promote particle breakage are possible. ▪ The simulated wavelength of asperities will be limited by the spatial extent of the impact surface. A plane IS will be simulated first. ▪ A compromise between the size of the system and the total number of simulated impact events is necessary. A cubic NaCl nanocrystal with edge length 170 Å contains approximately 216000 atoms; one with edge length 226 Å contains 512000 atoms.

Targets and accomplishments in each of the three years

First year. Setup of the single particle impact simulation engine for given impact angle, velocity and angular velocity of aspirin particles. We will use the freely available Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD software [47,48]. Selection of suitable force field for aspirin and IS (Fe). Computational generation of the particle/IS system. Automatic scheme for generating atomistic nanoparticles of given linear dimensions and habit. Application for preparatory access project (code scaling & optimization) to HPC centers [40,41]. Surface/bulk characterization of structure/energetics of the known aspirin and NaCl polymorphs. Mechanical characterization of aspirin for the selected force field (material model). Estimation of the elastic stiffness matrix and yield strength of the particle bulk phase and comparison with previous simulation/experimental work. Impact simulations of small/moderate size Aspirin systems and validation of setup. Development of software for post processing analysis of the observables to be tracked.

Second year. Effect of system parameters. Preparatory large-scale simulations of aspirin, estimation of computing and storage needs according to system size. Application for computationally intensive project to HPC centers. Optimization and selection of system parameters (especially size) for large-scale impact simulations of Aspirin. Visualization of impact trajectories with color filters for detecting generated surface/bulk defects and regions of high local stress in particle and its fragments. Large scale Aspirin simulations. Analysis of observables. Setup and deployment of large scale NaCl impact simulations.

Third year. Continuation of large scale Aspirin, NaCl impact simulations. Variation of initial conditions; initial particle orientation, etc. Analysis and collection of data/results for as many possible impact events. Setup of the multiscale simulation scheme. Integration of MD with FEM for the thermomechanical problem for one of the systems.

How this project could leverage into existing programs in which your research team is engaged. The Computational Materials Science and Engineering (CoMSE) group at NTUA is engaged in several research programs aiming at the design, development, and implementation of powerful, yet tractable multiscale modeling and simulation strategies for the prediction of properties of materials from chemical constitution and processing conditions. Ongoing programs relevant to the proposed project focus on dispersing nanoparticles in polymer matrices by tuning interactions or use of surface-grafted chains, as well as on the thermal and mechanical properties of the resulting nanocomposites [49-53]; on predicting surface tension, work of adhesion, and dynamics at interfaces from atomic-level interactions [57,58]; on cavitation of soft materials under imposition of external stress [54]; on polymer crystallization [55]; and on nonlinear rheology under high deformation rates [56]. The knowhow, methodology, software, and collaborative ties with Industry developed in the context of these research programs will be highly useful in the proposed project.

Indications where IFPRI members could support the program through provision e.g. of model test materials, test methods, industrial experience. Consultation on particle characteristics and impact conditions relevant to real milling processes; prioritization of system parameters for study according to their relevance for industry; validation of predicted material properties and impact simulation outcomes based on experimental findings and accumulated industrial knowhow; guidance in planning next steps.

References

1. Roberts, R.J. "Particulate Analysis - Mechanical Properties" (2011) in '*Solid State Characterization of Pharmaceuticals*', pp. 357-386, John Wiley and Sons
2. Vogel, L., Peukert, W. "Breakage behaviour of different materials - Construction of a mastercurve for the breakage probability" (2003) *Powder Technology*, 129 (1-3), pp. 101-110.
3. Ghadiri, M., Zhang, Z. "Impact attrition of particulate solids. Part 1: A theoretical model of chipping" (2002) *Chemical Engineering Science*, 57 (17), pp. 3659-3669.
4. Kwan, C.C., Chen, Y.Q., Ding, Y.L., Papadopoulos, D.G., Bentham, A.C., Ghadiri, M. "Development of a novel approach towards predicting the milling behaviour of pharmaceutical powders" (2004) *European Journal of Pharmaceutical Sciences*, 23 (4-5), pp. 327-336.
5. Vogel, L., Peukert, W. 'From single particle impact behaviour to modeling of impact mills' (2005) *Chemical Engineering Science*, 60 (18), pp. 5164-5176.
6. Meier, M., John, E., Wieckhusen, D., Wirth, W., Peukert, W. "Influence of mechanical properties on impact fracture: Prediction of the milling behaviour of pharmaceutical powders by nanoindentation" (2009) *Powder Technology*, 188 (3), pp. 301-313.
7. Williams, D.R. "Particle engineering in pharmaceutical solids processing: Surface energy considerations" (2015) *Current Pharmaceutical Design*, 21 (19), pp. 2677-2694.
8. Luner, P.E., Zhang, Y., Abramov, Y.A., Carvajal, M.T. "Evaluation of milling method on the surface energetics of molecular crystals using inverse gas chromatography" (2012) *Crystal Growth and Design*, 12 (11), pp. 5271-5282.
9. Heng, J.Y.Y., Bismarck, A., Williams, D.R. "Anisotropic surface chemistry of crystalline pharmaceutical solids (2006) AAPS *PharmSciTech*, 7 (4), art. no. 84, .
10. Heng, J.Y.Y., Thielmann, F., Williams, D.R. 'The effects of milling on the surface properties of form I paracetamol crystals' (2006) *Pharmaceutical Research*, 23 (8), pp. 1918-1927.
11. Scheler, S. "Micro- and Nanosizing of Poorly Soluble Drugs by Grinding Techniques" (2013) in *Drug Delivery Strategies for Poorly Water-Soluble Drugs*, pp. 509-550, John Wiley and Sons
12. Mende, S. "Industrial Production of Nanomaterials with Grinding Technologies" (2015) in '*The Nano-Micro Interface: Bridging the Micro and Nano Worlds*', Second Edition, 2-2, pp. 629-646, Wiley Blackwell
13. Knieke, C., Steinborn, C., Romeis, S., Peukert, W., Breitung-Faes, S., Kwade, A. "Nanoparticle production with stirred-media mills: Opportunities and limits" (2010) *Chemical Engineering and Technology*, 33 (9), pp. 1401-1411.

14. Guo, D., Xie, G., Luo, J. "Mechanical properties of nanoparticles: Basics and applications" (2014) *Journal of Physics D: Applied Physics*, 47 (1), art. no. 013001, .

15. Peltonen, L., Hirvonen, J. "Pharmaceutical nanocrystals by nanomilling: Critical process parameters, particle fracturing and stabilization methods" (2010) *Journal of Pharmacy and Pharmacology*, 62 (11), pp. 1569-1579.

16 Tavares, L.M., Austin, L.G., King, R.P. "Breakage and damage of particles by impact" (2006) in '*SME Annual Conference - Advances in Comminution*', pp. 205-223.

17. Meier, M., John, E., Wieckhusen, D., Wirth, W., Peukert, W. "Characterization of the grinding behaviour in a single particle impact device: Studies on pharmaceutical powders" (2008) *European Journal of Pharmaceutical Sciences*, 34 (1), pp. 45-55.

18. Olusanmi, D., Roberts, K.J., Ghadiri, M., Ding, Y. "The breakage behaviour of Aspirin under quasi-static indentation and single particle impact loading: Effect of crystallographic anisotropy" (2011) *International Journal of Pharmaceutics*, 411 (1-2), pp. 49-63.

