IFPRI

International Fine Particle
Research Institute

Research Project Brief

Aeration and Deaeration of Geldart Type C Powders

The International Fine Particle Research Institute (IFPRI) wishes to fund a research project on aeration and deaeration of Geldart Type C powders that occurs in bulk handling operations such as packaging. Controlled fluidization (i.e., fluidized bed operation or pneumatic conveying) is out of scope of this project.

Geldart Type C powders – fine and cohesive – exhibit unpredictable packaging behavior, for example highly variable packing rates and densities. This is especially true at large-scale production rates, > 100 kg/hour. Different powders behave qualitatively and quantitatively differently, and it is difficult to characterize them in a way that is predictive of their aeration and deaeration behavior. This project should focus on this problem: development of reliable characterization methods for Group C powders that enable prediction of packaging behavior (rate, density, variability) when the material is aerated during handling processes. The work should investigate the effects of single particle properties and particle interactions such as size distribution, surface roughness, particle cohesivity, and electrostatics. Ideally, the proposal should include a representative validation system.

In the packaging operations of interest, the powder is loaded into (semi) bulk containers (flexible or hard walled), 5-20 kg bags, or 1–4-liter bottles. Dosing into small packages (die filling, encapsulation) is out of scope, as this is the subject of other IFPRI projects. Uncontrolled aeration takes place during flow into the package, for example gravity flow in a chute or in a high-speed screw conveyer. Deaeration in the package is time-dependent and often is influenced by compaction (due to the weight of powder in a package or by stacking of multiple packages). Vibration is sometimes used to increase bulk density.

IFPRI
Research Project Brief
Aeration and Deaeration of Geldart Type C powders

Controlling Adhesion between Particles for a better understanding of Compaction and Aeration of Powders.

CAPCAP

- **Principal investigator (PI):** Olivier Pouliquen
- **Host institution:** Aix Marseille University-CNRS, France
- **Proposal duration:** 36 months

To address the problem of powder packaging raised by the IFPRI research program, we propose a fundamental approach consisting in using model materials, for which the inter-particle adhesion can be precisely controlled. We believe that being able to tune the cohesion at will is a necessary condition to develop a fundamental understanding of the flow of cohesive materials and powders. In our group we have recently developed a technics to coat silica particles with polymers and we are able by controlling the coating thickness to continuously varies the cohesion properties, and goes from a cohesionless to a highly cohesive medium. We are also planning to collaborate with chemists able to synthetize polymer particles with tailored surface properties. The proposed project consists in using these materials to investigate the packaging process. We will first study the rheology of model materials, before analysing a simplified version of a packaging process. We should be able to investigate the role of cohesion and of the rheology of the material in the different steps of the process, from the flow in the hopper to the formation of the deposit, looking also at the stability of the final packing to tap perturbations.

A. General context and state of art

Powders are omnipresent in many industrial processes but predicting their behavior still represents a challenge (Schulze 2008). Whereas the description of coarse granular media has notably progressed during the last 20 Years (Andreotti et al. 2013), our understanding of the physical mechanisms involved during powder flow remains sparse, which represents a real challenge both for engineers designing new industrial processes and for physicists seeking for a unified framework to predict particulate flows. The difficulty comes from the presence of adhesion forces between the grains at the origin of problems of clogging, flow heterogeneities, agglomeration, intermittent flows encountered during the storage, the transportation, the processing of the material. No unified framework exists that can predict and describe the rich variety of behaviors observed with powders, and industry relies on empirical characterization to measure the so-called "flowability", the ability of powders to flow (Castellanos 2005; Tay et al. 2016). This concept that lacks solid physical bases, consists in estimating different properties (compaction, heap angles . . .) mostly related to static properties. Recently, powder rheometers have been developed based on the measurement of the torque experienced by a helix rotating in the powder (Hare et al. 2015). All these measurements are of crucial importance in many industrial processes, but do not not have a predictive power, and no framework is nowadays relevant to describe and capture the complex properties of cohesive granular media. Understanding the concept of ”flowability” from a physical point of view is still a challenge.

The challenge posed by IFPRI in this call concerns the aeration and deaeration of fine particles encountered when handling powders and particularly during the filling and packaging process (Rathbone et al. 1987). The control and the reproducibility of the filling process pose major problems such as intermittent flow rates, air trapping, intempestive recompaction of the material during manipulation. Despite the apparent simplicity of the configuration of filling a bag with powders, the process involves different physical phenomena, from the rheology of powders to two-phase flow when the interaction between the powder and the air is important. To improve our fundamental understanding of the mechanics controlling the packaging processes, I think three main questions need to be addressed: the role of particle properties and of the rheology of the powder, the role of the feeding process, and the role of air.

The rheology of powder flows

The first and perhaps most important question concerns the role of the grain properties on the flow characteristics and in particular understanding the crucial role of the adhesion forces. Characterising the rheology of powders and its links to the grain properties is to my opinion a necessary step to progress in our understanding of the aeration problem. We need a detailed knowledge of the powders rheology in the regime encountered during packaging, which is a regime where the material is dense but flow rapidly under low level of stress, typically its own weight. This is a regime not captured by the classical characterisation of quasi-static properties of powders as measured in a Schulze’s shear cell, and there is a need for a controlled and relevant rheological protocol to characterize the "fluid regime". This question is currently motivating numbers of fundamental studies in the granular community (Vo et al. 2020). In absence of adhesion between particles, i.e for dry granular material made of grains interacting through frictional contacts only, a lot of progresses have been achieved. A key property of these materials is that in the limit of rigid particles, no internal stress scale exists in the system. This dimensional argument fully constrains the constitutive relations, leading to the writing of a rheology in terms of a friction law, relating the shear stress to the pressure through a macroscopic friction coefficient function of a single dimensional number called the inertial number I (Jop et al. 2006). This approach and its tensorial extension predict flows in many configurations like silo, avalanches, drums,..and can be enriched to capture transient effects due to dilatancy. One would like to get the same level of description with powders. However, adding adhesion between the grains dramatically changes the problem, as it introduces a new internal force scale, which modifies the scaling laws.

Recent numerical studies based on DEM simulations have shown that in presence of adhesion, the same framework might be relevant, but that a new dimensionless parameter has to be taken into account in addition to the inertial number to describe the rheology (Rognon et al. 2008; Vo et al. 2020). This number called the cohesion number measures the relative importance of adhesion and confining forces. Numerically, we have recently shown in my group that the story is more complex, that other parameters like stiffness and dissipation play also a crucial role when adhesion is present (Mandal et al. 2020), and that the rheological laws are non monotonic, leading to shear banding (Mandal et al. 2021) and instabilities that may be crucial to understand the concept of "fluidity". These results open new ideas to try do describe from a continuum perspective the flow of powders, and any advance in this direction will help in better understand the dynamics observed in packaging processes.

The role of the feeding technics

The second question of importance in the packaging process concerns the influence of the mode of supply. One would like to understand how powders flow from a hopper, on a chute, from a screw, how the flow characteristics change when changing the powders properties, and how the final deposit obtained in the container depends on the way the powder has been transported. This challenge, which is about to be achieved for simple granular materials are still fully open for cohesive materials, and there is a real need for controlled experiments in simplified flow configurations. One of the main question would be to understand to which extend the heterogeneities observed in the final bag are related to heterogeneities developing during the flow. Looking at the different instabilities that may arise in the different flow configurations is a way to improve our understanding of the origin of the variability in packaging processes.

The role of Air

Finally, a last crucial point for the dynamics at high flow rates and using fine particles concerns the coupling with air. Air might be entrained during the flow, and get trap in the deposit. It may then affect the structure of the deposit, and also can be a source of strong instabilities during the manipulation of the filled container. If mechanical perturbations of vibration are imposed, for exemple during transportation, the packing initially in a very loose state might be destabilized, and dramatic phenomena, including sudden fluidisation and compaction, may occur. This phenomenon similar to the well-know liquefaction in soil mechanics, is not really studied in details for powders, and a challenge would be to understand the role of the cohesion in this transient fluidisation process.

Our approach

The ambition of the CapCap Project is to study a simplified version of a packaging process on model materials, for which cohesion is controlled. We believe that being able to tune the cohesion at will is a necessary condition to develop a fundamental understanding of the flow of cohesive materials. We just develop in our group a method to coat in a control manner particles with polymers, a promising way to tune at will the adhesion. Another promising approach that we would like to test, is to use polymer particles with tailored properties that have been recently synthetized for the study of the rheology of suspension. We these materials, we should be able to go from cohesionless particles to very cohesive material, and study how the rheology, the flow in a hopper and chute, and the resulting deposit in the bag varies with inter-particle adhesion.

B. Research Program

Ideally to understand the role particle interaction in the flow of cohesive materials, one would like to be able to experimentally tune the cohesion at will, in order to follow how the dynamics is modified when increasing gradually the inter-particle adhesion from the well known case of granular materials. Whereas in suspensions, playing with the chemical properties of the solvent is a way to change the

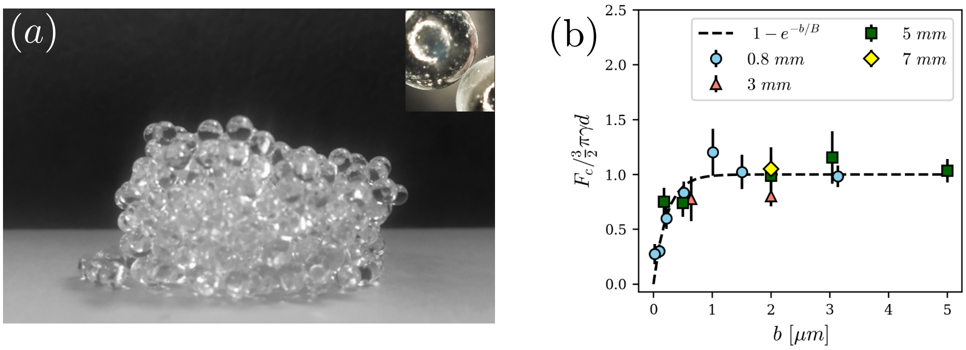


Figure 1: The model material: a) exemple of cluster formed by the coated particles b) rescaled interparticle adhesion force as a function of the averaged coating thickness.

interaction from repulsive to attractive (Van De Laar et al. 2016; Clavaud et al. 2017), for grains in air, the task is more difficult. Fundamental studies on cohesive granular media have then focused on mixture of grains and liquid, in which cohesion is controlled by the amount of liquid through the formation of capillary bridges (Scheel et al. 2008). However, capillary bridges appear to migrate during flows, leading to strong heterogeneities (Badetti et al. 2018). Humid sand is thus of interest per se, but does not represent a model material to understand powders. Working with real powders is also a challenge as they are very sensitive to environment (humidity, temperature) preventing a precise characterization of their rheology.

To circumvent this difficulty, we have recently developed in our group a simple method to introduce controlled adhesive forces between silica beads (Gans et al. 2020). The idea is inspired by the "kinetic sand", a toy for kids made of a mixture of sand and polymers which can be moulded and sculpted at will indefinitely. Our recipe is based on a mixture of PDMS, acid boric and water, mixed and heated with the particles during one hour. After cooking, the particles are coated with a layer of PolyBoroSiloxane (PBS), which makes them sticky (see Fig. 1a). The stickiness is stable, remains after many contacts, is present on every particle. The adhesion force is controlled by the thickness of the coating (see Fig. 1b). We have shown that this system is very stable in time, can be re-used with the same properties, making it an ideal material to study how adhesion may change the flowing properties of granular media, and thus a relevant model for powders. With this rather simple technics we are able to coat particles from 100μm to few millimetres. The research program proposes to use this new and unique model material to investigate how in the process of filling a container adhesion changes the dynamics and the deposit. Our hypothesis is that working with different particle sizes, we should be able to separate the role of adhesion and the role of air in the process. Using coarse but cohesive particles, we will investigate only the role of adhesion between the grains, without interaction with air, whereas working with 100μm particles, we should be able to study also the influence of air.

A second technics to control adhesion we have in mind relies on the recent progresses made by chemists regarding the synthesis of cross-linked polymer microparticles with tailored stiffness and attraction. We are starting a collaboration with the group of Pf. E. Drockenmuller in Lyon, who develops such particles (size between 10-1000μm) that have been used to study the rheology of suspensions (Moratille et al. 2022) but never in dry conditions. This alternative technics is very promising for precisely control particle interaction down to small particle size, however it is more difficult to create large quantities of particles.

Three main tasks are planned with the two model materials. First, the rheology will be analysed. Once the rheology characterized, we plan to study the flow in a simplified filling process consisting in emptying a silo in container. The aim is to understand how cohesion modifies the flow in the hopper, the heterogeneities at the exit, the formation and the structure of the resulting deposit. Finally the role of air will be studied in a second step using fine particles, with a focus on the stability of the packing

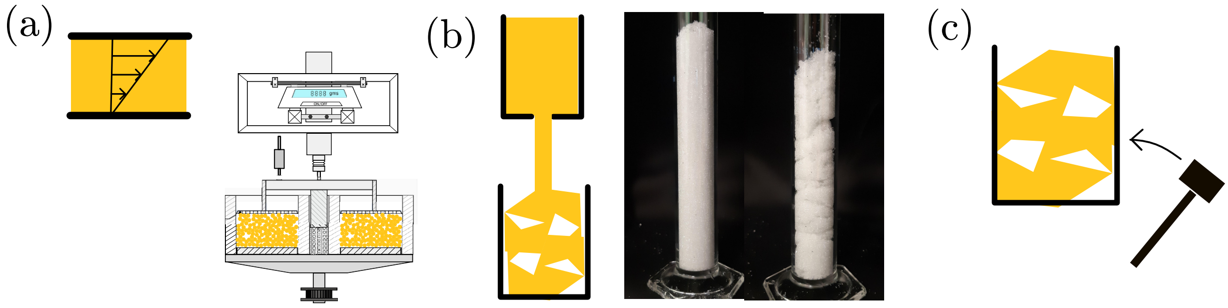


Figure 2: The three proposed tasks: a) Rheological characterisation of the model material; b) Studying a simplified feeling process (pictures show packings obtained for a low cohesion (left) and high cohesion(right) material; c) Compaction of a cohesive material.

submitted to tap perturbations.

Rheology of the model material

As a first task, we aim at characterizing the rheology of our model cohesive granular material. We will use the pressure imposed rheometer build in my group (Tapia et al. 2019) (Fig. 2a), where the grains are confined under a controlled pressure in an annular cell and sheared by a rotating top cover. The torque and position of the top plate provide accurate measurement for the shear stress and the volume fraction and thus a measure of the friction law and the volume fraction law. Our aim is to understand the role of the coating and how it changes the rheology under steady shear. The questions we would like to answer are : does adhesion induce a shear weakening branch in the friction law as observed in simulation (Mandal et al. 2021)? Can we put in evidence some scaling with adhesion as suggested in the literature (Vo et al. 2020) ? How transient flows starting from different controlled volume fraction are affected by adhesion and how it may affect dilatancy or compaction ? The results of the rheological study will serve as a base to analyse the flow characteristic in a filling process. In order to prevent the formation of shear bands and insure that we measure a bulk rheology, we will consider thin layer of material, of about 10 particle diameter. Our recent DEM simulation shows that under these conditions shear banding instability is stabilised, giving access to unstable shear weakening branches and to the "bulk" rheology.