19 Hammond, R.B., Pencheva, K., Ramachandran, V., Roberts, K.J. "Application of grid-based molecular methods for modeling solvent-dependent crystal growth morphology: Aspirin crystallized from aqueous ethanolic solution" (2007) *Crystal Growth and Design*, 7 (9), pp. 1571-1574.

20. Greiner, M., Elts, E., Briesen, H. "Insights into pharmaceutical nanocrystal dissolution: A molecular dynamics simulation study on aspirin" (2014) Molecular Pharmaceutics, 11 (9), pp. 3009-3016.

21. Range, S., Bernardes, C.E.S., Simões, R.G., Epple, M., Da Piedade, M.E.M. "Size matters: An experimental and computational study of the influence of particle size on the lattice energy of NaCl" (2015) *Journal of Physical Chemistry C*, 119 (8), pp. 4387-4396.

22. Bond, A.D., Solanko, K.A., Parsons, S., Redder, S., Boese, R. "Single crystals of aspirin form II: Crystallisation and stability" (2011) *CrystEngComm*, 13 (2), pp. 399-401.

23. Reilly, A.M., Tkatchenko, A. "Role of dispersion interactions in the polymorphism and entropic stabilization of the aspirin crystal" (2014) *Physical Review Letters*, 113 (5), art. no. 055701.

24. Zhang, S., Chen, N.-X. "Molecular dynamics simulations for high-pressure induced B1-B2 transition in NaCl by Möbius pair potentials" (2003) *Modelling and Simulation in Materials Science and Engineering*, 11 (3), pp. 331-338.

25. Li, J., Fang, Q., Zhang, L., Liu, Y. "The effect of rough surface on nanoscale high speed grinding by a molecular dynamics simulation" (2015) *Computational Materials Science*, 98, pp. 252-262.

26. June, R.L., Bell, A.T., Theodorou, D.N. "Molecular Dynamics Study of Methane and Xenon in Silicalite" (1990) *J. Phys. Chem.*, 94, 8232-8240; erratum (1991) *J. Phys. Chem.*, 95, 1014.

27. Berro, H., Fillot, N., Vergne, P., Tokumasu, T., Ohara, T., Kikugawa, G. "Energy dissipation in non-isothermal molecular dynamics simulations of confined liquids under shear" (2011) *Journal of Chemical Physics*, 135 (13), art. no. 134708.

28. Duncan-Hewitt, W.C., Weatherly, G.C. "Evaluating the hardness, Young's modulus and fracture toughness of some pharmaceutical crystals using microindentation techniques" (1989) *Journal of Materials Science Letters*, 8 (11), pp. 1350-1352.

29. Boese, R., Desiraju, G.R. "On the polymorphism of aspirin: Crystalline aspirin as intergrowths of two "polymorphic" domains" (2007) *Angewandte Chemie - International Edition*, 46 (4), pp. 618-622.

30. Crowell, E.L., Dreger, Z.A., Gupta, Y.M. "High-pressure polymorphism of acetylsalicylic acid (aspirin): Raman spectroscopy" (2014) *Journal of Molecular Structure*, 1082, pp. 29-37.

31. Varughese, S., Kiran, M.S.R.N., Solanko, K.A., Bond, A.D., Ramamurty, U., Desiraju, G.R. "Interaction anisotropy and shear instability of aspirin polymorphs established by nanoindentation" (2011) *Chemical Science*, 2 (11), pp. 2236-2242.

32. Bauer, J.D., Haussühl, E., Winkler, B., Arbeck, D., Milman, V., Robertson, S. "Elastic properties, thermal expansion, and polymorphism of acetylsalicylic acid" (2010) Crystal Growth and Design, 10 (7), pp. 3132-3140.

33. Zhang, Z., Ghadiri, M. "Impact attrition of particulate solids. Part 2: Experimental work" (2002) *Chemical Engineering Science*, 57 (17), pp. 3671-3686.

34. Hagan, J.T. "Impossibility of fragmenting small particles: brittle-ductile transition" (1981) *Journal of Materials Science*, 16 (10), pp. 2909-2911.

35. Knieke, C., Sommer, M., Peukert, W. "Identifying the apparent and true grinding limit" (2009) *Powder Technology*, 195 (1), pp. 25-30.

36. Saether, E., Yamakov, V., Glaessgen, E.H. "An embedded statistical method for coupling molecular dynamics and finite element analyses" (2009) *International Journal for Numerical Methods in Engineering*, 78 (11), pp. 1292-1319.

37. Saether, E., Yamakov, V., Glaessgen, E. "New developments in the embedded statistical coupling method: Atomistic/continuum crack propagation" (2008) *Collection of Technical Papers - AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference*

38. Thomas, L.M., Shanker, J. "Temperature dependence of elastic constants and thermal expansion coefficient for NaCl crystals" (1996) *Physica Status Solidi (B) Basic Research*, 195 (2), pp. 361-366.

39. Yamakov, V.I., Warner, D.H., Zamora, R.J., Saether, E., Curtin, W.A., Glaessgen, E.H. "Investigation of crack tip dislocation emission in aluminum using multiscale molecular dynamics simulation and continuum modeling" (2014) *Journal of the Mechanics and Physics of Solids*, 65 (1), pp. 35-53.

38. Kelchner, C.L., Plimpton, S.J., Hamilton, J.C. "Dislocation nucleation and defect structure during surface indentation (1998) *Physical Review B*, 58 (17), pp. 11085-11088.

39. Olusanmi, D., Wang, C., Ghadiri, M., Ding, Y., Roberts, K.J. 'Effect of temperature and humidity on the breakage behaviour of Aspirin and sucrose particles' (2010) *Powder Technology*, 201 (3), pp. 248-252.

40. Partnership for Advanced Computing in Europe (PRACE), http://www.prace-ri.eu

41. Greek research and technology network; Advanced Research Information System (ARIS) https://grnet.gr/en/

42. Germann, T.C. "Large-scale molecular dynamics simulations of hyperthermal cluster impact' (2006) *International Journal of Impact Engineering*, 33 (1-12), pp. 285-293.

43. Yamaguchi, Y., Gspann, J. "Large-scale molecular dynamics simulations of cluster impact and erosion processes on a diamond-surface" (2002) *Physical Review B*, 66 (15), art. no. 155408, pp. 1554081-15540810.

44. Doye, J.P.K., Wales, D.J. "Structural transitions and global minima of sodium chloride clusters" (1999) *Physical Review B*, 59 (3), pp. 2292-2300.

45. Kendall, K., Yong, C.W., Smith, W. "Deformation of NaCl particle in contact at the nano-scale" (2007) Powder Technology, 174 (1-2), pp. 2-5.

46. Miesbauer, O., Götzinger, M., Peukert, W. “Molecular dynamics simulations of the contact between two NaCl nano-crystals: Adhesion, jump to contact and indentation” (2003) *Nanotechnology*, 14 (3), pp. 371-376.

47. Pavia, F., Curtin, W.A. “Parallel algorithm for multiscale atomistic/continuum simulations using LAMMPS” (2015) *Modelling and Simulation in Materials Science and Engineering*, 23 (5), art. no. 055002.

48. Silani, M., Talebi, H., Arnold, D., Ziaei-Rad, S., Rabczuk, T. “On the coupling of a commercial finite element package with LAMMPS for multiscale modeling of materials” (2012) *Steel Research International*, SPL. ISSUE, pp. 1371-1374.

49. Vogiatzis, G.G., Voyiatzis, E., Theodorou, D.N. “Monte Carlo simulations of a coarse-grained model for an athermal all-polystyrene nanocomposite system” (2011) *Eur. Polym. J.*, 47, 699-712.

50. Ndoro, T.M., Voyiatzis, E., Ghanbari, A., Theodorou, D.N., Böhm, M., Müller-Plathe, F. “Interface of grafted and ungrafted silica nanoparticles with a polystyrene matrix: Atomistic Molecular Dynamics simulations” (2011) *Macromolecules*, 44, 2316-2327.

51. Vogiatzis, G.G., Theodorou, D.N. “Structure of polymer layers grafted to nanoparticles in silica-polystyrene nanocomposites” (2013) *Macromolecules*, 46, 4670-4683.

52. Skountzos, E. N., Anastasiou, A., Mavrantzas, V.G., Theodorou, D.N. “Determination of the mechanical properties of a poly(methyl methacrylate) nanocomposite with functionalized graphene sheets through atomistic simulations” (2014) *Macromolecules*, 47, 8072-8088.

53. Mathioudakis, I.G., Vogiatzis, G.G., Tzoumanekas, C., Theodorou, D.N. “Multiscale simulations of PS-SiO_2 nanocomposites: from melt to glassy state” (2016) *Soft Matter*, 12, 7585-7605.

54. Morozinis, A.K., Tzoumanekas, C., Anogiannakis, S.D., Theodorou, D.N. “Atomistic simulations of cavitation in a model polyethylene network” (2013) *Polym. Sci. – Ser. C*, 55, 212-218.

55. Romanos, N.A., Theodorou, D.N. “Melting point and solid-liquid coexistence properties of α_1 isotactic polypropylene as functions of its molar mass: A molecular dynamics study” (2016) *Macromolecules*, 49, 4663-4673.

56. Vogiatzis, G.G., Megariotis, G., Theodorou, D.N. “Equation of state based slip spring model for entangled polymer dynamics” (2017) *Macromolecules*, 50, 3004-3029.

57. Theodorou, D.N., Vogiatzis, G.G., Kritikos, G. “Self-consistent field study of adsorption and desorption kinetics of polyethylene melts on graphite and comparison with atomistic simulations” (2014) *Macromolecules*, 47, 6964-6981.

58. Sgouros, A.P., Vogiatzis, G.G., Kritikos, G., Boziki, A., Nikolakopoulou, A., Liveris, D., Theodorou, D.N. “Molecular simulations of free and graphite capped polyethylene films: Estimation of the interfacial free energies” (2017) *Macromolecules*, 50, DOI: 10.1021/acs.macromol.7b01808

IFPRI Research Project Brief

Rheology of Suspensions at High Solids Content: Bridging the Gap from Colloids to Grains

Pumping, flow, conveyance, and the long-term flow stability of highly concentrated particle systems remain and industrial challenge. Advancements in understanding surface turnover and chemistry-mediated particle interactions have improved our understanding of highly concentrated colloidal systems. Improvements in understanding of jamming phenomena, particle shape and inertial streams have similarly improved understanding of granular systems. A recent revolution has taken place in understanding the rheology of high-solid-content dispersions (HSCDs), viz., that at sufficiently high stress, particles are pressed into contact, so that many ideas from granular flow may become transferable to suspension flow in this regime. This project aims to explore how this new paradigm can be applied to optimize the processing of HSCDs by understanding how their rheology is controlled by many of the classic variables (e.g. morphology and size distribution) viewed under the new paradigm, and by some of the variables made relevant by these recent advances themselves (e.g. roughness, friction).

A key idea from recent advances is that HSCDs jam at a packing fraction ϕ_m substantially below random close packing, so increasing solid content involves increasing ϕ_m. *The overall objective is therefore to understand what controls φ_m.* Research themes under this heading may include:

- The friction coefficient matters, but how this can be systematically modified on the micro to nano scales is not yet mastered.
- Roughness almost certainly matters on some scale, but again, no systematic study yet exists.
- Badly packed aggregates lower ϕ_m, so that it may be fruitful to study wet milling in this context. In particular, wet milling applies stress to an HSCD at $\phi > \phi_m$ to break up aggregates, thereby lowering ϕ_m in the process; the new paradigm should give insight into how best to do this.
- Polydispersity is known to affect random close packing; how it affects ϕ_m is largely unknown.
- Identify key/dominant particle characteristics (e.g., morphology, surface friction, modulus, size distribution) that impact particle assembly, jamming and overall rheological behavior across the transition zone between low and high particle Peclet number concentrated (>40% vol) slurry systems for predictive modeling applications.
- Explore the link between system level and particle level characteristics on the packing/jamming transitions and corresponding rheology of concentrated suspensions across the transition regime between surface dominated interactions and inertially dominated particle systems.

To make progress, the contractor should be able to perform studies in well characterized systems using one or more of the following methodologies: monitor structure and dynamics under flow using a mixture of real-space and scattering methods; develop framework linking measured structure and dynamics to constitutive properties of suspension; develop toolkit for systematic variation of relevant parameters (friction, roughness, etc.).

Bridging the Rheological Gap:
Exploring Shear Thickening in non-Ideal Dispersions

Daniel L. Blair, Dept. of Physics and Institute for Soft Matter Synthesis and Metrology
Georgetown University, USA

The response of concentrated collections of solid particles subjected to external shear stresses exhibit a rich variety of nonlinear behavior [1, 2]. In particular, colloidal dispersions and granular slurries can undergo dramatic increases in viscosity. For low to moderate concentrations, the increase in viscosity as a function of shear stress (or strain) will remain smooth resulting in continuous shear thickening (CST). However, above a critical, and in many cases suspension specific concentration, the viscosity increase can become divergent leading to a dramatic solidification of the suspension at a finite applied stress, known as discontinuous shear thickening (DST). In this proposal, we will outline a set of experiments designed to quantify the impact that shear thickening transitions have on non-ideal particle suspensions. Our hope is to work closely with academic and industrial partners within IFPRI to identify systems and measurements that provide the best possible feedback between our work and broader needs.

Leveraging current work and results: One focus of my lab over the past five years centers around the development of experimental techniques that extend our ability to quantify the mechanical aspects of soft materials subjected to shear deformations. Of particular interest is our ability to enhance our platform that combines confocal microscopy and rheology to provide time resolved quantification of shear and normal stresses at the boundary of our rheometer with micron scale resolution. Our approach, known as *Boundary Stress Microscopy* (BSM) is a generalization of the traction force microscopy (TFM) method used by biological physicists to determine spatially resolved, localized forces exerted by cells as they translocate across 2-D substrates. TFM has also been used in non-rheological soft matter experiments to study fracture of slurries, dewetting of films and adhesion (see [4]). Briefly, both techniques utilize thin gel or elastomeric substrates of known stiffness and thickness that are typically placed on a glass or other rigid substrate. To elucidate the displacement at the boundary, colloidal particles are functionalized and linked to the surface of the elastomer to act as fiduciary markers. The displacements of the particles are recorded and analyzed through particle tracking or velocimetry methods; displacements are then analyzed using mathematical inversion methods that convert displacements to stresses. Our first application of this work was to investigate the spatially heterogeneous distribution of stresses in sheared collagen networks. We continue to explore this line of research to create three dimensional micro-environments for quantifying cell motility in materials with spatially varying stiffness.

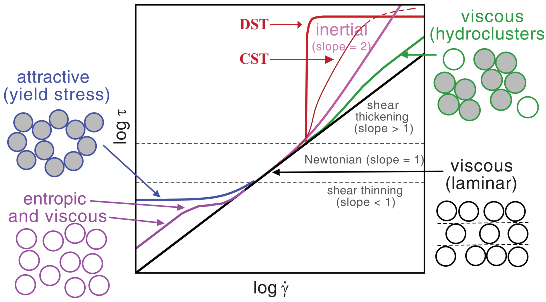


Figure 1: Typical strain rate vs. shear stress curves for suspensions of hard spherical particles, with schematics of the microstructural arrangements associated with some of the regimes (modified from [3]).