Filling a container from a hopper

Once the rheology of the model cohesive material characterized, we plan to study the emptying of a silo in a container as sketched in Fig. 2b. The presence of cohesion is known to dramatically affect the flow in hopper, leading to channellisation and clogging (Schulze 2008). The ability to continuously modify the adhesion between the particles in our model material, gives us the opportunity to study and understand what controls the flow regime and when clogging appears. We will also carefully look at the heterogeneities that may appear at the exit of the hopper, to understand how cohesion affects the formation of clusters at the exit. Lastly we will study how the deposit is created from the flow. When preparing this proposal, we have conducted preliminary experiments to test the feasibility and check the interest of the proposed approach. Results of the filling of a tank is shown in Fig 2b for two different levels of cohesion. One clearly observes that the packing looks homogenous and dense when cohesion is low (left picture), whereas strong heterogeneities are observed at high level of cohesion (right picture), with the formation of clusters at the exit of the silo that keep their identity in the final deposit, trapping air. A detailed analyse of the formation of the deposit, of its structure (we have access in our university to an X-Ray microtomographe to measure the 3D structure of granular packing), of its stability during the feeling process should provide important information about the dynamics at work during the process and the role of cohesion. This analysis will be first conducted with coarse particles (typically 1mm), for which air play no role. This will informe us about the role of the adhesive inter particle forces in the final compaction of the packing. In a second step, we will use smaller particle of about 100μm for which the coating is still controlling the adhesion, but which are sensitive to the air drag during the filling. We hope to be able to disentangle the role of the air and the role of the cohesion in the aeration of the final packing. By varying independently the size and the adhesion of the particles, we hope to be able to identify the relevant dimensionless number controlling the process.

Compaction of a cohesive material

The last task we would like to investigate in a longer term is the coupling of the packing with air. In the limit of very cohesive materials, the packing resulting from the emptying of the hopper is very loose. A perturbation, a shock or a vibration might destabilize the deposit and compact it. During compaction, the trapped air escapes. If the particles are coarse, air flows easily through the pores and the dynamics of compaction is simply controlled by the inertia of the particles. When the grains are fine, the air flow induces additional stresses due to viscous drag, which fluidizes the powder. This phenomenon called liquefaction when the fluid is water has been intensively studied in soil mechanics community. We propose to try to understand the role of cohesion in the his transient fluidisation of powders, using our model material. Traina et al (Traina et al. 2013) have shown that tap experiments, which consists in imposing a sudden acceleration to the packing, is an interesting test to discriminate between different powders. With our new model material, playing with both the adhesion force between particles and the particle size, we should be able to disentangle the role of cohesion and the role of air in the compaction under tap, by performing controlled experiments measuring simultaneously compaction and evolution of the air pressure during the dynamics. The result will be analyzed in the framework of two phase flow continuum descriptions, in the spirit of what is done to describe soil liquefaction, the difficulty being to introduce the role of the cohesion in the particle phase.

C. Expected achievements

This experimental project focus on the understanding of the role of cohesion in the packaging process. We hope to be able to improve our physical understanding of the flowability of cohesive granular materials, to evidence how inter-particle adhesion influences flow in a hopper and the formation of heterogeneous structures during the filling procedure. This experimental project is part of a wider project in our group, with also numerical and theoretical approaches on the powder rheology, with the ultimate goal being to be able to propose relevant continuum description of the flow of powders.

D. Risks and critical unknowns

One of the main unknown of this research program is the use of new model granular materials. Our first studies have shown the potential to use PDMS coated particle for controlling cohesion, a key challenge to improve our understanding of cohesive granular media. However, the coating of the particles might introduce more complexity than expected, for example one risk being that it might introduce also lubrification effects. This will be checked in our rheological investigation. The possibility to investigate other ways of controlling particle properties in collaboration with chemists, based on the click chemistry technics allowing to graft almost any kind of molecules at the interface of polymer particles, is an opportunity.

E. The team

Our group in Marseille has a strong expertise in granular flows, suspensions and in the rheology of complex fluids. With Maxime Nicolas and Pascale Aussillous, both professors at Aix Marseille University, we started four years ago a long term program on cohesive granular materials, with the hope that the recent progress on dry granular flows we have achieved in the last decade will help us to tackle the much more difficult challenge of the rheology of powders. Beside the fact that we believe that our fundamental approach based on the design of a model material to control adhesion might provide useful information in the aeration problem raised in the IFPRI call, we are convinced that our research program would strongly benefit from the IFPRI Community. It would give us the opportunity to share our results with imminent colleagues working in the field, but also and more importantly would provide contacts and discussion with engineers from various industries and learn from their unique knowledge of the rich and complex behaviour of powders.

Bibliography

Andreotti, B., Y. Forterre, and O. Pouliquen (2013). *Granular media: between fluid and solid*. Cambridge University Press.

Badetti, M., A. Fall, D. Hautemayou, F. Chevoir, P. Aimedieu, S. Rodts, and J.-N. Roux (2018). “Rheology and microstructure of unsaturated wet granular materials: Experiments and simulations”. In: *Journal of rheology* 62.5, pp. 1175–1186.

Castellanos, A. (2005). “The relationship between attractive interparticle forces and bulk behaviour in dry and uncharged fine powders”. In: *Advances in physics* 54.4, pp. 263–376.

Clavaud, C., A. Bérut, B. Metzger, and Y. Forterre (2017). “Revealing the frictional transition in shear-thickening suspensions”. In: *Proceedings of the National Academy of Sciences* 114.20, pp. 5147–5152.

Gans, A., O. Pouliquen, and M. Nicolas (2020). “Cohesion-controlled granular material”. In: *Physical Review E* 101.3, p. 032904.

Hare, C., U. Zafar, M. Ghadiri, T. Freeman, J. Clayton, and M. Murtagh (2015). “Analysis of the dynamics of the FT4 powder rheometer”. In: *Powder Technology* 285, pp. 123–127.

Jop, P., Y. Forterre, and O. Pouliquen (2006). “A constitutive law for dense granular flows”. In: *Nature* 441.7094, pp. 727–730.

Mandal, S., M. Nicolas, and O. Pouliquen (2020). “Insights into the rheology of cohesive granular media”. In: *Proceedings of the National Academy of Sciences* 117.15, pp. 8366–8373.

– (2021). “Rheology of Cohesive Granular Media: Shear Banding, Hysteresis, and Nonlocal Effects”. In: *Physical Review X* 11.2, p. 021017.

Moratille, Y., M. Arshad, C. Cohen, A. Maali, E. Lemaire, N. Sintes-Zydowicz, and E. Drockenmuller (2022). “Cross-linked polymer microparticles with tunable surface properties by the combination of suspension free radical copolymerization and Click chemistry”. In: *Journal of Colloid and Interface Science* 607, pp. 1687–1698.

Rathbone, T., R. Nedderman, and J. Davidson (1987). “Aeration, deaeration, and flooding of fine particles”. In: *Chemical engineering science* 42.4, pp. 725–736.

Rognon, P., J. Roux, M. Naaim, and F. Chevoir (2008). “Dense flows of cohesive granular materials”. In: *Journal of Fluid Mechanics* 596, pp. 21–47.

Scheel, M., R. Seemann, M. Brinkmann, M. Di Michiel, A. Sheppard, B. Breidenbach, and S. Herminghaus (2008). “Morphological clues to wet granular pile stability”. In: *Nature Materials* 7.3, pp. 189–193.

Schulze, D. (2008). “Powders and bulk solids”. In: *Behaviour, characterization, storage and flow. Springer* 22.

Tapia, F., O. Pouliquen, and É. Guazzelli (2019). “Influence of surface roughness on the rheology of immersed and dry frictional spheres”. In: *Physical Review Fluids* 4.10, p. 104302.

Tay, J. Y. S., C. V. Liew, and P. W. S. Heng (2016). “Research Article Powder Flow Testing: Judicious Choice of Test Methods”. In: *AAPS PharmSciTech* 18.5, pp. 1–12.

Traina, K., R. Cloots, S. Bontempi, G. Lumay, N. Vandewalle, and F. Boschini (2013). “Flow abilities of powders and granular materials evidenced from dynamical tap density measurement”. In: *Powder technology* 235, pp. 842–852.

Van De Laar, T., R. Higler, K. Schroën, and J. Sprakel (2016). “Discontinuous nature of the repulsive-to-attractive colloidal glass transition”. In: *Scientific reports* 6.1, pp. 1–7.

Vo, T., S. Nezamabadi, P. Mutabaruka, J.-Y. Delenne, and F. Radjai (2020). “Additive rheology of complex granular flows”. In: *Nature Communications* 11.1, pp. 1–8.

Dear IFPRI Members,

Thank you for your comments about the CapCap proposal. Your question about the particle size and the role of air is very relevant. The point of view adopted in this study is that the aeration obtained during packaging processes result from both the cohesive nature of the powder and the coupling with air. The proposed strategy is to try to disentangle the two, by first studying how interparticle adhesion gives rise to very loose samples, even when the particles are coarse and the influence of air is negligible, before studying finer particles for which air is expected to play a role. We believe that the first step towards a better understanding of the behavior of powders is the control of the adhesion.
Please find the response to your detailed comments. The text has been modified accordingly.

Overall, the members are enthusiastic about your proposal, however they note that you really aren't proposing to study Geldart Group C particles, rather you are studying Group D. Your particles are too large for aeration and deaeration to be relevant.
While your plan to grapple explicitly with particle cohesion is welcome, the coupling of aeration and cohesion is a key element to the brief. You weren't specific about the particle size you'll investigate, but the implication that they are O(millimeters). It would be useful to clarify this point.

We now specify in the text that our method to coat particles and to control the adhesion works down to 100 micro particles. For this particle size, air flow starts to play a role during compaction or decompaction under earth gravity. For smaller particles, other adhesive forces become of the same order of magnitude as the one introduced by the coating, meaning that we no longer control the adhesive force. Our hope is that playing with both the particle size (from 100μm to 1mm) and the coating, we will be able to disentangle between the role of adhesion and the role of air in the control of the final compacity of the sample.
Moreover, since the writing of the first version of the proposal, we have been in contact with chemists from university of Lyon, who have developed new technics to synthetize polymer particles with tailored mechanical and surface properties. These particles have been recently used to investigate the role of particle interaction in suspensions but have never been tested in dry conditions. These particles can be synthetize in the range (10 to 500 micrometers), which will be an alternative to our PDMS coated particles.

Also, your proposal was vague about the theoretical framework you will apply to analyze the data. It would be useful to discuss how you will apply what you learn in these experiments to address the questions posed in the project brief. (I should note that there is interest in Group D powders as well, and the general question of how cohesivity affects fundamental phenomena like yielding, compaction, and the Janssen effect is always of interest to IFPRI).

The proposed research program is mainly experimental. The data and experimental analysis should help rationalizing theoretically the flow of powders. First, by controlling adhesion and size independently, we should be able to identify the relevant dimensionless parameters controlling the aeration during the packaging process, a key point to generalize to different kind of powders. The ultimate goal would be to propose constitutive equations to describe the flow of powders as a continuum, to inject them in a two phase-flow description and to be able to simulate flow in any configurations taking into account both cohesion and coupling with air… This represents the long-term project we have in mind, starting with the proposed program.

Some more specific questions include:

- **how thick are your PDMS films? Are they significant relative to particle diameter?**

The PDMS film is about few tens of nanometers, much smaller than the particle size.

- **do these films contribute to lubrication or create viscoelastic interactions between particles?**

This is a very good question. For very thick coating, viscoelastic interactions are certainly present, but not in the range of coating we have tested. However, we do not know yet about the lubrification, and more characterization about the particle interaction should be conducted.

- **can you confirm that you create a viscometric flow (i.e. shear stress spans the gap) in your annular shear cell? The gap is approximately 30x the particle diameter - how do you assure that a shear band doesn't form?**

To prevent shear banding we propose to study the rheology in very thin gap, less than 10 particle diameters. We have tested in DEM numerical simulation that using small system stabilize shear banding and provide the « bulk » rheological curves.
This can be easily tested experimentally by performing experiments varying the gap, and checking that the measured flow curve are independent of the gap, in this thin regime.

IFPRI
International Fine Particle
Research Institute

Research Project Brief

Drying Wet Powders With Shear to Prevent Agglomerate Formation

The International Fine Particle Research Institute (IFPRI) wishes to fund a research project on elucidating how the method of drying, and more specifically the intensity of shear in a dryer, affects the state of agglomeration of the dried product and its redispersibility.

IFPRI has supported strong work on spray drying in recent years which has provided insight into the mechanisms of atomisation (affects granule PSD) as well as the dewatering modes of the droplets (drying outside-in vs inside out) and how they affect the granule strength and porosity. However, industrially, drying is diverse, with tray and belt dryers at low/no shear, fluid bed and rotary dryers at medium shear, and flash and agitated dryers at high shear - with diverse mechanisms of heat exchange. The choice of the right dryer for a given situation is multifactorial - it can be driven by cost (capex/energy efficiency), by the delicacy of the material, or by the resulting bulk density, flowability or dustiness of the product.

The state of agglomeration of the dried powder, and the ability to redisperse the powder later is also very important. For many fine materials, drying results in unavoidable agglomeration, sometimes this is beneficial, sometimes it presents problems. The degree and nature of this agglomeration is influenced by the particle’s surface chemistry and morphology (size and shape) but is also strongly influenced by the type of dryer used, as well as the presence or absence of solutes in the water. The intensity of shear in the dryer clearly is a key variable that influences both agglomeration and granule attrition in conjunction with the time-temperature history of the powder and understanding interplay between these variables in controlling the ultimate particle structure of the *dried* powder is the general objective of this project.

While we expect this project to be largely experimental, we place no restriction on the approach. For example, development of a regime map in terms of fundamental variables (e.g., time, temperature, moisture content, shear stress) would be acceptable, as would be a focused study on drying of particle clusters under appropriate mechanical stresses. IFPRI is interested in drying of both organic and inorganic powders, so the primary restriction of material system is that the powders be fine (volume mean particle size smaller than 100 microns) and hydrophilic. Drying in the presence of soluble species is in-scope as well.

A REGIME MAP APPROACH FOR PREDICTING THE AGGLOMERATION OF FINE WET POWDERS AFTER DRYING UNDER VARYING LEVELS OF SHEAR

IFPRI Research Project Proposal: Drying Wet Powders with Shear to Prevent Agglomerate Formation

Dr. Heather Emady, Associate Professor of Chemical Engineering, Arizona State University

BACKGROUND

Wet powder drying is a unit operation used in a variety of industries, yet the many variables involved in this process make it very difficult to predict the dried powder product attributes. A particular concern for drying of fine powders is the tendency for agglomerate formation and also attrition, which are highly dependent upon the level of shear in the dryer. The extents of both agglomeration and attrition can be characterized by the change in particle size and size distribution between the initial powder and the dried powder product.

Important dried powder product attributes include particle size and size distribution, particle shape, and bulk density. Formulation properties (e.g., particle size and size distribution, particle shape, particle density, bulk and tapped density) and process variables (e.g., liquid content, temperature, shear rate, time) can all influence the product attributes.

A regime map can be a useful tool to guide formulation choices and process operation, and is an improvement upon just performing many experiments to test variables, and is a positive step toward predictive model development.[1] Regime maps for wet granulation (the process of adding a liquid binder to a powder bed, usually with some level of agitation, for particle size enlargement) were established over 20 years ago, with separate regime maps for nucleation[2] and growth.[3,4] More recently, we expanded this regime map framework for single drop granule formation in static powder beds (see **Figure 1**).[5] Two distinct mechanisms and corresponding granule shape regimes were discovered, based upon the powder bed porosity and the granular Bond number. Spreading occurred with granular Bond numbers <65,000 (roughly corresponding to surface mean particle sizes >30 μm) for all bed porosities below the minimum fluidization porosity and formed flat granules, while Tunneling occurred with granular Bond numbers >65,000 (roughly corresponding to surface mean particle sizes <30 μm) for all bed porosities and formed round granules. These two regimes in particle size, from coarser particles that naturally form a smooth, packed bed of individual particles, down to finer particles that form a fluffy powder bed comprised of dry agglomerates, are expected to be critical components in the development of a drying regime map for this proposed work.