We have recently published two rheological studies of shear thickening in colloidal dispersions [6, 5]. In our first work, we explored the signatures of frictional interactions through the exploration of the first normal stress difference N_1. We found that for low concentrations, N_1 reveals the relative contributions from hydrodynamic lubrication and frictional contact forces; a hotly debated subject within the community. Our results can be summarized in the following way: At moderate volume fractions we find $N_1 < 0$, consistent with a hydrodynamic picture, while at higher volume fractions and shear stresses hydrodynamics alone cannot completely explain our results. We instead observe dilatancy ($N_1 > 0$) which is indicative of frictional contact networks similar to those found in granular flows. What is also remarkable about this apparent transition is the lack

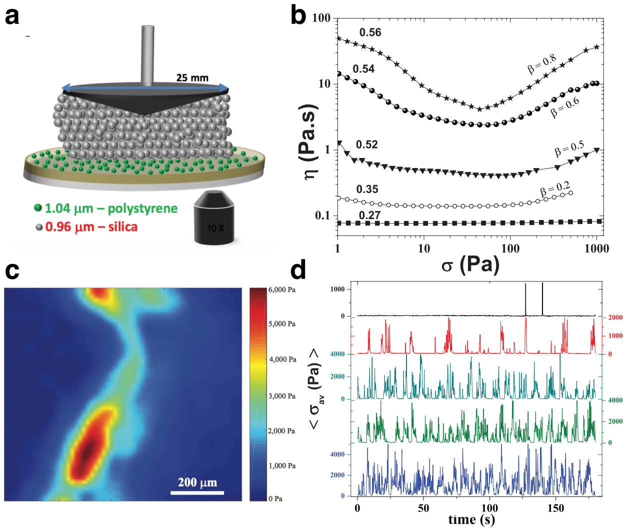


Figure 2: (a) Schematic of Boundary Stress Microscopy setup. The bottom cover slide is shown in silver and the thin elastic PDMS layer in light green. Fluorescent microspheres attached to the PDMS are shown in green and the silica colloids in silver. The rheometer cone defines the top surface of the suspension and is attached to a stress controlled rheometer. (b) Viscosity vs. applied stress flow curves for suspensions of different concentrations ϕ with the approximate shear-thickening exponent β. (c) Representative calculated stress field (component of the stress in the flow direction) showing heterogeneous boundary stress for a concentration $\phi = 0.56$ in the CST regime. The field of view, slightly less than 1x1 mm, is large compared to the particle size (1 μm) and small compared to the radius of the rheometer tool (25 mm), but the extent of the high stress region in the velocity (flow) direction is of the order of the space between the rheometer plates (200 μm). (d) Time series of average stress per frame from BSM in the CST regime ($\phi = 0.56$). From top to bottom, applied stress of $\sigma = 100$, 200,500,750, 1000 Pa (From [5]).

of any signature in the viscosity, which remains continuous and increasing even while N_1 changes sign. These results suggest a scenario where shear thickening is driven primarily by the formation of frictional contacts, with hydrodynamic forces playing a supporting role at lower concentrations.

More recently, we have investigated high concentration colloidal dispersions that exhibit shear thickening using the BSM technique described above. This work will serve as the basis for the project outlined in this proposal (see below), and due to the importance of our findings I will review them here. The experimental system consists of an Anton-Paar MCR301 stress controlled rheometer with a 25 mm 1^o cone and as the upper fixture (see Fig. 2a). We utilize a cone geometry to ensure the shear rate is uniform throughout the sample. BSM measurements are made by replacing the bottom rheometer plate with a glass slide with an elastomeric film that is spun coat resulting in a uniform thickness and known stiffness with a sparse and uniform coating bound fluorescent microspheres. The attached microspheres are imaged from below with a commercial high speed confocal microscope, and the measured bead displacements converted to surface stresses using our algorithms.

From the perspective of bulk rheology, each measurement consists of measuring the stress controlled flow curve for suspensions of varying concentration. For each of these measurements, we use BSM to determine the local stresses. The average viscosity, as determined by the rheometer as a function of applied stress for varying concentrations is shown in Figure 2b. At the lowest volume fraction $\phi = 0.3$, where $\phi = \frac{N_p}{v_{total}} v_p$ is the number density times the single particle volume, the viscosity is slightly enhanced above the solvent, but the curve is flat for all stress. For intermediate values, $0.3 < \phi < 0.5$ the flow curves exhibit behavior typical for solid particle suspensions, modest shear thinning followed by CST indicated by a shear thickening exponent $\eta \sim \sigma^\beta$, where $\beta < 1.0$. At larger values of the applied shear stress, and for higher values of ϕ, the shear thickening exponent can approach the limiting value of $\beta = 1$ indicating DST. In the shear thickening regime, we observe the appearance of localized surface deformations that are much higher than the average displacement. Figure 2c shows an example of the spatial map of the component of the boundary stress in the velocity (flow) direction calculated from the measured displacement fields. The deformations of the elastic substrate arise from the stresses exerted by the suspension at the boundary, $\bar{\sigma}_b \cdot \hat{n}$, where $\bar{\sigma}_b$ is the suspension stress tensor evaluated at the boundary with the substrate, and $\hat{n}$ is the normal to the boundary surface. In the figure and in what follows, we report the component of the boundary stress in the velocity direction. The field of view is 890×890 μm^2 and the regions of high stresses are large compared to the particle size. Moreover, the total area imaged represents 0.16% of the total surface area of the system, indicating that the spatial scale of the stress variation is much smaller than the scale of the lateral system size (25 mm). The regions of high stress at the boundary appear with increasing frequency as the applied stress is increased, as can be clearly seen in a time series of the average stress in each image (Fig. 2d). At the start of the shear thickening region (top curve), most images do not exhibit high stress regions, and thus have a small average stress. High stress fluctuations are clearly separated from the smooth background and appear intermittently separated by large quiescent periods. As the applied stress is increased (successive curves offset vertically), the high stress events do not get substantially larger (in terms of total stress), but occur much more frequently. Thus these high-stress regions represent a larger fraction of the total surface area, and quantitative analysis showed that this increase accounts for the observed shear thickening [5].

We found that the high stress regions appear and evolve stochastically, with an overall average translation in the velocity (flow) direction. The average size of the regions, assessed from 2-D spatial correlations analyses, indicated that the spatial extent of the high stress regions in the velocity direction is determined by the rheometer gap). The average motion of the high stress regions, quantified by spatiotemporal cross-correlations analyses, show propagation in the velocity direction that scales with the shear rate, and is consistently equal to half the velocity of the upper boundary, which is the velocity of the suspension at the middle of the gap, assuming a symmetric shear profile. These results suggest that the high boundary stresses reflect high viscosity fluid phases that span the gap of the rheometer, sheared equally from above and below and at rest in a frame co-moving with the center of mass of the suspension. The high viscosity phases are transient, but live for times long compared with the inverse of the shear rate , so the thickened clusters stays intact despite substantial flow of particles into and out of the region. Quantitative analysis of the stress patterns further revealed that the apparent viscosity of the high viscosity phase is nearly independent of shear rate but increases rapidly with concentration.

In summary, our initial results demonstrated that: (a) CST is associated with intermittent, localized high stresses at the suspension boundary, (b) the characteristic size of the high stress regions (in the flow direction) is much larger than the particle size and appears to be set by the gap between the rheometer plates, (c) on average, the large boundary stresses propagate in the flow direction with a speed equal to the speed of the suspension halfway between the top and bottom boundaries, (d) the high stresses at the boundary are consistent with a high viscosity fluid phase that spans the rheometer gap and has an approximately constant shear rate and a roughly Newtonian viscosity that increases rapidly with concentration, and (e) the dramatic shear thickening observed in the macroscopic rheology arises from an increasing fraction of the suspension existing in the high viscosity phase[5].

Connections with industrial partners and IFPRI members: Industrial processing of High Solids Content Dispersions (HSCDs) must consider the physical aspects of both colloidal and granular phenomenon. HSCDs consists of particles suspended in fluids at high solids loading and are often processed and transported at extreme shear rates to enhance the transport efficiency. Of course, as one might expect, shear thickening transitions can lead to deleterious effects such as abrupt changes in the flow rate and shear stress. Additionally, somewhat less well understood processes may be simultaneously occurring at the particle scale, potentially leading to the physical breakdown of individual particles. Understanding the impact of high flow rates and the resulting particle-level fluctuations in stress should provide insights into how shear flows alter the physicochemical aspects of the particle surfaces. Enhanced local stresses like we observe in our BSM measurements should impact any materials that are chemically bound to suspended solids while also creating microscopic fractures resulting in the removal of asperities or even the wholesale breakup of individual particles. The production of so-called "fines" may provide a tell-tale sign that local stresses, through contact forces may impact the overall integrity of the HSCDs have a dramatic impact on the final state of transported solids. With this in mind, we will explore the cases of particles with high surface roughness and surface asperities using BSM. We will look to IFPRI partners for guidance, and perhaps even materials, to guide our work.

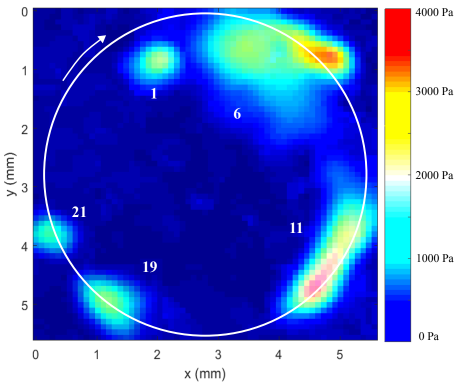


Figure 3: Superposition of stress maps obtained from the 5 mm diameter tool. The frame number associated with each distinct location of the high stress region is indicated by the associated numerals. The images were produced at 7 frames per second, so the lifetime of this event was $\sim 21/3 = 3$ seconds. The solid line indicates the extent of the tool. The field of view, 5x5 mm, is substantially larger than Fig. 2 ($\phi = 0.52$, 1.5 micron diameter rough particles).

Outline of Proposed Work During the initial three year time window, we will quantify the impact of shear flow on the properties of HSCDs. We will utilize a combination of confocal-rheology boundary stress microscopy, and light scattering and other imaging techniques to quantify the impact of CST and DST on two specific properties of interest within ideal and non-ideal particle systems. *i*) We will explore the lifetime of shear thickening clusters through a temporal analysis of local stress heterogeneities measured with BSM. *ii*) We will quantify the impact that the nonlinear increases in viscosity, both in CST and DST has on the stability and fidelity of particles surfaces through an post-shear analysis of particle size distributions.

Variation of particle surface friction and morphology – It is clear that shear thickening occurs in highly polydisperse repulsive particles with surface structures and asperities with a variety of length-scales from the nanometer to the micrometer range. Our recent work has focused on idealized spherical colloids in the size range of 1.0-1.5 micron in diameter to simplify the picture and to establish a baseline study to describe the physical mechanisms. However, the applicability of idealized scenarios may be limited. Moreover, the existence of surface structures may lead to additional factors, at the particle scale, when stress localization in thickening clusters dramatically exceed the applied stress (see Figure 2c).Therefore, we will utilize three different particle systems that represent ideal to non-ideal conditions for each of our proposed experiments. "Ideal" micron-scale silica spherical particles of varying surface roughness will provide a basis for understanding the impact of nanometer scale surface asperities on the onset of shear thickening, providing insights into the role of inter-particle friction. We will also synthesize non-spherical particles using modifications to the protocols found in Ref.[7] to make sphere-like particles that have a "snowman" shape. We will also used a combination of fumed particles and finely milled cornstarch particles[8]. The last two particle choices will provide us particles with surface aperities that could potentially fracture during thickening events.

Quantifying high stress cluster lifetimes – Our picture of continuous increase in viscosity when suspensions are sheared above a critical stress states that an increasing number of localized and discontinuous events are responsible for the increase in viscosity. However, the exact nature of the temporal evolution of these clusters of the high viscosity phase is currently unexplored due to the small size of our region of interest. We were able to quantify how the average surface coverage of the phase increases as a function of concentration and applied shear stress, and showed that this increase accounts for the macroscopic viscosity increase. What remains a mystery is the origin is how the increased number of events connects to either the increased nucleation rate or if there is an increased lifetime, or some combination of the two. Here we propose studies that will enable us to directly measure the determining factors, providing critical constraints on models to describe the dynamics of the underlying instability while also quantifying the role of surface roughness and shape have on determining the lifetime of the thickened portion of the system.

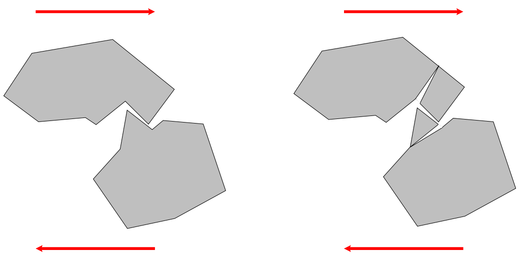


Figure 4: Schematic of the expected influence of high local stresses on the integrity of particle with non-idealized shapes. Left if solid particles with large surface asperities are within thickening clusters, they may experience local stresses orders of magnitude higher than the applied stress and may result in the breakup of the particles.

In order to image the entire system, we have extended our measurements to lower magnification, using a 1.6X objective and 10 micron fiduciary beads. This provides a field of view approximately 5.5 mm on a side, which is still too small to cover the entire domain of the smallest tools avail able from the manufacturer. Thus we have machined a custom rheometer tool with a 5 mm diameter flat surface, so the entire sheared region can be imaged simultaneously. We have confirmed that neither the modified rheometer tool nor the larger fiduciary beads significantly alters the bulk rheology.
Figure 3 shows a superposition of images of a high stress region obtained in this configuration. The numerals adjacent to each cluster indicate the frame number from which that image was taken. The birth, migration, and demise of the high stress region can be clearly resolved. In th is regime (where a relatively small fraction of the surface has high stresses), image segmentation to track the evolution of the high viscosity phases will be relatively straightforward, allowing a direct measurement of the nucleation rate and distribution of lifetimes of the high viscosity phase. We will measure these quantities as a function of applied stress, suspension concentration, and particle morphology in order to determine the role each quantity plays in the changes in surface coverage [5]. We will apply this technique to our various particle types, we will use this method to understand the role that particle roughness and shape have on the temporal evolution of thickened regions which will provide a way to understand how particle details impact the route to thickening.