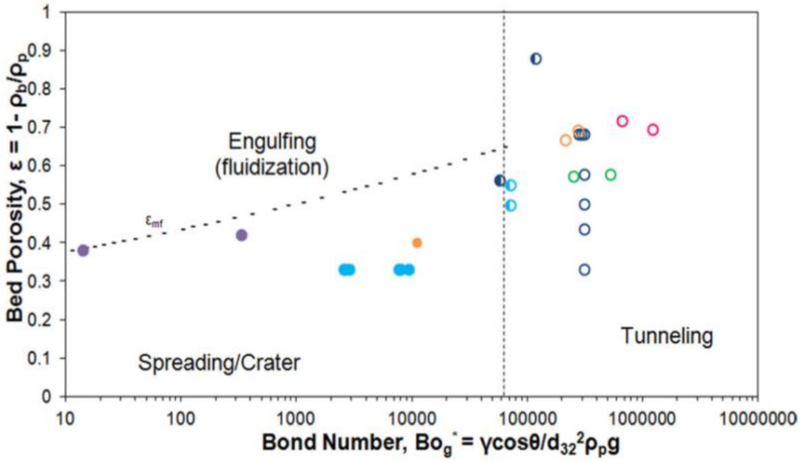


Figure 1. Granule formation mechanism regime map.[5]

PROPOSED RESEARCH PLAN

The overall goal of this research is to develop a particle drying regime map that determines the conditions under which agglomerate formation will occur in drying processes with varying shear rates. Toward this end, the following research objectives will be explored:

(**RO 1**) Raw Material Characterization and Preparation of Wet Particle Assemblies;
(**RO 2**) Tray Drying of Wet Particles [***no shear***];

(**RO 3**) Rotary Drying of Wet Particles [***low-medium shear***];
(**RO 4**) Jet Milling of Wet Particles [***high shear***];
(**RO 5**) Dried Product Characterization; and
(**RO 6**) Regime Map Development.

Details of each objective are provided in the subsequent sections, and a proposed timeline for carrying out the work for all objectives is included at the end of the proposal, in **Table 3**. More details are given for **RO 3** to demonstrate the capability of our in-house rotary drum dryer system, while the drying tests for **RO 2** and **RO 4** use standard commercial equipment.

(RO 1) Raw Material Characterization and Preparation of Wet Particle Assemblies:

The selection of materials will be done with the input of IFPRI members and will cover the two important particle size regimes (e.g., <30 μm and 30-100 μm). In addition to particle size, thorough raw material characterization is essential for elucidating the powder properties that will be relevant for regime maps. The techniques available in our powder characterization lab and at the ASU imaging facility, outlined in **Table 1**, will be utilized for this purpose.

Table 1. Equipment and corresponding measurements used for material characterization.

Equipment	Measurement
Malvern Morphologi G3 Automated Particle Characterization System with Automated Sample Dispersion Unit	Particle size and shape, and their distributions
AccuPyc II 1340 Automatic Gas Pycnometer	Particle density
SOTAX Tap Density Tester	Bulk and tapped density
Bruker MultiMode 8 Atomic Force Microscope (AFM)	Particle surface topography and particle adhesion
Zeiss Auriga FIB-SEM	Particle surface topography

The wet particle assemblies will be prepared by mixing the powder with the desired amount of liquid and kneading until the mixture appears homogeneous. The mixtures will be prepared immediately before each test in order to minimize evaporation.

(RO 2) Tray Drying of Wet Particles [no shear]:

Oven tray drying will be performed in order to have a control drying case without shear. We have a Fisher Scientific 60L Gravity Oven in our lab that is capable of operating at temperatures up to 250°C. In these experiments, the weight of the drying particles will be monitored at regular intervals throughout the drying process. The weight loss in the system will be equal to the quantity of water lost from the wet particles upon drying. This mass balance can be used to determine the drying kinetics and heat transfer rate within the wet particles. Since the particles are tray dried without any particulate motion within the system, the shear rate will be zero for these experiments.

(RO 3) Rotary Drying of Wet Particles [low-medium shear]:

Rotary drying will be performed in order to test the low-medium shear regimes. We will use our in-house rotary drum experimental setup that is designed for conductive and convective granular heat transfer, with particle temperature quantification via a thermal IR camera. Rotary drum systems have been used to explore mixing of fine particles, as characterized by the axial dispersion coefficient,[6,7] but little experimental work on the heating and drying of this class of materials in rotary drums is available in the literature.

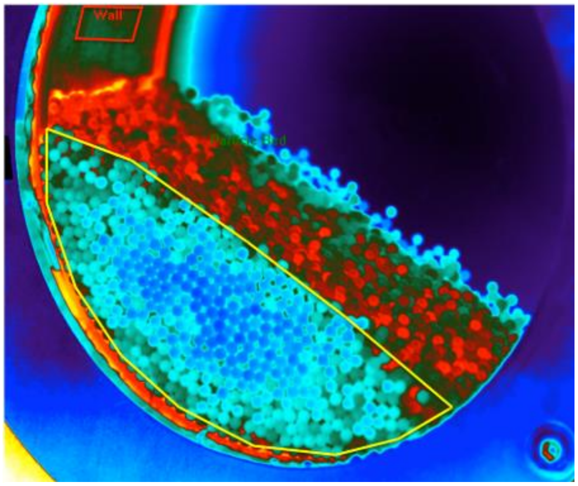


Figure 2. Sample IR camera image, with region of interest selection for the drum wall (red) and the particle bed (yellow).

Details of our experimental rotary drum setup and thermal IR camera are presented in Adepu et al.[8] The setup consists of a stainless-steel cylinder (ID = 15.24 cm, OD = 16.51 cm, L = 7.62 cm) that is closed on each end by 6 mm thick windows. One end of the drum is closed by a sapphire window (D = 15.24 cm) that provides optical and thermal access to the interior particle bed, and the other side of the drum is closed by a quartz window (D = 16.51 cm) that provides optical access to the particle bed. Both windows are held in place using 1.27 cm thick titanium rings that are specifically chosen due to the low conductivity, thereby preventing direct contact of the drum walls with the rollers used for rotating the drum and reducing heat loss through any contact. The sapphire window is held using a 14.478 cm ID, 27.94 cm OD titanium ring, and the quartz glass is held using a 15.24 cm ID, 27.94 cm OD titanium ring. The drum rotates on the two 27.94 cm OD titanium wheels using rollers with variable rotational speed. Three heat guns are placed with equal spacing, at 120° apart, around the drum, to provide effective uniform heating. An infrared radiation (IR) camera (FLIR A6701SC) is used to capture the temperature profile through the sapphire window (see **Figure 2)**. Therefore, the sapphire window is specifically chosen to give a high transmittance to IR light, with a transmission range from 0.17 µm to 5.5 µm.

This rotary drum system was designed for conduction heat transfer via the drum walls. However, to incorporate convection heat transfer, the setup has been modified to introduce forced convection into the drum system. For the conduction setup, one side of the drum is closed using a quartz window and another side is covered using a sapphire window. For convection, besides the sapphire window that is used for IR imaging, a quartz window with holes to pump hot air into the drum is used. The quartz window used features a central inlet hole for hot air to be forced into the drum for internal heating. It also has four smaller holes around the edge to let air outside, in order to release the pressure from inside the drum. The internal heat gun is attached to an air duct that connects with pipe fittings to a temperature sensor and the air inlet port. This heat gun serves to insert a hot air stream into the drum to heat the particle bed inside the drum via forced convection. The rotary drum experimental setup, showing the placement of all four heat guns, is provided in **Figure 3**.

The FLIR A6701SC infrared camera is a non-contact device that detects and transforms infrared radiation (heat) into a visual image through digital video outputs. A lens, a heat sensor, processing circuitry, and a mechanical housing comprise the IR camera's components. The lens focuses infrared radiation on the sensor. This perceived energy could be carefully quantified and recorded – as low as 0.1ºC – as a picture or video, which can then be evaluated for additional calculations.[9] The IR camera records the temperature evolution as a video, coupled with the temperature scale for the region of interest, while the particles are heated/dried inside the rotating drum. The rotating drum's outer drum wall temperature can be measured with a thermocouple, and the internal drum wall temperature can be measured with the IR camera. As the heating advances, the temperatures on the exterior and interior drum walls will equalize. The IR camera captures the front and top faces of the particles inside the rotating drum, which will be utilized to calculate the temperature profile. Since the rotary drum is short (7.62 cm in length) and cylindrical, it is reasonable to assume that the cross-sectional area and temperature profile remain consistent along its length. Thus, the heat transfer rate in the rotary drum can be measured.

We will control the shear rate inside of the drum via the rotation rate, which can operate from 1-15 rpm (if the IFPRI members would like to see higher shear in the rotary drum than is achievable from 15 rpm, then we could modify the system by replacing the motor). Particle image velocimetry (PIV) is a noninvasive method that employs the idea of particle displacement over a defined tiny finite separation period, which offers a quantifiable, immediate velocity vector field that can be used to determine shear rates.[10] As the IR camera records the temperature evolution as well as the particle motion inside the rotary drum, it can be used to apply PIV and hence calculate the shear rates.

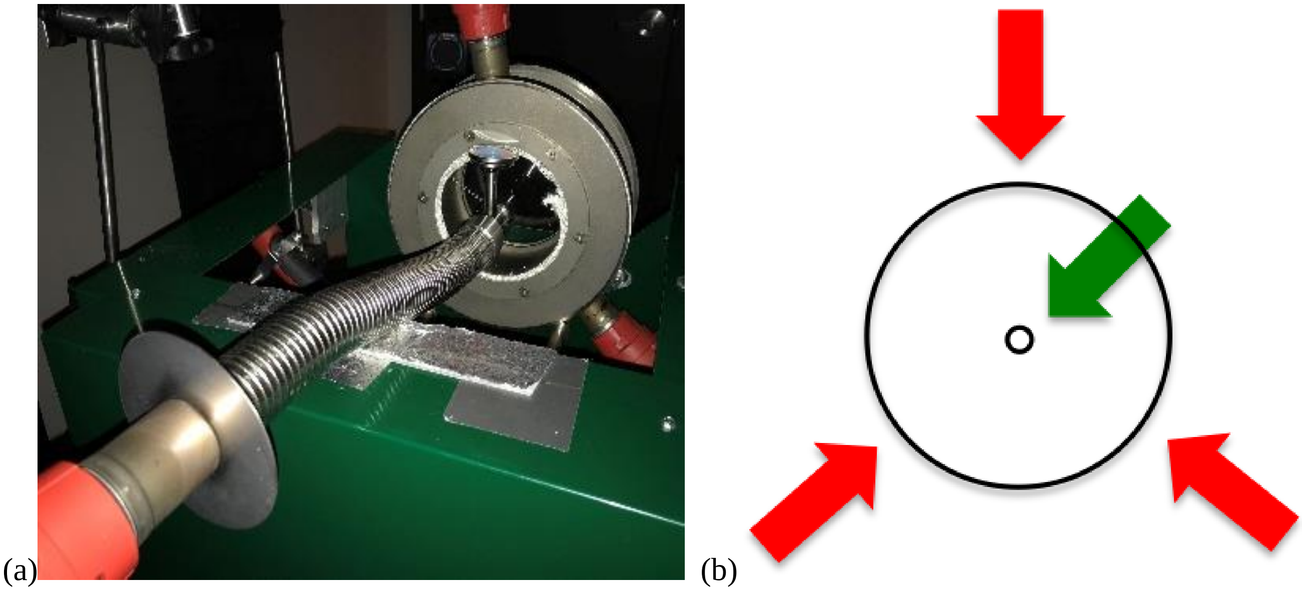


Figure 3. Rotary drum experimental setup. (a) Rear view of empty drum with air inlet duct and quartz window. The opposite end of the drum is enclosed with a sapphire window, where the thermal IR camera is positioned in order to obtain the particle temperature profile within the drum. (b) Schematic of the heat addition to the rotary drum, with the red arrows indicating external heat guns, and the green arrow indicating an internal heat gun.

(RO 4) Jet Milling of Wet Particles [high shear]:

Jet milling will be performed in order to test the high shear regime. We have a Fluid Energy Model 00 Jet-O-Mizer Mill in our lab, which can process 0.75-15 g/min of material. We wanted to include a high shear case in our experimental plan, but our control and measurement of the temperatures and shear rates for this mill are not as sophisticated as those we are able do with the rotary drum in **RO 2**. The operating variables for this mill include the supply air flow rate, the grinding nozzle pressure, and the pusher nozzle pressure. We will manipulate these variables in an attempt to vary the shear rate, although accurately quantifying this may be challenging. We will attempt to measure the heat transfer rates using the mass balance approach presented in **RO 1**, but we acknowledge that there will likely be some loss of material within this milling system. Thus, this research objective will be more qualitative than quantitative, but should nonetheless provide some useful insights into the dried product resulting from a high shear system.

(RO 5) Dried Product Characterization:

The dried powder will be characterized using the same techniques outlined in **RO 1**. A key attribute of the dried powder product is the extent of agglomeration. The product particle size, shape, and their distributions will be measured using the Malvern Morphologi G3. These product size and shape characteristics will then be compared with those of the original powder, as obtained in **RO 1**, to quantify the extent of agglomeration. The surface properties of the dried powder are also critical, and will be characterized using AFM and SEM and compared with the measurements of the original powder, as obtained in **RO 1**, to quantify the change in surface properties.

(RO 6) Regime Map Development:

The regime map will incorporate fundamental properties of the particles (e.g., particle size and shape), as well as process conditions (e.g., moisture content and shear rate), into dimensionless groups. **Table 2** provides a summary of all of the variables that will be tested, and the results will be obtained from **RO 1-5**, which will be used for derivation of the dimensionless groups and development of the regime map that will predict agglomerate formation upon drying under shear. From the literature in the areas of unsaturated porous media[11] and the general dynamics of wet particle systems,[12,13] we found some relevant quantities that incorporate these variables, to be used as a basis for the regime map development. These quantities include the van der Waals binding energy, capillary force or pressure, degree of saturation, Weber number, Bond number, and capillary number.

Table 2. Tested variables for inclusion in regime map.

	Variable
Formulation	Particle size and size distribution
	Particle shape
	Tapped and bulk density
	Root mean square of roughness
	Hamaker constant or force/work of adhesion
Process	Temperature
	Shear rate
	Mass of material
	Moisture content
Product	Particle size and size distribution
	Particle shape
	Tapped and bulk density
	Root mean square of roughness
	Hamaker constant or force/work of adhesion

CRITICAL UNKNOWNS

The primary uncertainties in the proposed work are: (1) the quantification of the shear rate, and (2) determination of the dimensionless groups to be used in the resulting regime map. Shear rate is variable across various equipment designs, but we strive to develop a single dimensionless group that quantifies shear rate across a variety of process equipment. For example, in the rotary drying process, there will be a balance between the shear of drum rotation versus the shear of air flow into the drum. We will not have an understanding of what this balance looks like until we actually perform the experiments. Additionally, we do not know the dominating variables in each of these drying processes before we do the experiments (although we now have a mechanistic basis upon which to start), so our experimental results will dictate the formation of the dimensionless groups for the regime map. Despite these unknowns, we have experience using this framework of characterizing the feed material, performing experiments looking at the effects of varying process variables, and characterizing the product material; then, we combine all of these components to determine the dominating dimensionless groups and corresponding regime map.

INTEGRATION INTO EXISTING RESEARCH PROGRAM

The proposed research combines our lab's two main research thrusts, namely single drop granulation and granular heat transfer. The regime map framework comes from the granulation project, which is currently funded by the NSF CAREER award. However, we do not currently have external funding for our granular heat transfer project, and the proposed work can leverage our existing infrastructure for this project, namely the rotary drum with the thermal IR camera.

OPPORTUNITIES FOR IFPRI MEMBER SUPPORT

The proposed research would benefit from the supply of appropriate particulate materials from IFPRI members. The two categories of particles needed are as follows: particles with surface mean sizes <30 μm, and those between 30-100 μm. Beyond these size requirements, we would be open to any type of particulate materials from relevant industries.

In addition to the supply of test materials, we would appreciate the input of IFPRI members for industrially relevant drying conditions (e.g., liquid saturation levels, temperature, drum rotation rate, etc.) to test in our setups.

PROPOSED TIMELINE

The proposed research will take place in Dr. Heather Emady's laboratory at ASU from August 1, 2022 – July 31, 2025, and the details are provided in **Table 3**.

Table 3. Timeline of research activities for the proposed work.