Impact of thickening on particle integrity – One of the most important aspects of connecting shear thickening behavior to the stability and processability of suspensions at high solids fraction is understanding the effect that inter-particle contacts have on the integrity of the particles; a quantity that has largely not been quantified during the processing of dispersions. Until very recently, surface interactions were considered to be only important at granular length-scales, but our recent work and that of others indicates that contact forces, and therefore dilatancy are very important at colloidal scales[9, 10, 11, 12]. Taken together, contacts, clustering, and high localized shear stresses could result in stresses large enough to either destabilize particles or perhaps lead to an unexpected *milling* of the particles, where fines are produced through fracturing even at lower shear rates that would normally found in commercial milling systems (see Fig.4).

Using particles with anisotropic morphologies that we produce through synthesis and purchase commercially, we will explore the impact of CST and DST on the morphology of particles within HSCDs. First, we will quantify the magnitude of the inter-particle stresses by relating the magnitude of the cluster boundary stresses to the number of particles participating within the high stress cluster. Throughout the range of shear thickening, we expect large local stresses within clustered regions. Therefore, we anticipate that high local stresses will exist for all concentrations that exhibit thickening. We will systematically quantify the effect of thickening on the particle morphology by removing and processing the HSCD from the rheometer after a fixed amount of time spent above the critical stress for various solids fraction. Using centrifugation and filtration techniques we will isolate the initial solids from the expected fines. The "filtrate" will then be quantified using light scattering, SEM, and optical microscopy. We anticipate that if the particles are brittle enough, the fractures may go beyond simply rounding the edges at contact points, but may even fracture individual particles. Therefore, we will also compare size distributions and polidispersity indices for suspensions before and after shear.

Y1. We will investigate the flow behavior of suspensions of varying surface friction using BSM to quantify the role that surface interaction play in the nonlinear rheology of HSCDs. While also starting our synthesis methods leading into Y2.

Y2. We will perfect and utilize our synthesis techniques, while requesting feedback from Industrial partners in particles that may be interesting to supplement the ones we are planning to study. In this year of work we plan to begin systematically investigating the influence of CST on the morphology of particles.

Y3. In the final year of support we will synthesize our efforts and apply BSM to non-ideal particle types that are even higher stresses by working in the limit of DST.

References

[1] N. J. Wagner and J. F. Brady. "Shear thickening in colloidal dispersions." *Physics Today* 62, 27–32 (2009).

[2] M. Wyart and M. E. Cates. "Discontinuous shear thickening without inertia in dense non-brownian suspensions." *Phys. Rev. Lett.* 112, 098302 (2014). URL `https://link.aps.org/doi/10.1103/PhysRevLett.112.098302`.

[3] E. Brown and H. M. Jaeger. "Shear thickening in concentrated suspensions: phenomenology, mechanisms and relations to jamming." *Reports on Progress in Physics* 77, 046602 (2014).

[4] R. W. Style, R. Boltyanskiy, G. K. German, C. Hyland, C. W. MacMinn, A. F. Mertz, L. A. Wilen, Y. Xu, and E. R. Dufresne. "Traction force microscopy in physics and biology." *Soft Matter* 10, 4047 (2014).

[5] V. Rathee, D. L. Blair, and J. S. Urbach. "Localized stress fluctuations drive shear thickening in dense suspensions." *Proc. Natl. Acad. Sci. U.S.A.* 114, 8740–8745 (2017).

[6] J. R. Royer, D. L. Blair, and S. D. Hudson. "Rheological signature of frictional interactions in shear thickening suspensions." *Physical Review Letters* 116, 188301 (2016).

[7] P. Datskos and J. Sharma. "Synthesis of segmented silica rods by regulation of the growth temperature." *Angew Chem Int Ed Engl* 53, 451–4 (2014). URL `https://www.ncbi.nlm.nih.gov/pubmed/24272918`.

[8] M. Hermes, B. M. Guy, W. C. Poon, G. Poy, M. E. Cates, and M. Wyart. "Unsteady flow and particle migration in dense, non-Brownian suspensions." *Journal of Rheology* 60, 905–916 (2016).

[9] N. Y. Lin, M. Bierbaum, P. Schall, J. P. Sethna, and I. Cohen. "Measuring nonlinear stresses generated by defects in 3D colloidal crystals." *Nature Materials* 15, 1172–1176 (2016).

[10] C. Ness, Z. Xing, and E. Eiser. "Oscillatory rheology of dense, athermal suspensions of nearly hard spheres below the jamming point." *Soft Matter* 13, 3664–3674 (2017).

[11] C. Clavaud, A. Bérut, B. Metzger, and Y. Forterre. "Revealing the frictional transition in shear-thickening suspensions." 114, 5147–5152 (2017).

[12] J. Comtet, G. Chatté, A. Niguès, L. Bocquet, A. Siria, and A. Colin. "Pairwise frictional profile between particles determines discontinuous shear thickening transition in non-colloidal suspensions." *Nature Communications* 8, 15633 (2017).

IFPRI Project proposal: Erin Koos

1. State of the art

Suspensions can exhibit a wide range of rheological behaviors such as shear thinning, shear thickening, and normal stress differences. These behaviors are closely linked, not necessarily to the bulk particle structure, but more to the microstructure and direct particle contacts. For instance, discontinuous shear thickening (DST) is closely linked to friction, and hence on the number of number of particle contacts. In their numerical study, Mari et al. showed a link between the fraction of frictional contacts and the shear stress [1]. This fraction of frictional contacts, defined as the number of contacts where the normal force exceeds the critical load for the onset of friction in their model divided by the total number of particle contacts, was independent of volume fraction.

Confocal microscopy allows us to image model suspensions to gain information about their microstructure [2–4]. Recently, we have used this method to determine the structure of suspensions with attractive capillary interactions [5, 6]. Confocal microscopy is a powerful tool that can be used to study the link between the network microstructure and the rheological response of the material. Typically, the structure is analyzed using the local volume fraction ϕ_{local} or coordination number z [7, 8]. We propose using an additional parameter c, the clustering coefficient. The clustering coefficient is a measure, taken from graph theory, describing the clique-ishness of a network. The difference between the coordination number and the clustering coefficient is shown in Figure 1. In this figure, the center two configurations both have a coordination number of 3. In the case were the particles are distributed around the particle, the bonds are able to rotate as shown by a low clustering coefficient ($c = 0$). The case where the particles form close-packed dimers will be much more rigid and the clustering coefficient is closer to unity ($c = 2/3$).

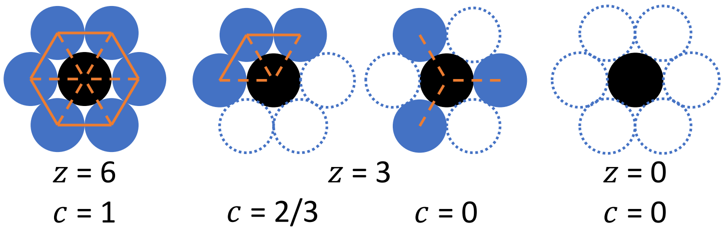


Figure 1: Difference between the coordination number z, the number of bonds per particle (dashed lines), and the clustering coefficient c. The clustering coefficient is defined as $c = \frac{2e}{z(z-1)}$, where the number of bonds between neighbors (solid lines) is e.