	Year 1	Year 2	Year 3
RO 1: Raw Material Characterization and Preparation of Wet Particle Assemblies			
Select materials of the following surface mean particle sizes: (1) <30 μm binary, and (2) 30-100 μm Characterize materials: particle size and size distribution, particle shape, particle density, bulk and tapped density, surface topography and adhesion Prepare wet particle assemblies for each drying test	■ ■ ■	 ■ ■	 ■
RO 2: Tray Drying of Wet Particles [***no shear***]			
Perform oven tray drying experiments and test for the effects of: (1) temperature, (2) mass of material, and (3) moisture content	■		
RO 3: Rotary Drying of Wet Particles [***low-medium shear***]			
Perform rotary drying experiments and test for the effects of: (1) temperature, (2) mass of material, (3) moisture content, and (4) shear rate	■	■	
RO 4: Jet Milling of Wet Particles [***high shear***]			
Perform jet milling experiments and test for the effects of: (1) mass feed rate, (2) moisture content, and (3) air pressure/shear rate			■
RO 5: Dried Product Characterization			
Measure dried powder product properties, including size, shape, and their distributions, in order to quantify the extent of agglomeration; also measure surface topography and adhesion	■	■	■
RO 6: Regime Map Development			
Develop regime maps that predict agglomerate formation after drying based on dimensionless groups involving the formulation properties and the process variables			■

RESPONSES TO IFPRI REVIEWER COMMENTS

Overall, the members feel that your proposal meets the project brief and believe that development of a regime map for agglomerate breakage in drying will be useful. They are concerned, however, about your vagueness about the controlling dimensionless groups and worry that your approach is too empirical. You note that the Bond number is very large in these systems (in the pendular regime), indicating that they are capillary-dominated. You may find it useful to draw from the unsaturated porous media literature to develop a mechanistic basis for your regime map.

We understand the concerns in using an empirical approach for developing the regime map, and we appreciate the reviewers directing us toward the unsaturated porous media literature. However, from our experience, a mechanistic basis is usually too ambitious a goal for powder systems. Our approach in gaining an understanding of the controlling variables of the material and process will help us better understand the mechanisms, but we will not necessarily end up with a useful mechanistic description. As an example, our past work looked at granule formation mechanisms, which can be determined from a regime map of dimensionless groups that include formulation properties and operating parameters (see **Figure 1**). We did attempt to provide a mechanistic description of the granule formation mechanisms via a force balance approach, but due to the inhomogeneous packing tendencies of fine powders, a single ideal model was unable to accurately predict the formation mechanism behavior, as compared to the empirical regime map.[14] Nonetheless, we have now discovered some useful existing mechanistic quantities in the literature (thank you again to the reviewers for pointing us in this direction) that will be relevant to our system and will give us a more mechanistic basis to start for our dimensional analysis, and have now included the discussion of these under **RO 6**.

Also, you are unspecific about how you will measure heat transfer rates (including temperature profiles) and shear rates, A more detailed description about how you plan to do this would be useful.

We apologize for neglecting to include this information in our original proposal. We have now added details about the temperature and shear rate measurements for each of our three types of experiments, under **RO 2-4**, at the end of each of these sections.

Your characterization plan doesn't include surface characterization. This seems to be a significant omission, as the surface properties of the particles are likely to dominate adhesion at the very end of drying.

We agree that surface characterization is critical to the success of this project, and thus we have now included that as part of our proposed work. We have added information about the equipment we will use for surface characterization in **Table 1**, as well as some text about this characterization under **RO 5**. We have also now included surface characterization with our regime map development in **Table 2**. Further details about how we will characterize the particle surfaces using this equipment are provided here.

The particle-particle adhesion in a powder is due to the following forces: van der Waals, electrostatic, and capillary. The contact area between the particles heavily influences these forces, and can be influenced by the size of asperities on the surface.[15,16] Atomic force microscopy (AFM) has been commonly used to acquire information on the nature of particle-particle and particle-surface interactions, as well as surface topography.[17] The use of the colloidal probe method, where a particle is mounted onto the tip of a cantilever of an AFM, allows for the measurement of the adhesion of the particle to other particles or surfaces.[15,17–19]

Scanning electron microscopy (SEM) has also often been used to characterize the surface features of particles. The SEM stereoscopy technique has been used to obtain data of the three-dimensional particle surface for analysis of the topography.[20]

An AFM and an SEM will be used to characterize the surface topography of the particles. The images and the root mean square (RMS) of the roughness will be reported to give insight into the area of interaction for the adhesion of the particles. The colloidal probe method will be used to determine the adhesion of the particle-particle system. The SEM will be used to confirm and determine how the particle is mounted on the cantilever tip. The adhesion of the particle-particle system will be quantified from the force-distance curves as one or more of the most-used values in literature: force of adhesion, work of adhesion, and/or a Hamaker constant (assuming only van der Waals forces are present).[21]

REFERENCES

(1) Kayrak-Talay, D.; Dale, S.; Wassgren, C.; Litster, J. Quality by Design for Wet Granulation in Pharmaceutical Processing: Assessing Models for a Priori Design and Scaling. *Powder Technology* **2013**, *240*, 7–18. https://doi.org/10.1016/j.powtec.2012.07.013.

(2) Hapgood, K.; Litster, J. D.; Smith, R. Nucleation Regime Map for Liquid Bound Granules. *AIChE Journal* **2003**, *49* (2), 350–361.

(3) Iveson, S. M.; Litster, J. D. Growth Regime Map for Liquid-Bound Granules. *AIChE Journal* **1998**, *44* (7), 1510–1518.

(4) Iveson, S. M.; Wauters, P. A. L.; Forrest, S.; Litster, J. D.; Meesters, G. M. H.; Scarlett, B. Growth Regime Map for Liquid-Bound Granules: Further Development and Experimental Validation. *Powder Technology* **2001**, *117* (1–2), 83–97.

(5) Emady, H. N.; Kayrak-Talay, D.; Litster, J. D. A Regime Map for Granule Formation by Drop Impact on Powder Beds. *AIChE Journal* **2013**, *59* (1), 96–107.

(6) Koynov, S.; Wang, Y.; Redere, A.; Amin, P.; Emady, H. N.; Muzzio, F. J.; Glasser, B. J. Measurement of the Axial Dispersion Coefficient of Powders in a Rotating Cylinder: Dependence on Bulk Flow Properties. *Powder Technology* **2016**, *292*. https://doi.org/10.1016/j.powtec.2016.01.039.

(7) Paredes, I. J.; Yohannes, B.; Emady, H. N.; Muzzio, F. J.; Maglio, A.; Borghard, W. G.; Glasser, B. J.; Cuitiño, A. M. Measurement of the Residence Time Distribution of a Cohesive Powder in a Flighted Rotary Kiln. *Chemical Engineering Science* **2018**, *191*, 56–66. https://doi.org/10.1016/j.ces.2018.06.044.

(8) Adepu, M.; Boepple, B.; Fox, B.; Emady, H. Experimental Investigation of Conduction Heat Transfer in a Rotary Drum Using Infrared Thermography. *Chemical Engineering Science* **2021**, *230*, 116145. https://doi.org/10.1016/j.ces.2020.116145.

(9) FLIR Teledyne. How Do Thermal Cameras Work? https://www.flir.com/discover/rd-science/how-do-thermal-cameras-work/.

(10) Hochareon, P.; Manning, K. B.; Fontaine, A. A.; Tarbell, J. M.; Deutsch, S. Wall Shear-Rate Estimation within the 50cc Penn State Artificial Heart Using Particle Image Velocimetry. *Journal of Biomechanical Engineering* **2004**, *126* (4), 430–437. https://doi.org/10.1115/1.1784477.

(11) Xu, J.; Louge, M. Y. Statistical Mechanics of Unsaturated Porous Media. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* **2015**, *92* (6). https://doi.org/10.1103/PhysRevE.92.062405.

(12) Herminghaus, S. Dynamics of Wet Granular Matter. *Advances in Physics* **2005**, *54* (3), 221–261. https://doi.org/10.1080/00018730500167855.

(13) Liu, P. Y.; Yang, R. Y.; Yu, A. B. Dynamics of Wet Particles in Rotating Drums: Effect of Liquid Surface Tension. *Physics of Fluids* **2011**, *23* (1). https://doi.org/10.1063/1.3543916.

(14) Emady, H. N.; Kayrak-Talay, D.; Litster, J. D. Modeling the Granule Formation Mechanism from Single Drop Impact on a Powder Bed. *Journal of Colloid and Interface Science* **2013**, *393* (1). https://doi.org/10.1016/j.jcis.2012.10.038.

(15) Jaiswal, R. P.; Kumar, G.; Kilroy, C. M.; Beaudoin, S. P. Modeling and Validation of the van Der Waals Force During the Adhesion of Nanoscale Objects to Rough Surfaces: A Detailed Description. *Langmuir* **2009**, *25* (18), 10612–10623. https://doi.org/10.1021/la804275m.

(16) Bowen, W. R.; Lovitt, R. W.; Wright, C. J. Atomic Force Microscope Studies of Stainless Steel: Surface Morphology and Colloidal Particle Adhesion. *Journal of Materials Science* **2001**, *36*, 623–629.

(17) Etzler, F. M.; Drelich, J. Atomic Force Microscopy for Characterization of Surfaces, Particles, and Their Interactions. In *Developments in Surface Contamination and Cleaning: Detection, Characterization, and Analysis of Contaminants*; Elsevier Inc., 2012; pp 307–331. https://doi.org/10.1016/B978-1-4377-7883-0.00006-7.

(18) Vaziri Hassas, B.; Caliskan, H.; Guven, O.; Karakas, F.; Cinar, M.; Celik, M. S. Effect of Roughness and Shape Factor on Flotation Characteristics of Glass Beads. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2016**, *492*, 88–99. https://doi.org/10.1016/j.colsurfa.2015.12.025.

(19) Louey, M. D.; Mulvaney, P.; Stewart, P. J. Characterisation of Adhesional Properties of Lactose Carriers Using Atomic Force Microscopy. *Journal of Pharmaceutical and Biomedical Analysis* **2001**, *25*, 559–567.

(20) Podsiadlo, P.; Stachowiak, G. W. Characterization of Surface Topography of Wear Particles by SEM Stereoscopy. *Wear* **1997**, *206*, 39–52.

(21) Liu, Y.; Song, C.; Lv, G.; Chen, N.; Zhou, H.; Jing, X. Determination of the Attractive Force, Adhesive Force, Adhesion Energy and Hamaker Constant of Soot Particles Generated from a Premixed Methane/Oxygen Flame by AFM. *Applied Surface Science* **2018**, *433*, 450–457. https://doi.org/10.1016/j.apsusc.2017.10.030.

DEVELOPMENT OF INNOVATIVE TOOLS TO CHARACTERIZE THE DRYING OF WET POWDERS UNDER SHEAR

Alban Sauret
Department of Mechanical Engineering, UC Santa Barbara
asauret@ucsb.edu (805) 618-5318 https://sauretlab.me.ucsb.edu/

1 PROBLEM STATEMENT AND PROJECT OBJECTIVES

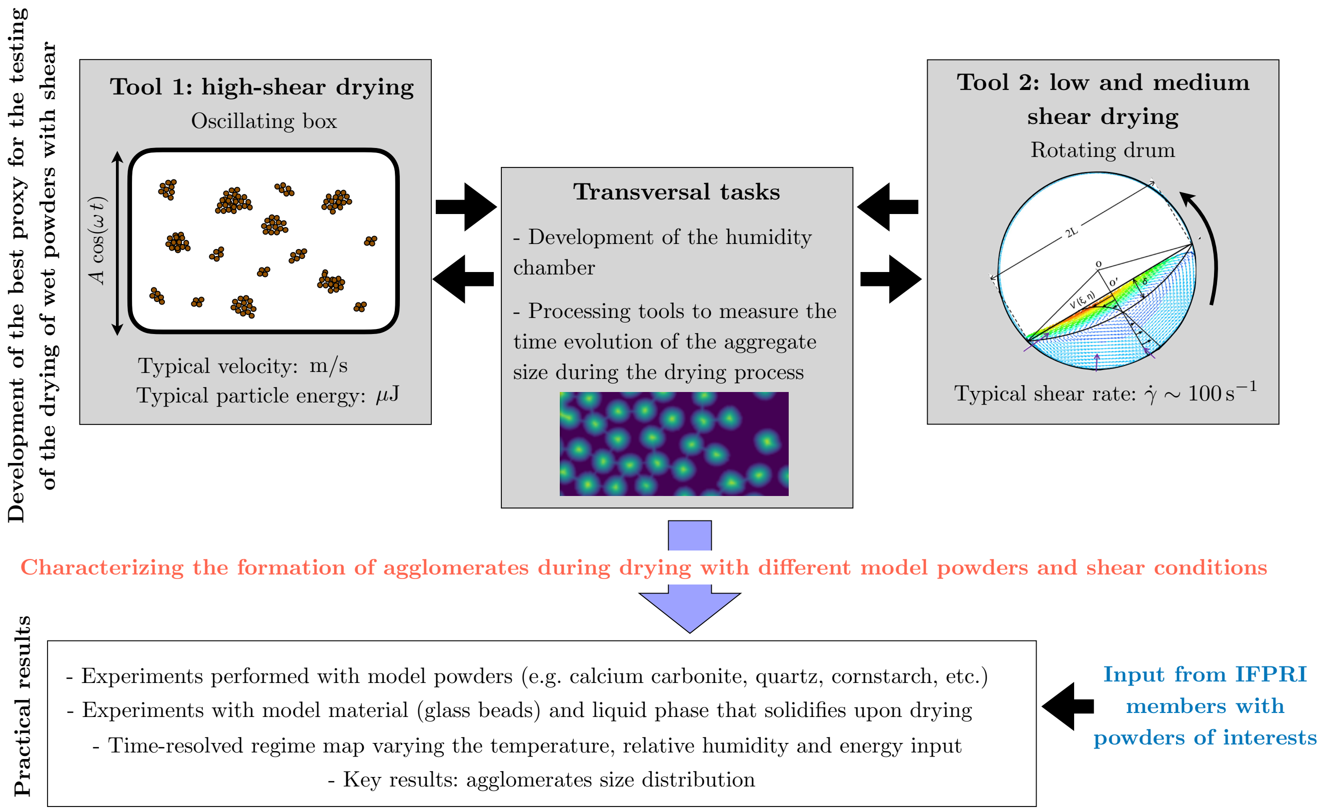
▷ **Granular matter and powders** are widely used in the manufacturing of numerous products and in many industries. In particular, powders are used as intermediate products but are also products consumed as such or, most often, after rehydration in the food industry [1]. They are also omnipresent in pharmaceutical products, but also in building materials, as the PI has experienced with Saint-Gobain. Despite this intense utilization, their behavior is still poorly understood, and empirical [2]. One significant difficulty in developing a general understanding is the range of possible powder properties (size, shape, wettability, etc.), the key role of the moisture and electrostatic force, and the flow conditions.

▷ **Drying of powders and formation of agglomerates.** Developing final products with powders often involves a wet agglomeration process, which is still very empirical [3]. Wet agglomeration of powders consists of coupling the agitation of solid particles to an operation of adding water or a binder to form granular structures of larger size, which after drying modify the properties of the final powder (flowability, rehydration properties, density, etc.) [4, 5]. At the industrial level, there is a great diversity of equipment (configuration, agitation mode) and modes of water supply (pulverization, flow...) allowing to realize this operation. The drying of wet powders ultimately leads to agglomerate formation because of solid bonds formed between the particles [3, 6]. The average size of the agglomerates produced can vary from ten to a few hundred microns. Nevertheless, in all cases, one can expect that two different drying techniques will lead to different final granules in terms of strength, size, compressibility, flowability, and ultimately result in products of varying quality and properties.

▷ **A complex (and impossible?) prediction.** As mentioned in the project brief, the question of how the intensity of the shear in a dryer affects the state of agglomeration of the dried product, and its redispersibility is broad and fascinating because of all the different physical and chemical ingredients involved. An approach to providing some first answers useful to a broad community would be to perform some real-scale experiments with a few selected powders and build a regime map for some well-chosen variables. However, this approach would have limited interest since the degree and nature of the agglomeration is influenced by the particle's surface chemistry and morphology (size and shape) but is also strongly influenced by the type of dryer used, as well as the presence or absence of solutes in the water. As a result, any particular characterization obtained may not be appropriate to describe or predict other configurations.

▷ **Should we give up? Towards a predictive tool.** The goal of this project is to develop two innovative experimental tools that will allow easy implementation and quick testing of a large variety of powders and liquid while controlling the input energy and/or shear rate during the drying process. We will base our approach on our expertise in granulation and blending of liquid and grains performed in the past with an industrial collaborator, Saint-Gobain. Deliverables will be the tools developed within this project from which we will obtain the final size distribution, but also the time evolution, of the agglomerates formed. The capabilities of such tools will be demonstrated through experiments with model powders, from which the PI will develop a modeling framework to gain some fundamental insights into potential optimization properties (evolution of the final size distribution of the agglomerate with the shear rate) that could later be transferred to industrial configurations.

▷ **Research objectives.** A schematic of the research objectives, tasks, and deliverables is shown in figure 1, highlighting the nature of the project and the cross-talk between the different stages. In particular, once the tools will have been developed, the PI will seek powders of interest among the IFPRI members to leverage these characterizing tools while simultaneously running experiments with model materials. The proposed research will lead to the development of two characterizing tools: (i) an oscillating box for high-shear rate and (ii) a rotating drum for medium shear rate, which could be used on any powders to provide the time-varying and final size distribution of the agglomerates formed upon the drying of wet powders with shear. These tools will provide a first, quick, and low-cost estimate of the influence of the different controlling parameters (shear rate, relative humidity, nature of the powders, drying dynamics, etc.) prior to running more elaborate tests in industrial settings.



- Development of the humidity chamber

- Processing tools to measure the time evolution of the aggregate size during the drying process

- Experiments performed with model powders (e.g. calcium carbonite, quartz, cornstarch, etc.)
- Experiments with model material (glass beads) and liquid phase that solidifies upon drying
- Time-resolved regime map varying the temperature, relative humidity and energy input
- Key results: agglomerates size distribution

Figure 1: Schematic overview of the proposed research.

2 EXPERTISE OF THE PI AND RELEVANCE TO ITS OWN RESARCH

▷ **Background of the PI.** The PI, Alban Sauret, is a faculty in the Department of Mechanical Engineering at UC Santa Barbara (USA) since 2018. He leads the Multiphase and Multiscale Flow Laboratory (*website*), which consists of 10-15 researchers. His group tackles problems in the area of fluid mechanics, soft matter, and granular materials. In particular, topics of current interest in the group include capillary flows of suspensions (dispensing of suspensions, dip coating of suspensions, additive manufacturing, etc.), clogging in confined systems, rheology and properties of granular material and powders, and blending of liquid and grains. Before joining UCSB, the PI was a CNRS Researcher between 2014 and 2018 in SVI (*website*), a joint academic-industrial laboratory between the CNRS and Saint-Gobain located in the Saint-Gobain Research center in Aubervilliers (France). In addition, he was a scientific consultant for Saint-Gobain Research in the field of granular materials, powders, and coating processes.

▷ **Why is PI well-qualified to develop new diagnostic tools for powders?** In the past, the PI, in collaboration with Saint-Gobain and Dr. Pierre Jop (SVI), has developed model approaches to gain some fundamental insights into the wet granulation processes. In these past projects, the goal was to work at constant water content and thus prevent any evaporation and drying of the liquid phase. However, similar approaches could easily be used and extended to control the drying of the liquid phase and provide relatively quick insights into the size distribution of the agglomerates resulting from the drying of wet powders. In addition, since 2019, the PI has started to investigate constitutive laws to provide a physical understanding of the concept of flowability of powders by studying the rheology of powders in various configurations in collaboration with researchers in France (Dr. Olivier Pouliquen and Prof. Maxime Nicolas, IUSTI, Marseille, France). Interestingly, whereas powders are handled at large scales, different simple tools have been developed to characterize powders in industrial environments (see, for instance, *Granutools*). The spirit of the present project is similar, *i.e.*, developing experimental tools to provide insights into the formation of agglomerates during the drying of wet powders under controlled shear. In particular, the goal is not to capture the complexity of full industrial configurations but instead to be able to provide first guidelines through experiments and scaling laws without the need for expensive tests.

▷ **Why focusing on an oscillating box and a rotating drum as model configurations?** We have performed similar work leveraging the simplicity of an oscillating box in the past with a postdoctoral student and an MS student at CNRS and Saint-Gobain (France) to mimic the wet granulation process using controlled granular systems (spherical glass beads and polystyrene beads, both monodisperse in size). We thus believe that combining this approach with a control of the relative humidity, temperature, water content, and nature of the powders could lead to the development of an innovative tool for characterizing wet powders drying under controlled shear. Similarly, the PI has also considered the rotating drum configuration during the Ph.D. thesis of G. Saingier (funded by Saint-Gobain) [7]. We have used this approach to model wet granulation processes at low shear rates [7, 8]. More specifically, we have considered the growth of a single wet agglomerate rolling in a dry granular flow inside a rotating drum. We have been able to measure the time evolution of its diameter for different grains and liquids and various shear rates. Using X-ray tomography, we were also able to characterize the internal structure of the granular agglomerate at different times during the process and proposed a model that captured the growth dynamics. Therefore, extending this approach to provide low-cost tools to build a regime diagram of the drying of wet powders at low shear rates is feasible.

> The proposed project relies on the expertise of the PI and controlled flow configurations and drying kinetics. The goal is the development of innovative tools for characterizing the drying of wet powders with shear and the resulting formation of agglomerates. The tools that will be developed could be used with any powders and binding agents at high shear rates (oscillating box) and medium shear rates (rotating drum).

3 RESEARCH WORK-PLAN

Objective 1: Drying powders at high-shear

The first objective of this project will be to investigate and characterize the drying dynamics and the resulting agglomerates formed under *high-shear drying*, typically as encountered in flash and agitated dryers [9]. A large part of this process is controlled by the impact of the agglomerates with the impellers during the drying process that brings energy to the agglomerates [10]. Performing such an approach with an actual high-shear drying system would only result in the characterization of a specific situation (specific powder, for given relative humidity and temperature). While very useful these kinds of large-scale tests could be quite time and money-expensive while only providing limited opportunities for optimizing the formation of the agglomerates. Therefore, we aim to develop a controlled setup where we will be able to visualize the drying agglomerates during the drying process using high-speed visualization and post-mortem. During the drying process under agitation, the visualization of the agglomerates and the dynamical evolution of the size distribution may provide precious information on what controls the final size distribution (collision of agglomerates between themselves, on the solid boundaries, leading to the formation of larger agglomerates or break-up in smaller agglomerates).

▷ **From wet granulation to drying with shear.** Beyond the difference due to the drying phase, the wet granulation process [11] and the drying of wet powder under high shear rates share common key features. In the context of high shear wet granulation, the process often takes place in a tank in which rotating blades set the material in motion. The shape of the blades only impacts the intensity of the velocity field within the granulator, and they serve to set the material in motion and to give it enough energy for shocks to occur. Indeed, during the granulation stage, it is assumed that it is the shocks between agglomerates that will determine the average value of the final diameter of the latter [12]. It is, therefore, possible to assume that such an analogy can be made with the shear drying process. The approach is to use a large-amplitude vibrating pot where the two main control parameters to impose the energy input and shear are the amplitude A and the frequency of oscillation $f = 2\pi/\omega$ [see figure 2(a)].

▷ **A simplified approach.** Although a vibrated box seems to be a simple system, in the context of wet granulation, the size distribution of the final agglomerate size with the water content has shown that the data obtained with this system are similar to data from high-shear granulation systems at an impeller rotation speed that would lead to a similar input energy in the system (close to 1 m/s with a typical size of the impeller of 10 cm and a typical particle size 10 µm) although the details of the process are different [13]. Moreover, it is worth mentioning that the effects of the typical velocity on the final size are also similar in industrial processes, suggesting that this setup was a promising model system to understand high-shear granulation, but also to extend it to high-shear drying of powders [14].

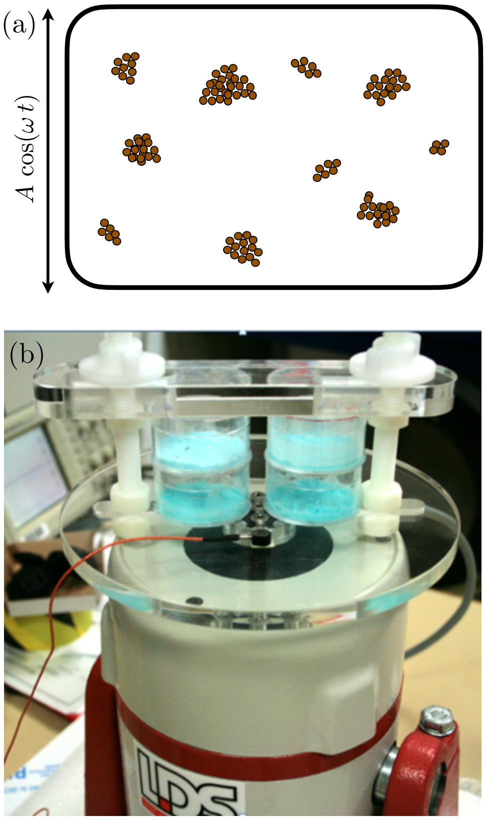


Figure 2: (a) Schematic and (b) picture of the previous oscillating box experiment.

▷ **The apparatus.** We will initially base our approach on a setup similar to the one we used in the past, shown in figure 2(b). A small amount of the initial powder, mixed with the liquid, will be placed in a rectangular plastic box of typical dimensions $10 \times 3 \times 5$ cm. Within this box, shocks between agglomerates will also take place, similar to what would be observed in other high-shear drying processes. In addition, the agglomerates will also impact the solid boundaries during the entire drying process. This experiment should allow us to reach comparable values for the acceleration, velocity, and input with those obtained using a tank (the frequency and amplitude of the oscillations could be extended to reach a different range of shear). The mechanisms involved are likely similar, and this procedure seems to be a good alternative to provide a benchmark to test different powders, liquid, initial moisture, time variation, etc. To make this box oscillate, we will use a vibrating pot. The amplitude and frequency will be controlled by an amplifier and a low-frequency generator. We will also be able to add an accelerometer on this plate to measure the acceleration experienced by the box, thus estimating the input energy in our system.

▷ **Preparation of the initial sample.** We will initially use a plastic bag in which we will weigh the desired quantity of powders, and the volume of liquid will be added to obtain the desired liquid content, and the bag will be sealed, the powder homogenized, and then placed in the plastic box to run a test.

▷ **Environmental chamber: control of the temperature and the relative humidity.** An important modification to this setup will be to implement a control in temperature and relative humidity in the box. Since our system is quite simple, this should easily be done by connecting on the side of the box an inlet leading to a full range humidity control with an elevated temperature that would allow control from 10 to 98% RH (at 20°C) and a temperature from ambient to 55°C. We have used such a system in the past, purchased from Electro-Tech Systems, within an environmental chamber, to study the drying dynamics in fibrous media [15] (this overall project was later continued with Saint-Gobain Research Paris within the framework of the glass wool business [16]). The airflow can then be exchanged between this environmental chamber and the test box. An alternative will be to place the entire setup within the environmental chamber since its footprint is moderate. In both cases, we will have a total control over the temperature and the relative humidity. Furthermore, we would also be able to investigate the influence of the time-temperature history on the agglomerate.

▷ **Micro-High-Speed Imaging.** One of the specialties of our group is to characterize high-speed phenomena, such as, for instance, the formation of droplets of suspensions for manufacturing application [17, 18] or the blending of grains and liquids [19, 20]. These situations require reaching a recording speed of typically 10,000 frames per second and a spatial resolution of order 5 μm/pixels. We will use a similar approach here, where the motion and evolution of the agglomerate inside the oscillating box will be recorded using a Phantom VEO 710 high-speed camera (available in our laboratory), equipped with a macro lens (Nikkor 200 mm), on which, if we need to reach a higher resolution, we could add a microscopic lens (Mitutoyo) as we have done in the past to study the coating of tubings by suspensions [21]. Even if high-speed imaging is not intended to record an entire drying under shear process, we will record a few seconds at different times along the process so that it will give us a picture of the entire drying dynamics, as well as information on the state of the agglomerates at a given time. This approach is particularly unique, as it provides a direct visualization *in situ* of the dynamical process.

▷ **Image analysis.** For each experiment, the analysis of the size distribution of the agglomerates over time will be done using methods commonly used in our group (via custom-made routines). From the videos obtained with the high-speed camera during the dynamics drying process, we will detect the agglomerates as distinct ”objects” to obtain each equivalent diameter (defined through the surface area A by $D_{eq} = \sqrt{4\,A/\pi}$). The different steps are illustrated in figure 3 with an example for polystyrene beads [figure 3(a)]. The images of the agglomerates are first thresholded to differentiate the agglomerates from the background of the image [figure 3(b)]. Then a segmentation allows us to separate the agglomerates

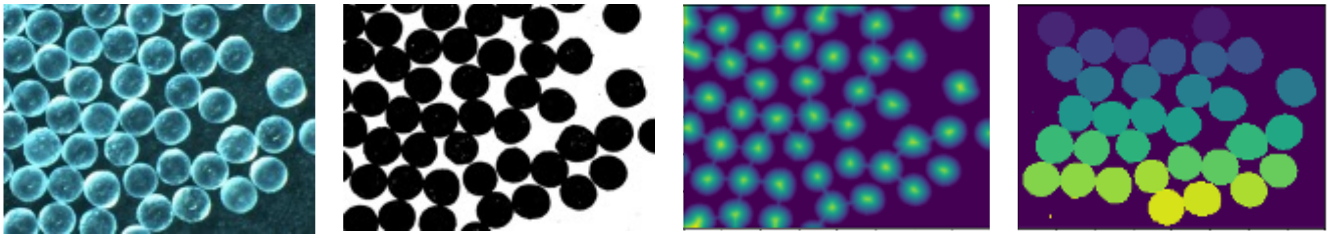

(a) (b) (c) (d)

Figure 3: (a) Example of a zoomed picture of agglomerate of glass beads and water formed during the model granulation process. (b) Example of resulting probability ditribution function of the agglomerate sizes and (c) Example of the evolution obtained when varying the size of the beads (blue: 60 μm, green: 200 μm)

[figure 3(c)]. This step being done, the next step, the label, allows us to number these different objects to define each agglomerate as an object from which we can recover some characteristics, the diameter being the one we are interested in [figure 3(d)]. This method also has the advantage of following the fragmentation and coalescence processes of agglomerates and thus obtaining unique information on the dynamics during drying, such as, for instance, the time evolution of the agglomerate size distribution.

Post-mortem characterization. Once the drying process is over, we expect to have a distribution of agglomerates that will depend on the particles' surface chemistry and morphology but also on the temperature, shear stress, and other physical parameters (and their time-evolution during the process). We will be able to collect the samples and measure the relevant powder properties such as the bulk density and the flowability. In addition, we will image the resulting agglomerates using a microscope that will allow us to characterize more finely the final agglomerate size distribution as we have done for the granulation process, as shown in figure 4(a)-(c).