We have applied this concept to networks with capillary interactions (Figure 2). A slice of the confocal image is shown on the left in this figure. As the solid phase, we used monomodal silica spheres with a mean particle size of $d_{50,3} = 6.40 \pm 0.02$ µm and a polydispersity of $(d_{90,3} - d_{10,3})/d_{50,3} = 0.697 \pm 0.005$. The nanoporous particles were fluorescently dyed with rhodamine B isothyocyanate and are shown in red in this image. The secondary fluid, aqueous glycerine is dyed using PromoFluor-488 premium carboxylic acid and shown in yellow in this image. The oil, a mixture of 1,2-cyclohexane dicarboxylic acid diisononyl ester (Hexamoll DINCH) and n-dodecane, is undyed. The three components are all index matched and the silica contact angle modified (see [5] for more information). The computationally reconstructed body for this network is shown on the right where the particles are colored using their individual clustering coefficient. To determine the particle positions and sizes, the computational code of Weeks [9] (based on the method of Crocker and Grier [10]) was used where multiple mask sizes were employed to account for the polydispersity in the particle diameters. Particle contacts were determined using a separation threshold.

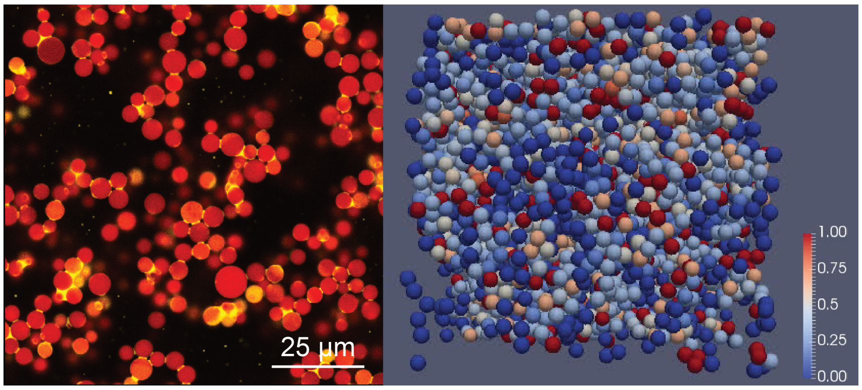


Figure 2: (left) Confocal image and (right) reconstructed body colored by the clustering coefficient for each particle. This solid-liquid-liquid system has $\phi_{\text{solid}} = 0.25$ and $\phi_{\text{sec}}/\phi_{\text{solid}} = 0.09$.

The average coordination number and clustering coefficient compare well with transitions observed in the rheology of these capillary networks as shown in Figure 3. The transition from a granular pile to a pendular network corresponds to a drop in both z and c as a loose sample-spanning network is formed. (There is no rheological data for $\phi_{\text{sec}}/\phi_{\text{solid}} = 0$ as phase separation prevented these measurements.) The transition from a pendular network, where particles are connected by binary bridges, to the funicular state, where larger clusters are formed, occurs at $\phi_{\text{sec}}/\phi_{\text{solid}} = 0.09$ (case shown in Figure 2), which corresponds to a peak in the coordination number and beginning of a plateau in clustering coefficient. While not shown here, the distribution of clustering coefficients in the system changes from a monomodal to bimodal distribution.

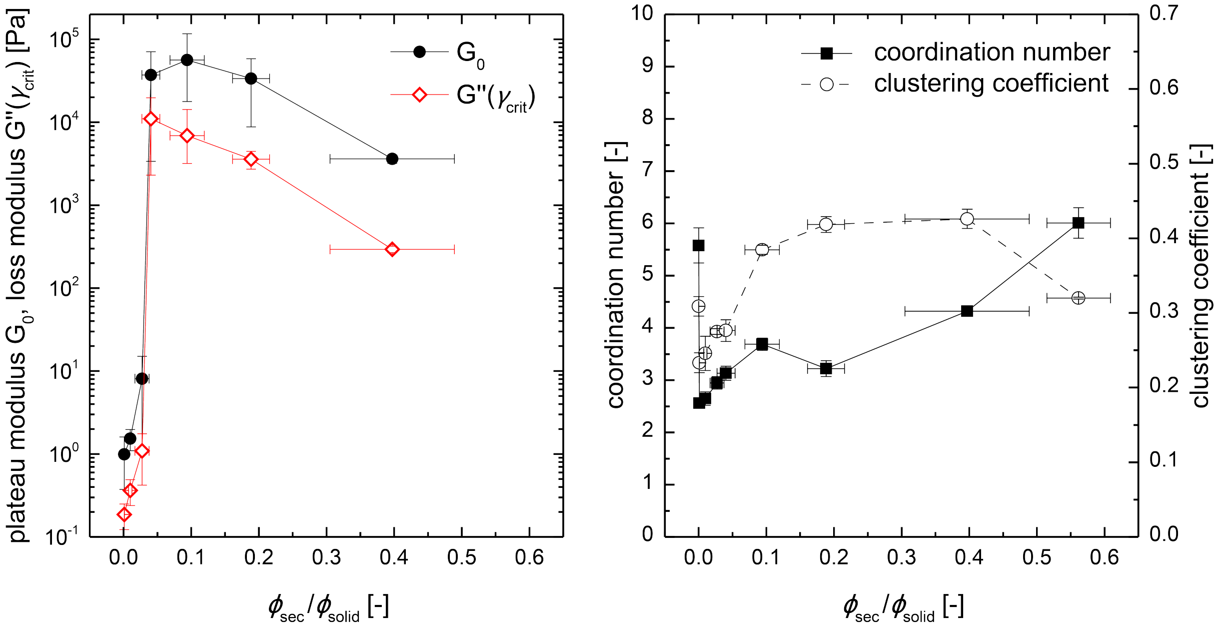


Figure 3: (left) Plateau modulus G_0 and loss modulus G'' at the critical oscillatory amplitude γ_{crit}. (right) Mean coordination number and clustering coefficient computed from confocal imaging. The rheological properties at $\phi_{\text{sec}}/\phi_{\text{solid}} = 0$ (granular bed) and $\phi_{\text{sec}}/\phi_{\text{solid}} = 0.56$ (inside a dense floc) were not measured as phase separation occurred in these systems.

This method can be used to investigate several phenomena in granular systems. One particularly promising area is in understanding yield. Yield occurs on a plane with some critical number of defects or where key rearrangements are possible. As these materials are disordered, this is a statistical process. A better understanding of the specific microstructure around yielding plane. These particle contacts are equally important in situations where chains of particles lead to a dramatic increase in the shear stress or even the stoppage of flow.

2. Proposed work

2.1. General methodology

The general methodology can be described as follows:

1. Samples for confocal microscopy will be created using an index matched system of SiO_2 in a suitable oil (Hexamoll DINCH, BASF) or aqueous glycerol. The particle surface chemistry can be controlled to create attractive or repulsive interactions. Irregularly shaped particles can be created using a Stöber silica growth around appropriate seed particles.
2. The micro-and network structure will be imaged using confocal microscopy and analyzed using a custom-designed IDL code. This code determines the particle positions and their size (for polydisperse particles) as well as the size and location of the secondary fluid. From this information, various parameters can be calculated.
3. The particle positions and microstructure will be monitored during shear using a thermo-shear cell that fits on top of the confocal microscope. This shear cell applies a linear shear profile using the deformation of microscope slides. The structure can be either monitored continuously during shear (if the continuous shear profile is sufficiently slow) or using a step profile.
4. The bulk rheological properties of the materials will be measured under steady and oscillatory shear. In addition to the shear stress, the first normal stress differences will be measured.