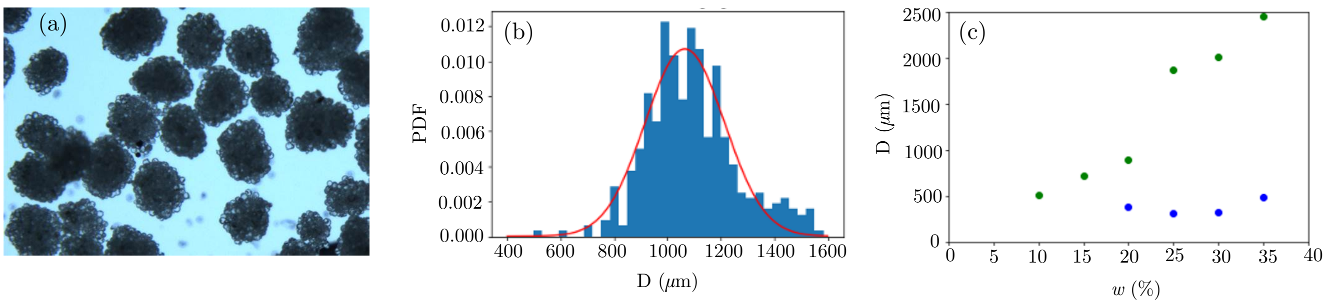


Figure 4: (a) Example of a zoomed picture of agglomerate of glass beads and water formed during the model granulation process. (b) Example of resulting probability ditribution function of the agglomerates size. The solid red line shows a Gaussian distribution. (c) Example of the evolution obtained when varying the the water content w for two different size of beads (blue: 60 µm, green: 200 µm)

▷ **Modeling framework to interpret the experimental results.** The two main quantities of interest are the size distribution and the mean size of the resulting agglomerates. We should emphasize that considering the size distributions of agglomerates rather than just the average size will be required. Indeed, two different operating conditions could have a similar mean size but very different distributions that would result in different properties in the final products. We have considered a similar approach in the past for a project in partnership with Saint-Gobain, where we were interested in understanding how the presence of particles dispersed in an interstitial fluid modifies the atomization and final size distribution of the spray (some of these results with the model system have been published [17]). Based on atomization modeling, we showed that the size distribution of all sprays obtained is well captured by a Gamma distribution when rescaled by the mean droplet radius $\langle r \rangle$ and that the mean droplet size can be estimated by accounting for the viscosity of the suspension and other physical properties.

Size distribution. Here, we believe that the size distribution, once rescaled by the mean size, will be captured by a log-normal distribution as observed for the wet granulation in high shear mixer (see *e.g.*, [13]):

$$\mathcal{P}\left(r; A, B\right) = \frac{1}{r\,B\,\sqrt{2\,\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln x - A}{B}\right)^2\right] \tag{1}$$

where the mean radius of the agglomerate and the variance are given by $\langle r \rangle = \exp(A + B^2/2)$ and $\sigma^2 = \exp(B^2 + 2\,A)\,[\exp(B^2) - 1]$, respectively. If our experiments were to show different behaviors, we would also be able to consider other distributions common for coalescence-fragmentation processes (such as the Gamma distribution, *e.g.*, [22]).

Evolution of the mean size with the input parameters. The more challenging task will be to develop a model accounting for the evolution of the average size of the agglomerates. Numerous approaches have been developed in the wet granulation community (*e.g.*, [23,24], among many others), and our goal within this project is not to develop full numerical models of the process (for instance trough discrete elements simulations) as it will be impossible to account for the complexity of each configuration. Instead, we want to develop scaling laws that, combined with our experiments, could predict the evolution of the state of agglomeration in the final product when varying the intensity of shear, the particle size, and the binding agent. Without trying to capture the entire complexity of such systems, we will rely on a scaling approach to predict how the change in one parameter, for instance, the input energy, can influence the final average diameter of the agglomerate D. In this process, the size of the agglomerates results from a balance between the cohesive energy E_c, which tends to increase the size of the agglomerates, and the breaking energy E_b, which tends to decrease their sizes. Our past experiments with a simplified approach to the wet granulation process have shown that scaling laws can capture the influence of the different effects at play, and in particular, the influence of the particles' size, the binding agent, and the input energy. For the cohesive energy, the force between two grains connected by a capillary bridge was proportional to $\gamma\, d$ where γ is the surface tension between the liquid and the grain. To break the capillary bridge, the two grains must be moved away from each other by a distance of the order of d, so that the cohesion energy is $E_c \sim \gamma\, d^2\, D^2/d^2$. Note that here, we will use cohesive energy associated with solid bonds since the drying process may lead to different cohesive effects. The breaking energy in our experimental approach will be the energy brought by the vibrations of the box, *i.e.*, $E_r \sim \rho D^3 (A\omega)^2$. We will consider the balance between the energy of cohesion (that may evolve over time) and the breaking energy of the agglomerates. We will not seek to determine the energy of cohesion, although this could empirically could be investigated through the impact of agglomerates [10, 12]. Instead, we will report the evolution of the average diameter of the agglomerates as a function of the diameter d of the particles (other parameters kept constant), and as a function of $A\,\omega$ (other parameters kept constant) for varying drying kinetics. We will seek scaling laws to describe the evolution of D that could be extrapolated to additional intensity of shear. The experiments will be used to obtain the numerical prefactors in our scaling laws.

Can we break agglomerates down to the particle size? We should emphasize that since the breaking energy of the agglomerate scales as D^3, whereas the cohesive energy scales as D^2, there will be a limit in the diameter of the agglomerates, $D_{\min}$, below which it will likely be impossible to break the agglomerates. We should be able to obtain the expected intensity of shear required for a given system to reach this limit through the combination of experiments and scaling laws approach. However, this particular limit may not be reached experimentally with our model system for some configurations of small particles. We should be able to estimate this threshold value by comparing the energy of cohesion to the input energy.

Expected outcome of objective 1. The development of the experimental setup and the characterization methods. The successful completion of this task will provide a unique tool to provide the final agglomerates size distribution but also the evolution during the process to identify which steps may be the more important. This tool will then be used to characterize some powders and develop regime maps to identify the role of the time, temperature, relative humidity, and high shear stress on the drying of wet powders. A modeling framework that will consider the energy input versus the energy of cohesion will be considered to capture the mean size of the agglomerates. Such an approach should allow a first extrapolation of these results to actual processes.

Objective 2. Drying at low and medium shear

Industrially, the processes of drying wet powders in the presence of shear to avoid agglomeration are diverse involving configurations with large differences in input energy and shear. The tool that will be developed in objective 1 aims at reaching high-shear and input energy, similar, for instance, to an agitated dryer. However, other methods, such as belt or rotation dryers, involve low or medium shear that will not be captured with the previous approach. The second main objective of the proposed project will rely on the development of a thin experimental drum, shown in figure 5(a), in which the shear will be imposed by the rotation rate, and the temperature and ambient humidity will be controlled in a similar approach while allowing in the same time to observe the drying dynamics.

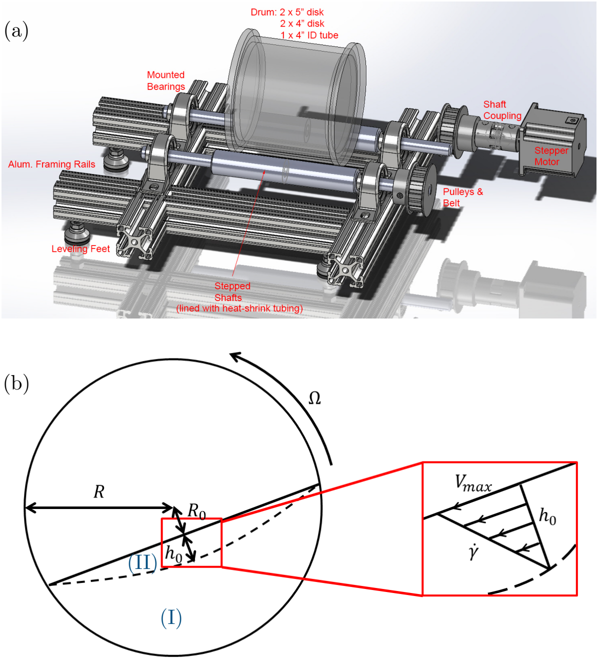


Figure 5: (a) Schematic of the rotating drum available in the PI's lab. (b) Schematic describing the properties of the flow in a rotating drum.

▷ **Why is a rotating drum a good approach to model medium shear rates?** The rotating drum is one of the classical experimental configurations for the study of granular flows, which allows obtaining a stationary and cyclic flow. This system can also be used as a mixer [25] and has been shown to provide relevant information regarding the flow of powders [26]. In our study, the interest of the rotating drum lies in the periodicity of the flows that it generates, which makes it possible to observe the evolution of the agglomerates over long times, *i.e.*, during the entire drying process. The flows encountered in a rotating drum depend on the rotational speed of the cylinder, Ω. We will work in the continuous regime characterized by a stationary flow of grains at the surface. The flow of grains in the continuous regime occurs in two stages: (1) a rotation phase where the grains are at the bottom of the pile and have a solid rotational motion following the cylinder wall and then (2) an avalanche flow phase when the grains reach the surface. These two phases can be seen in figure 5(b). Models of the velocity field in a granular drum flow are well-known in the literature. The flow field exhibits a linear profile in the active layer (region II in figure 5(b)), which concentrates most of the shear, and a tail of exponentially zero-trending profile in the passive zone, having a solid-body rotation with the cylinder. The shear rate in the linear part is approximately constant and its amplitude is of the order of $\dot{\gamma} \simeq \sqrt{g/(4\,d)}$ [27], where d is the size of the particle or agglomerate. Since the velocity profile is linear in this region, the shear rate can be written as $\dot{\gamma} = V_{max}/h_0 = \bar{V}/(2h_0)$, where $\bar{V}$ is the average velocity in the layer and h_0 the thickness of the flowing layer that can be controlled with the rotation rate and the filling rate of the drum [28]. We will work in the situation where the thickness of the flowing layer is larger than the mean radius of the agglomerate so that it will be advected by the granular flow and subject to a controlled shear. We plan to perform the first tests in a range of rotational speed between 15 and 60 rpm. In summary, this configuration allows to quantitatively impose a rather low shear of the order of $\dot{\gamma} \sim 100\,\mathrm{s}^{-1}$.

▷ **Apparatus.** The experimental system that we have in our laboratory is illustrated in figure 5(a). This system consists of a cylinder with a diameter that can be varied (the first tests will be done with a diameter of about 10 cm, but this could be adjusted to provide more control over the shear rate). We will choose small drum thicknesses, typically of the order of the centimeter, to be able to measure in real-time the evolution of the roughness of the free surface, which ideally will give us information on the characteristic size of the agglomerates flowing at the surface. The cylinder is rotated by two rollers and driving at a rotation speed of 0 to 60 rotations per minute.

▷ **Principle of the measurements.** Similarly to the oscillating box described in the previous objective, we will prepare a sample of wet powders that will be placed in the rotating drum. The axis of the cylinders will be made of two holes so that the temperature and humidity will be controlled by placing the setup in the same environmental chamber. The experiments will start at $t = 0$, and we will visualize the flow within the rotating drum from the side. The roughness of the interface should provide us with information on the evolution of the agglomerates and, in particular, the cohesion between the grains. The main challenge with this setup is that the direct measurement of the agglomerate size during the process is much harder. However, the rotating drum could easily be stopped during the experiments to pick up a small sample and measure the properties and size distributions of the agglomerate before resuming the experiments, as we have done for the blending process in the past [8]. Methods similar to the one developed in the previous objective will be used to obtain the size distribution and the average agglomerate size.

▷ **Modeling.** For this system, we will use a similar approach to the one presented in the previous objective. The cohesive energy between the particles is expected to remain similar, but the force exerted on the grains will be different. Past experiments with wet granular materials have shown that the force exerted on an agglomerate of diameter D scales as $F \sim \pi D^3 \rho g$ or $F \sim \pi D^2 \rho g h \mu$ depending on the size of the aggregate [29]. We will compare this force to the cohesive force to provide a scaling law of the mean agglomerate size (note here also that the prefactors will rely on experimental measurements).

Expected outcome of objective 2. The development of an experimental setup to characterize the drying of powders under medium shear and visualize the agglomerates during the process. The image analysis to obtain the time evolution of the particle size distribution will be similar to the methods developed in parallel to objective I.

Objective 3. Leveraging the tools: regime map of the resulting agglomerates formed

▷ **Validation of the methods.** The PI will use these two setups with model powders. The following ones have been identified as good candidates for hard inorganic powders: calcium aluminate, calcium carbonate, and silica glass sphere as they will not (or little) react with the liquid phase, *i.e.*, water within the framework of the project. Our goal is to choose materials that will not be too soluble to not precipitate when mixed with water. We will characterize the initial size distribution of each powder before using them in the experiments. Typically, we aim for powders of the size of order $10\,\mu$m and initially, the liquid phase that will be used is water. We will consider the role of the following parameters on the size distribution of the agglomerates to build a regime map of the outcome of the agglomeration following drying of wet powders under shear: (i) shear rate $\dot{\gamma}$, (ii) initial water content, (iii) dynamics of drying (controlling the relative humidity and the temperature), (iv) size distribution of the initial powders. Of particular interest, especially with the oscillating box, is that we will be able to track the dynamic evolution of the size distribution. We also aim to rationalize the evolution of the mean agglomerate size by considering the balance between the input energy to the system and the cohesion between particles.

▷ **Interactions with IFPRI.** The core of the project is the development of these two innovative tools and their testing on some model powders. After the first characterization made with the model powders, the PI will seek candidate materials (samples) from interested companies within the IFPRI consortium. In particular, it could be interesting to also qualitatively consider the configuration of soft inorganic materials.

Expected outcome of objective 3. The last objective of this project will be to demonstrate the relevance of the two diagnostic tools with model and more realistic powders. The main result will be the size distribution and the mean size of the agglomerates under different drying dynamics and shear and simple models to account for their evolution with the input parameters.

4 CONCLUSION

Outcome. The proposed project will develop innovative tools to characterize the resulting size distribution of agglomerates resulting from the drying of wet powders under controlled shear. The oscillating amplitude and frequency will control the input energy in the case of the oscillating box, whereas it will be controlled through the size and rotation rate of the container for the rotating drum experiments. In both experiments, the temperature and the relative humidity will be controlled thanks to an environmental chamber. Using these systems, we will be able to collect experimental data and rationalize the evolution with the different parameters through scaling laws.

Tentative timeline. Year 1 will be devoted to the development of the oscillating box, the diagnostic methods, and model experiments with silica beads and water. Year 2 will be devoted to running experiments with more complex powders in the oscillating box (from which the PI will seek the input of the IFPRI members), as well as the development of the rotating drum experiments and its testing with the same model powders. Finally, year 3 will be used to build the regime map (dynamics and final size distribution of the agglomerate) for varying powders, shear rate, and temperature/humidity conditions. The key results will be the resulting average agglomerate size and dispersion of the distribution around the mean value. Similar to his past works, the PI will also look for theoretical approaches that could capture, at least qualitatively, these evolutions and could thus be used to provide some guidelines for industrial processes involving the drying of wet powders. Interactions with the IFPRI members will be sought to consider relevant powders and refine our approach during the project.

References Cited

[1] G. V. Barbosa-Cánovas, E. Ortega-Rivas, P. Juliano, and H. Yan, *Food powders*. 2005.

[2] J. N. Michaels, “Toward rational design of powder processes,” *Powder technology*, vol. 138, no. 1, pp. 1–6, 2003.

[3] A. Goldszal and J. Bousquet, “Wet agglomeration of powders: from physics toward process optimization,” *Powder Technology*, vol. 117, no. 3, pp. 221–231, 2001.

[4] D. G. Bika, M. Gentzler, and J. N. Michaels, “Mechanical properties of agglomerates,” *Powder technology*, vol. 117, no. 1-2, pp. 98–112, 2001.

[5] K. Dhanalakshmi, S. Ghosal, and S. Bhattacharya, “Agglomeration of food powder and applications,” *Critical reviews in food science and nutrition*, vol. 51, no. 5, pp. 432–441, 2011.

[6] S. H. Schaafsma, P. Vonk, P. Segers, and N. W. Kossen, “Description of agglomerate growth,” *Powder technology*, vol. 97, no. 3, pp. 183–190, 1998.

[7] G. Saingier, *Mécanismes et dynamiques d'interactions entre grains et liquide: du matériau granulaire sec au mélange saturé*. PhD thesis, Sorbonne université, 2018.

[8] P. Jop, G. Saingier, and A. Sauret, “Wet rolling stones: Growth of a granular aggregate under flow,” in *EPJ Web of Conferences*, vol. 249, p. 09012, EDP Sciences, 2021.

[9] H. Hayashi, “Drying technologies of foods-their history and future,” *Drying technology*, vol. 7, no. 2, pp. 315–369, 1989.

[10] J. Fu, G. K. Reynolds, M. J. Adams, M. J. Hounslow, and A. D. Salman, "An experimental study of the impact breakage of wet granules," *Chemical Engineering Science*, vol. 60, no. 14, pp. 4005–4018, 2005.