2.2. Specific work packages

WP1: Particle tracking under shear

Using the custom IDL code and the thermo-shear cell, we can track the particle positions and interactions under step or oscillatory shear profiles. Of particular interest is the development of the coordination and clustering coefficient during shear. We hypothesize that particles clusters with a high clustering coefficient undergo rigid-body motion and should be associated with frictional shear thickening. By tracking the individual particle deformation and that of the neighboring particles, we can correlate this motion to the local clustering. We will begin using a very slow, step shear profile to test and optimize the particle tracking. We will then investigate profiles with a larger shear step. As the tracking of individual particles may be difficult at large steps, we may employ a small proportion of tracer particles with a fluorescein isothiocyanate (FITC) dye and track their dynamics. Using the microscope, we can look at the number and type of particle collisions and bonds at yield, during shear thickening, and also between the different layers in the shear banding system.

These shear profiles will be repeated on the rheometer so that the force measurements can be compared to the changes in microstructure. These rheometer tests can also be used to highlight interesting regions for the confocal study. The thermo-shear cell uses piezoelectric actuators to create a smooth shear profile, which means that the force data cannot be independently measured. We might be able to use the applied voltage to monitor changes to the force, but this cannot be used to make reliable rheometric measurements. Thus, we must rely on correlations between the two devices.

WP2: Particle size distribution and particle shape

The particle size distribution influences both the packing of particles and the resultant rheological properties. We will first investigate systems with mixtures of large and small particles. The relative fractions and size ratios will be varied. Such mixtures are associated with a decrease in the effective viscosity at intermediate fractions of small spheres, with the degree of reduction depending on the relative size ratio of the spheres. With our method, we can investigate the local packing around both sphere sizes individually as well as the influence on the direct local deformation of the system.

We will then investigate a unimodal particle size distribution having wider and narrower size ranges. A narrow distribution is particularly interesting as it can be associated with a very high degree of local ordering or crystallization. Such ordering is interesting as yielding typically occurs at regions with low local order. As with bimodal distributions, wider particle distributions change the effective packing and the effective viscosity of these systems.

Finally, we will also modify the particle shape using Stöber silica shells grown on seed particles. This method has been effectively been employed to create ellipsoidal particles. The current IDL code (and the Week's algorithm) uses a cross correlation between the particle and a mask. The use of ellipsoids introduces an orientation as well as size parameter to this mask. Therefore, the IDL code will have to be modified appropriately.

WP3: Modification of particle interactions

By modifying the surface chemistry of the particles and using an adsorbing polymer, we can introduce attractive or repulsive particle interactions. These interactions modify the effective size and softness of the particles as well as the importance of frictional collisional interactions in the shear dynamics. Such repulsive interactions have been shown to reduce or even prevent shear thickening whereas attraction between the particles acerbate this problem. We can also roughen the particles to further increase the coefficient of friction between the particle pairs.

We must be careful in conducting experiments with repulsive systems, however. A very thin layer of fluid, below the optical resolution of the microscope, may separate the particles. This fluid layer complicates the calculation of particle bonds. Thus, we will probably need to look at the motion of neighboring particles to determine bonds. Therefore, we will begin with increasingly rough particles and then weak repulsive interactions.

2.3. Gantt chart

This research is divided into four work packages. The first three quarters will consist of improving the IDL code and tracking the particles under shear. This code will have to be improved for each subsequent work package. The other two work packages investigate particle size distribution and particle interactions. These will be investigated individually and then in combination.

	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q7	Q8	Q9	Q10	Q11	Q12
WP1	▨	▨	▨	▨	▨			▨		▨	▨		
WP2					▨	▨	▨	▨	▨			▨	▨
WP3										▨	▨	▨	▨

3. Leverage opportunities

3.1. Existing research programs

I have already started to investigate the structure of capillary suspensions using these confocal microscopy techniques. Thus, the developments we make within this proposal can benefit from and contribute to these efforts. Our initial study (highlighted above) shows that the microstructure can be used to predict the bulk rheological data under quiescent conditions. Naturally, we would like to adapt this method to monitor dynamic changes to the network, especially during yielding. The advanced made in this program, in combination with the work with capillary suspensions, also lends itself to a future expansion in the dynamics of wet granular media.

In addition, I have a doctoral student who recently started to model capillary suspensions using the coarse-grained MD code ESPResSo. He will determine the structure of these networks and to make pseudo-rheology experiments under various conditions. This student has experience in analyzing the particle networks once the particle positions and sizes are determined. In addition, we can use the confocal experimental results as the initial conditions for the MD model. The rheological results made in this project will improve the force-interaction curves in his model and give us more insight into the direct influence of the particle interactions on the resultant behavior, especially as such particle interactions can be selectively altered computationally.

3.2. Collaboration within IFPRI

The industrial expertise of the IFPRI members will be invaluable in identifying areas of specific interest for this project. This research should be a platform that we can use to gain a clear understand the dynamics on a limited scale. Thus, the problems and test methods should be used as a starting point in this project. We can then identify the specific microstructural changes occurring during these tests or under these specific conditions. By highlighting the microstructural changes, especially in relation to the particle interactions, we can have a positive feedback loop with industry to suggest minor changes and tackle increasingly more complex problems.

While this research project concentrates on the use of model systems due to the limitations of confocal microscopy, we should push towards making experiments on real systems. Assistance in bridging this gap using more ideal, industrial materials would be appreciated. Coating seed particles with silica can be used as one such method. This can even be used to create irregular particles that still have the necessary index of refraction for confocal microscopy. We aim to start with ellipsoidal particles (one axis of orientation), but angular and irregular particles are the natural end goal.

4. References

1. Mari, R., Seto, R., Morris, J. F., Denn, M. M. (2014). Shear thickening, frictionless and frictional rheologies in non-Brownian suspensions. *Journal of Rheology*, *58* (6), 1693–1724.
2. Cheng, X., McCoy, J. H., Israelachvili, J. N., Cohen, I. (2011). Imaging the Microscopic Structure of Shear Thinning and Thickening Colloidal Suspensions. *Science*, *333* (6047), 1276–1279.
3. Dinsmore, A D., Weitz, D. A. (2002). Direct imaging of three-dimensional structure and topology of colloidal gels. *Journal of Physics: Condensed Matter*, *14* (33), 7581–7597.
4. Dinsmore, A. D., Prasad, V., Wong, I. Y., Weitz, D. A. (2006). Microscopic structure and elasticity of weakly aggregated colloidal gels. *Physical Review Letters*, *96* (18), 185502.
5. Bossler, F., Koos, E. (2016). Structure of Particle Networks in Capillary Suspensions with Wetting and Nonwetting Fluids. *Langmuir*, *32* (6), 1489–1501.
6. Bossler, F., Maurath, J., Dyhr, K., Willenbacher, N., Koos, E. (2018). Fractal approaches to characterize structure of capillary suspensions using rheology and confocal microscopy. *Journal of Rheology*, *62* (1), 183.
7. Aarons, L., Sundaresan, S. (2006). Shear flow of assemblies of cohesive and non-cohesive granular materials. *Powder Technology*, *169* (1), 10–21.
8. Wenzl, J. (2013). *Wet and dry model granulates under mechanical load A confocal microscopy study*. PhD Thesis, Johannes-Gutenberg-Unversität, Mainz.
9. Weeks, E. R., Crocker, J. C., Levitt, A. C., Schofield A. B., Weitz, D. A. (2000). Three-Dimensional Direct Imaging of Structural Relaxation Near the Colloidal Glass Transition. *Science*, *287* (5453), 627–631.
10. Crocker, J. C., Grier, D. G. (1996). Methods of Digital Video Microscopy for Colloidal Studies. *Journal of Colloid and Interface Science*, *179* (179), 298–310.
11. Lee, M. H., Furst, E. M. (2008). Response of a colloidal gel to a microscopic oscillatory strain. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, *77* (4), 41408.