[11] J. D. Litster, K. Hapgood, J. N. Michaels, A. Sims, M. Roberts, S. Kameneni, and T. Hsu, "Liquid distribution in wet granulation: dimensionless spray flux," *Powder Technology*, vol. 114, no. 1-3, pp. 32–39, 2001.

[12] J. Fu, M. Adams, G. Reynolds, A. Salman, and M. Hounslow, "Impact deformation and rebound of wet granules," *Powder Technology*, vol. 140, no. 3, pp. 248–257, 2004.

[13] H. G. Kristensen, "Particle agglomeration in high shear mixers," *Powder Technology*, vol. 88, no. 3, pp. 197–202, 1996.

[14] B. J. Ennis, "Agglomeration and size enlargement session summary paper," *Powder technology*, vol. 88, no. 3, pp. 203–225, 1996.

[15] F. Boulogne, A. Sauret, B. Soh, E. Dressaire, and H. A. Stone, "Mechanical tuning of the evaporation rate of liquid on crossed fibers," *Langmuir*, vol. 31, no. 10, pp. 3094–3100, 2015.

[16] A. Sauret, F. Boulogne, B. Soh, E. Dressaire, and H. A. Stone, "Wetting morphologies on randomly oriented fibers," *The European Physical Journal E*, vol. 38, no. 6, pp. 1–9, 2015.

[17] P. S. Raux, A. Troger, P. Jop, and A. Sauret, "Spreading and fragmentation of particle-laden liquid sheets," *Physical Review Fluids*, vol. 5, no. 4, p. 044004, 2020.

[18] V. Thiévenaz and A. Sauret, "Pinch-off of viscoelastic particulate suspensions," *Physical Review Fluids*, vol. 6, no. 6, p. L062301, 2021.

[19] G. Saingier, A. Sauret, and P. Jop, "Accretion dynamics on wet granular materials," *Physical review letters*, vol. 118, no. 20, p. 208001, 2017.

[20] A. Cervantes-Álvarez, Y. Escobar-Ortega, A. Sauret, and F. Pacheco-Vázquez, "Air entrainment and granular bubbles generated by a jet of grains entering water," *Journal of colloid and interface science*, vol. 574, pp. 285–292, 2020.

[21] D.-H. Jeong, A. Kvasnickova, J.-B. Boutin, D. Cébron, and A. Sauret, "Deposition of a particle-laden film on the inner wall of a tube," *Physical Review Fluids*, vol. 5, no. 11, p. 114004, 2020.

[22] E. Villermaux, "Fragmentation," *Annu. Rev. Fluid Mech.*, vol. 39, pp. 419–446, 2007.

[23] S. M. Iveson, J. D. Litster, K. Hapgood, and B. J. Ennis, "Nucleation, growth and breakage phenomena in agitated wet granulation processes: a review," *Powder technology*, vol. 117, no. 1-2, pp. 3–39, 2001.

[24] P. Suresh, I. Sreedhar, R. Vaidhiswaran, and A. Venugopal, "A comprehensive review on process and engineering aspects of pharmaceutical wet granulation," *Chemical Engineering Journal*, vol. 328, pp. 785–815, 2017.

[25] J. M. N. T. Gray, "Granular flow in partially filled slowly rotating drums," *Journal of Fluid Mechanics*, vol. 441, pp. 1–29, 2001.

[26] F. Boschini, V. Delaval, K. Traina, N. Vandewalle, and G. Lumay, "Linking flowability and granulometry of lactose powders," *International journal of pharmaceutics*, vol. 494, no. 1, pp. 312–320, 2015.

[27] GDR MiDi, "On dense granular flows," *The European Physical Journal E*, vol. 14, pp. 341–365, 2004.

[28] J. Rajchenbach, "Granular flows," *Advances in physics*, vol. 49, no. 2, pp. 229–256, 2000.

[29] G. Lefebvre and P. Jop, "Erosion dynamics of a wet granular medium," *Physical Review E*, vol. 88, no. 3, p. 032205, 2013.

IFPRI
International Fine Particle
Research Institute

Research Project Brief

Spray-Drying of Pastes for Process Intensification

The International Fine Particle Research Institute (IFPRI) wishes to fund a research project on spraying of highly concentrated materials (pastes) as a means of improving process sustainability. Spray-drying of liquid products is a key technology that is widely used in many industries. Its environmental impact could be reduced through process intensification by increasing the concentration of the feed liquid to be dried, thereby reduce energy consumption and process footprint. This would require the ability to atomize highly viscous liquids (especially pastes) and achieve short drying times to produce a suitably dry product that does not stick to process surfaces without changing functionality of the dried product.

Key objectives of this project are:

- Identify and validate one or more atomization technologies that will enable spraying highly viscous liquids (up to 100 Pa.s) or dispersions with high solids fraction (pastes) and generate droplets smaller than 100 micron [see references below]
- Develop methods to measure drying kinetics of highly viscous liquid or paste droplets in controlled temperature and humidity conditions.
- Evaluate the impact of the composition and morphology of the atomized droplets on the drying kinetics and develop drying models for highly concentrated feeds.

The scope of this project is limited to viscous aqueous solutions and high solids fraction suspensions, with no limitation on the solute or dispersed particles. IFPRI members can provide recommendations for experimental systems and perhaps provide materials for study.

Some relevant papers on atomization approaches are:

1. Stähle, P., et al. (2017). "Comparison of an Effervescent Nozzle and a Proposed Air-Core-Liquid-Ring (ACLR) Nozzle for Atomization of Viscous Food Liquids at Low Air Consumption." Journal of Food Process Engineering 40(1)
2. García, J. A., et al. (2016). "Experimental characterization of the viscous liquid sprays generated by a Venturi-vortex atomizer." Chemical Engineering and Processing - Process Intensification 105: 117-124
3. Czisch, C. and U. Fritsching (2008). "Atomizer design for viscous-melt atomization." Materials Science & Engineering A 477(1-2): 21-25

Research proposal for IFPRI-Grant

Spray-Drying of Pastes with ACLR-Nozzle for Process Intensification

Creators:
P. D. Dr. Volker Gaukel, M.Sc. Miguel Ballesteros, M. Sc. Sebastian Höhne
Karlsruhe Institute of Technology
Institute of Process Engineering in Life Science
Chair for Food Process Engineering
Kaiserstr. 12
76131 Karlsruhe
Germany

Recipient:
Jim Michaels
Vice President, Industry-Academia Liaison
International Fine Particle Research Institute (IFPRI)
2045 Wooddale Dr. Woodbury
Minneapolis 55125
USA

Date: 19th April 2022

Description of research proposal

1 Topic of the research project

Spray-Drying of Pastes with ACLR-Nozzle for Process Intensification

2 Introduction and background

Spray-drying is a widely used process for the production of powdered products from liquid formulations. The spray-drying process can be divided into three main steps: Atomization, convective drying in a hot air stream, and powder separation [1]. A scheme is shown in Figure 1.

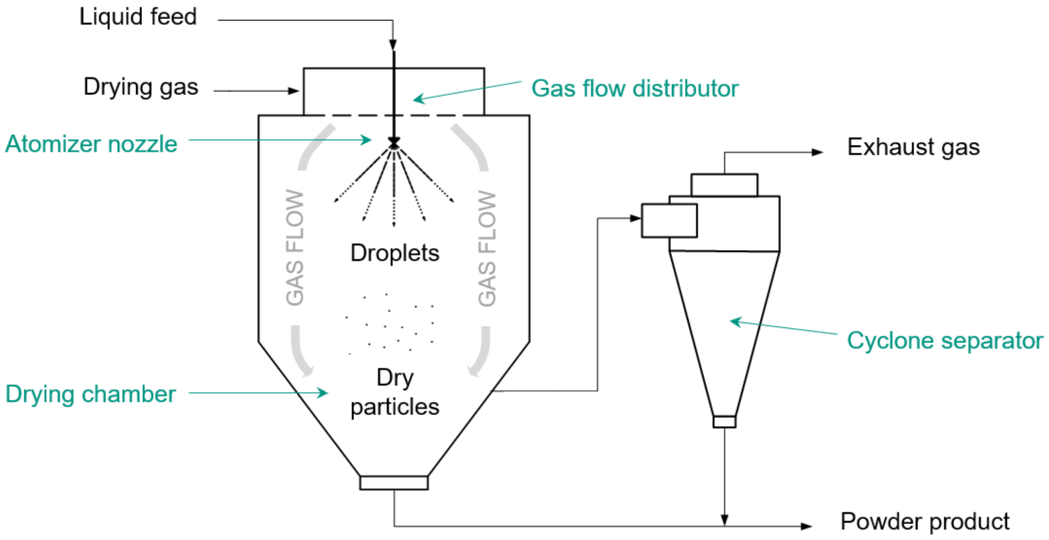


Figure 1: Schematic of the spray-drying process

The atomization of a bulk liquid into small droplets leads to a drastic enlargement of the surface-to-volume ratio, enhancing heat and mass flow in the subsequent convective drying step. The surface-to-volume ratio conditions product quality, since particles that are too small can burn, while particles that are too large do not dry sufficiently. The latter leads to increased stickiness of the particles, powder adhesion in the process equipment and storage problems [2]. Therefore, a narrow droplet size distribution is generally favorable. As with all drying processes, water removal is a very energy-consuming process, especially as internal-energy recovery is restricted in spray-drying [3]. Moreover, the powder throughput of a spray-dryer is limited by its specific water evaporation rate at given process conditions [2]. In industrial applications, the aim is therefore to feed the media into the drying process with the lowest possible water content (high dry matter content). This allows a higher product throughput with a constant water evaporation rate.

Using more energy-saving methods, such as membrane processes or multi-stage evaporation, for the upstream concentration, the total energy consumption and process footprint can be reduced. According to a model calculation on industrial spray drying by Fox et al. [4], an increase in feed dry matter content by 1% leads to a decrease in thermal energy consumption of the spray dryer by 3.8%. It also leads to a decrease in total energy consumption of 2.5%, when the energy for pre-concentration in an evaporator is taken into account. However, the dry mass content cannot be increased at will, since the viscosity of the liquid also increases with increasing solid concentration [5]. At high viscosities, the atomization step becomes more energy intensive, since the volume-specific atomization energy requirement for droplet breakup increases sharply as the internal resistance forces of the liquid increases. Larger droplets and/or wider spray droplet size distributions are then produced, up to the point where atomization is no longer possible.

For droplet formation, pressure-swirl (PS) nozzles are commonly used in spray-drying processes on industrial scale [1]. However, for PS nozzles the highest processable viscosity is considerably lower, compared to pneumatic nozzles [6].

Pneumatic atomizers are usually used for atomizing highly viscous liquids. The atomization energy is transferred via a gas stream [7]. In this type of atomizers, a distinction is also made between external-mixing and internal-mixing atomizers, depending on where the gas and liquid flows are combined [8]. An advantage of external mixing nozzles is that the gas and liquid flows can be set independently of each other. However, they tend to produce wide droplet distributions unless high rates of atomizing gas are used [9]. This makes the use of external-mixing pneumatic atomizers on an industrial scale not economically feasible.

In internal-mixing nozzles, an already formed two-phase flow exits through the nozzle channel. This allows for a more efficient transfer of energy from the gas to the liquid [9], as well as the ability to handle higher-viscosity liquids than with pressure swirl nozzles [10]. A drawback is that gas and liquid flow cannot be set entirely independently of each other [11].

With that in mind, the LVT-Institute developed a specific type of internal-mixing nozzle atomizer, the Air-Core-Liquid-Ring (ACLR) atomizer. A schematic of this nozzle can be seen on Figure 2 (left). The device is composed of two concentric tubes. The outer tube is where the liquid feed flows, while a capillary at the center carries the gas and injects it in the center of the mixing chamber. This forms an annular liquid flow, with a gas core. As this two-phase flow exits the nozzle through the outlet channel, the gas phase expands, and the liquid phase forms a cone like lamella that then disperses into droplets. The thickness of the lamella is correlated with the droplet size while the outlet diameter of the nozzle is much larger, typically larger than 1.5 mm. This nozzle design allows for relatively large particles in the feed stream, as the risk of clogging is low. The studies so far published, have involved both experimental and numerical analysis of the atomizer, to better understand its performance and its potential (see Figure 2 (right)). The ACLR nozzle has been proven successful for the atomization of highly viscous liquids up to 690 mPa·s [11].

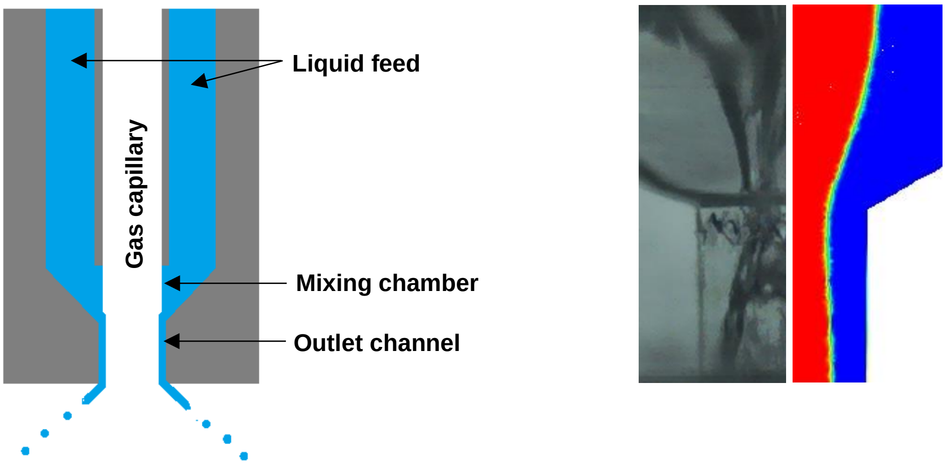


Figure 2: Scheme of the ACLR nozzle (left). Experimental high-speed image of the flow inside the nozzle and the computational simulations performed to represent the internal flow in the atomizer (right)

With the aid of high-speed images of the two-phase flow inside the atomizer, Stähle et al. [10] showed that, if a continuous liquid annular flow forms in the nozzle outlet channel, a stable spray is formed with small droplets. Wittner et al. showed the potential applicability of the ACLR for reducing total energy consumption in spray-drying processes, with theoretical energy savings of up to 29% [12].

Despite these major benefits of the ACLR nozzle, further studies on the scale-up potential of ACLR atomizers are still needed before a widespread application of the technology in industrial processes is conceivable. As reported by Wittner et al. [11], moisture content and water activity in the final powder product should be decreased to meet industrial demands. Additionally, based on Wittner et al. [13], we assume that in order to properly understand the process-function of the nozzle, and how spray performance relates to operating conditions and feed composition, we need to comprehend the flow behavior inside the ACLR nozzle. For this purpose, a CFD model is being developed in an ongoing project for the simulation of the internal flow of the ACLR-nozzle. Based on these investigations, it is assumed that the spray performance of the ACLR-nozzle can be enhanced by geometrical improvements. This should lead to a further reduction of the spray droplet size widths and increase the maximum possible viscosity that can be atomized for spray drying applications. In addition a further nozzle scale-up can be based on these results. Comprehending this process-function is therefore not only important for the atomization itself, but also for the subsequent drying step.

This process-function establishes the relation between the entry feed composition and droplet morphology. Nonetheless, it is well known that the droplet composition and morphology together with the process variables have a high impact on the final powder product [14–16]. Powder properties such as powder flowability, particle size, as well as particle and bulk density relate directly to the morphological structure of the powder particles. Although morphology is material-specific, it is also dependent on, for example, initial feed solids content, atomization and drying temperature [15]. The work of Hecht and King [17] also showed, that morphological changes, such as vacuole formation, can influence mass transfer rates and therefore drying kinetics. Consequently, it is very import to investigate the dynamic interactions between particle composition, morphology development and drying kinetics.

One way to examine the drying kinetics and morphology development is to directly observe the structure of the drying spray-droplets. This also allows acquiring accurate insights into the structural changes during the drying process. Direct observation of the drying droplets is unrealistic in a commercial spray-dryer or a modular nozzle test rig, due to the number of droplets and the difficult accessibility of the equipment. Furthermore, the transition from a droplet to a particle during spray-drying occurs quasi-instantaneously, which makes it almost impossible to track the drying kinetics and the morphology development of the particle. Consequently, for mechanistic studies of the drying process, experimental setups that center around drying a single droplet have been more and more the focus of research [18].

In single droplet drying (SDD) experiments, an isolated droplet is dried under a controlled drying environment [19]. The drying temperature, air humidity and air mass flow is set to mimic the convective drying process during spray-drying. Several experimental setups exist for SDD and are usually divided into levitation methods and free flight drying methods. Free flight drying methods are rather impractical for the examination of drying kinetics, as a continuous tracking of the droplet during drying is not possible. A commonly employed contact levitation method is a SDD experiment with a droplet suspended on a thin filament [20–22]. This allows easy monitoring of droplet mass and temperature changes of the droplet [23]. A drawback of this method is the intrusiveness of the filament on heat transfer.

An alternative to contact levitation is the immobilization of the droplet by acoustic levitation. In acoustic levitation, a single droplet is suspended due to a counterbalancing acoustic force while drying. [24]. A major benefit of this setup is that the drying of a droplet can be investigated non-intrusively, while one drawbacks is the not well-understood influence of the ultrasound on the drying kinetics.

Another tool to investigate one-dimensional drying kinetics is thin film drying [25]. Previous work has shown that a film thickness of micrometer- to nanometer-scale is feasible [26]. Schutyser et al. [18] has suggested that thin film drying technology could be a valuable tool to compliment the results generated by single droplet drying experimental setup.

Single droplet drying has been used extensively in literature for studying the morphology development, both by contact levitation [20,22,27] as well as by non-contact levitation [14,23,28,29]. The SDD setups are usually equipped with a CCD-camera with microscope optics for a continuous observation of the droplet during drying. Crust formation and structural changes can thus be determined directly. Nuzzo et al. [23] found for milk powder that it was possible to predict the morphology of spray-dried particles largely by means of SDD experiments, despite significantly longer drying times. The effects in the SDD tests were significantly more pronounced compared to the spray-drying tests. It is therefore expected that, despite the different drying systems, conclusions can be drawn between SDD and spray-drying tests with respect to the development of the particle morphology during drying.

The LVT-institute has many years of experience with single droplet experiments and equipment for the investigation of e.g. interfacial properties in single droplets. This mainly involves equipment with droplets suspended on filaments. In a just started research project financed by German Ministry BMWi, the LVT-Institute develops an experimental setup for SDD.

3 Project objectives

Spray-drying of liquid products is a key technology that is widely used in many industries. Its environmental impact could be reduced through process intensification by increasing the concentration of the feed liquid to be dried, thereby reduce energy consumption and process footprint. This requires the ability to atomize highly viscous liquids (especially pastes) and achieve short drying times to produce a suitably dry product that does not stick to process surfaces without changing functionality of the dried product. Key objectives of this project are:

- Validate the ACLR atomizer technology to enable spraying of highly viscous liquids for spray drying applications by improvement and upscale of the ACLR-nozzle.
- Evaluate the impact of the composition and morphology of the atomized droplets on the drying kinetics and develop drying models for highly concentrated feeds by single droplet drying.
- Investigation of the applicability of the ACLR nozzle for spray-drying of highly viscous liquids.

4 Methodology and work plan

The project is divided into three main working packages (WP). The ACLR nozzle is proposed as a suitable atomization technology for spraying of highly viscous liquids or pastes and generate droplets smaller than 100 micron. The central task of the first working package (WP) will be the validation of the ACLR nozzle to enable atomization of highly viscous liquids. CFD simulations will be used to optimize nozzle design. Process- structure-functions for the nozzle will then be established based on spray performance measurements. The gained insights can be used for further upscaling of the process. A period of 18 months is planned for this work package.

The objective of the second WP is to investigate the impact of the composition and process parameters on the drying kinetics and morphology development of highly viscous liquid or paste droplets in controlled conditions. For this purpose single droplet drying experiments will be carried out, in which droplets can be dried under precisely defined conditions. These studies will also be used to explore a possible relation between the morphology development and the drying kinetics. Taking into account the results of the first two WPs, a model for drying of highly concentrated feeds will be formulated as process-structure-function. Work on the second WP will start after viable formulations for the project are identified. It is currently estimated that the WP will be concluded after 18 months.

In the third WP, the applicability of the ACLR nozzle for industrial spray-drying processes of highly viscous liquids will be examined. For this purpose, spray-drying trials will be carried out. The results will be used to evaluate the validity of the in WP 2 formulated model. WP 3 will be the main workload during the project’s third year. It is estimated, that work on the final WP will start after the first two WPs have been completed and the process-structure-function has been elucidated in WP 2.

A working diagram is shown in Table 1.

Table 1: Working diagram for the planned project duration

Project year	1				2				3			
Quarter	I	II	III	IV	I	II	III	IV	I	II	III	IV
WP 1: Atomization with the ACLR nozzle	■	■	■	■	■	■						
WP 2: Evaluation of the impact of composition and morphology on drying kinetics			■	■	■	■	■	■				
WP 3: Industrial applicability of the ACLR nozzle for spray-drying									■	■	■	■

4.1 WP 1: Atomization with the ACLR nozzle

Numerical studies on the ACLR atomizer started with Wittner et al. [13], where an initial computational model to represent the multiphase flow inside the system was developed, using Ansys Fluent. This model is currently being refined, under a project financed by the DAAD. The objective of this research is that the predicted annular multiphase flow inside the nozzle can be used as an indication of whether a stable flow with the selected process and formulation conditions is possible, which corresponds with a stable atomization. In this way, the operational limits of the current nozzle design are determined, which serves as a basis for geometrical optimization or tailoring of the nozzle design for specific industrial applications.

In WP1 this model will be extended to the flow analysis of highly viscous liquid feeds. On the basis of the CFD results, the suitability and limitations of the nozzle design and atomization system will be determined, which allows the development of an improved nozzle concept. The focus of the research will be on the evaluation of process-structure-function for the nozzle. Therefore, the atomization capability of two different highly viscous liquids will be investigated. Process parameters are the nozzle design, the ratio of air-to-liquid flow rate (ALR) and the air pressure. Structure variables are the spray angle and the droplet size distribution, including its temporal stability. As model system, aqueous solutions of starch and derivatives (like maltodextrin) are proposed. Starch and its derivatives are commonly used as thickener and stabilizing agent and can form aqueous solutions and suspensions. To ease the transfer of knowledge between the research results and industry partners, the partners could also provide relevant model liquids and suspensions. Nonetheless, the model system has to be defined and characterized at the beginning of the experimental study, to allow a systematic investigation of the relevant process parameters.

For validation of the CFD model, the flow pattern inside the nozzle will be analyzed. Taking into account the numerical and experimental results, a comparative analysis can be done to investigate the feasibility of spraying highly viscous liquids and pastes to generate droplets smaller than 100 µm. The current CFD model has shown so far good agreement with experimental data up to 400 mPa·s, and will be further used with higher viscosities. The experimental study can be carried out on the institute's facilities. The setup has been proven successful for viscosities of up to 690 mPa·s with droplet sauter mean diameter of around 70 µm.

On the basis that Kelvin-Helmholtz instabilities lead to a disintegration of the liquid lamella which ends in droplet formation, one can roughly estimate the maximum viscosity that can be atomized by the current ACLR nozzle. For this rough estimation The droplet diameter was calculated, taking Kelvin-Helmholtz sheet instabilities into account (Equation 1). The equation for the droplet diameter x_d is given by

$$x_d = 1{,}882 \left(\frac{8a_b}{k_{max}}\right)^{\frac{1}{2}} (1 + Oh)^{\frac{1}{6}} \qquad (1)$$

with half of the width of the liquid sheet a_b in m, the wave number of the maximum instability k_{max} in 1/m and the dimensionless Ohnesorge number *Oh*, a dimensionless number that relates the viscous forces to inertial and surface tension forces [30]. For estimation of k_{max} eq. 1 was used with measured values at 140 mPa s. The development of lamella thickness was estimated in case 1 (C1) to develop linear with the droplet size for 690 mPas and then extrapolated for higher virtual viscosities. In a second case (C2) it was assumed that the lamella thickness is constant. The results are shown in table 2.

*Table 2: Estimations of lamella thickness depending on the liquid viscosity. *measured values*

Liquid viscosity η in mPa·s	**Lamella thickness d_l in mm, C1**	**Droplet diameter x_d in µm**	**Lamella thickness d_l in mm, C2**	**Droplet diameter x_d in µm**
140*	0.130*	43*	-	-
690*	0.228	70*	-	-
1000	0.290	86	0.290	86
2000	0.490	120	0.290	96
5000	1.09	195	0.290	112

Allowing the lamella thickness to increase leads to comparably large droplets e.g. 195 µm at 5 Pa s. Assuming the lamella thickness to be constant leads only to a moderate increase of the droplet size from 86 mm to 112 µm while the viscosity increases from 1 to 5 Pa s. This calculation is very limited in its significance but one can state that the lamella thickness has a much higher impact on the droplet size than the viscosity. This leads to the conclusion that if its possible e.g. by constructional means or process variables like the air pressure to limit the increase of the lamella thickness, it should be possible to produce droplets which are small enough for spray drying even at high liquid viscosities.

The available facilities for these investigations are: Air compressor which can be operated at pressures of up to 9 bar (RSF-Top 7.5, Renner GmbH, Güglingen, Germany); A pressure vessel and various eccentric screw pumps with volume flow between 5 and 100 L/h for the liquid supply; A test rig equipped with a temperature control for the feed liquid. Here the spray droplet sizes can be measured over time using a laser diffraction spectrometer (Malvern Spraytec, Malvern Panalytical Ltd, Malvern, United Kingdom) in a size range of 2-2000 µm; A high-speed imaging system (OS3-V3-S3, Integrated Design Tools Inc., Tallahassee, FL,USA) is available to analyze the spray angle and the flow pattern inside the atomizer. The rheological characterization of the model systems can be executed with a double gap system (Physica MCR 101/103, Anton Paar, Graz, Austria).

4.2 WP 2: Evaluation of the impact of the composition and morphology on the drying kinetics and model development by single droplet drying

The development of a suitable methodology for single droplet drying experiments is already being pursued at the institute as part of the AiF project 21662 N "Spray-drying of emulsions for microencapsulation". For this project, an experimental setup is will be installed that allows continuous monitoring of the drying kinetics and particle morphology during the drying of emulsion droplets.

In WP 2, the experimental setup for emulsion droplets will be extended to droplets of highly viscous solutions. This is expected to be fairly straightforward. A potential challenge is mainly seen in the production of uniform droplets from formulations with varying solids concentrations, as the rheological behavior differs between these formulations. Using of different droplet injection systems might be necessary. Nevertheless, as the development of the experimental setup is still in its early stages, advices and experiences of industry partners on single droplet drying could prove valuable. The experimental studies in WP 2 will focus on the influence of air temperature, air velocity and total solids content on the drying kinetics and morphology development during convective drying. Therefore, the same highly viscous liquids will be used as in WP 1. By monitoring droplet size, evaporation rate and temperature profiles of the droplet, the drying kinetics can be determined. For the morphology development, different structural changes are expected. Besides changes in particle size, other phenomena may occur during drying of a liquid droplet. These include the formation of an inhibitory skin, changes in the surface structure (smooth or wrinkled), and rupture of the particle. To observe these phenomena, various analytical methods are available at KIT. In addition to light microscopy and SEM (scanning electron microscopy) images, the particles can be examined in µCT (micro computed tomography). Solubility tests can provide information about the properties of the particle skin.

Based on the results of the experimental study a model for the drying of highly viscous liquids will be developed. The model will be formulated as a process-structure-function to elucidate the impact of feed composition and morphology development on the drying kinetics.

4.3 WP 3: Proof-of-concept of industrial applicability of the ACLR nozzle for spray-drying of highly viscous liquids

It is expected that from the results of WP1 and WP2 conclusions can be drawn on possible process windows for atomization (WP1) and drying (WP2) conditions for highly viscous liquids. In WP3 the applicability of these conditions on a spray drying process will be investigated. This will be executed in pilot scale on the institute's spray-dryer (Werco SD-20, Fa. Hans G. Werner, max. water evaporation capacity of 20 l/h, max. air inlet temperature 250 °C, max. air outlet temperature 100 °C). Solutions with the highest possible viscosity at acceptable spray droplet size are selected for this purpose. The spray-drying experiments can be conducted under variation of the air temperature at the inlet (160-220 °C) and outlet (65-95 °C), the air velocity and the spray droplet size. This way, the drying rate and the surface-to-volume ratio in the particle are varied. Measurements of the residual moisture content can be used to validate the drying kinetics determined in WP 2. After spray-drying, the structure of the produced powder will be characterized and compared to the results of WP 2. The same powder characterization methods can be used as in WP 2. The results allow a validation of the process-structure-function developed in WP 2, which will be modified if necessary.

Figure 3: The institute's pilot scale spray-dryer

5 Transfer of knowledge

Based on the results, solution concepts can be derived that contribute to a targeted and understanding-based process design for the production of powder products from highly viscous liquids. These solution concepts form the basis for an implementation by the industrial user with their own recipes and processes. The research results can be presented and discussed in accompanying meetings and appropriate international conferences and are summarized in annual reports. The results will be published in appropriate international journals.

6 References

[1] Mujumdar A. S., Ed., 2015. *Handbook of industrial drying,* 4th ed., CRC Press, Boca Raton.

[2] Masters K., 2002,"Spray Drying in Practice," SprayDryConsult International.

[3] Baker C. G. J., and McKenzie K. A., 2005,"Energy Consumption of Industrial Spray Dryers," Drying Technology, **23**(1-2), pp. 365–386.

[4] Fox M. B., Akkerman C., Straastma H., and Jong P. de, 2010,"Energy reduction by high dry matter concentration and drying," New Food(2).

[5] Rao M. A., 2014. *Rheology of Fluid, Semisolid, and Solid Foods: Principles and Applications,* 3rd ed., Springer, Boston, MA.

[6] Stähle P., Schuchmann H. P., and Gaukel V., 2017,"Performance and Efficiency of Pressure-Swirl and Twin-Fluid Nozzles Spraying Food Liquids with Varying Viscosity," Journal of Food Process Engineering, **40**(1), p. 1–12.

[7] Ashgriz N., 2011. *Handbook of Atomization and Sprays: Theory and Applications*, Springer Science+Business Media LLC, Boston, MA.

[8] Wozniak G., 2003. *Zerstäubungstechnik: Prinzipien, Verfahren, Geräte*, Springer, Berlin, Heidelberg.

[9] Hammad F. A., Sun K., Jedelsky J., and Wang T., 2020,"The Effect of Geometrical, Operational, Mixing Methods, and Rheological Parameters on Discharge Coefficients of Internal-Mixing Twin-Fluid Atomizers," Processes, **8**(5), p. 563.

[10] Stähle P., Gaukel V., and Schuchmann H. P., 2017,"Comparison of an Effervescent Nozzle and a Proposed Air-Core-Liquid-Ring (ACLR) Nozzle for Atomization of Viscous Food Liquids at Low Air Consumption," Journal of Food Process Engineering, **40**(1), e12268.

[11] Wittner M. O., Karbstein H. P., and Gaukel V., 2018,"Spray performance and steadiness of an effervescent atomizer and an air-core-liquid-ring atomizer for application in spray drying processes of highly concentrated feeds," Chemical Engineering and Processing - Process Intensification, **128**, pp. 96–102.

[12] Wittner M. O., Karbstein H. P., and Gaukel V., 2020,"Energy efficient spray drying by increased feed dry matter content: investigations on the applicability of Air-Core-Liquid-Ring atomization on pilot scale," Drying Technology, **38**(10), pp. 1323–1331.

[13] Wittner M. O., Ballesteros M. A., Link F. J., Karbstein H. P., and Gaukel V., 2019,"Air-Core–Liquid-Ring (ACLR) Atomization Part II: Influence of Process Parameters on the Stability of Internal Liquid Film Thickness and Resulting Spray Droplet Sizes," Processes, **7**(9), p. 616.

[14] Both E. M., Karlina A. M., Boom R. M., and Schutyser M., 2018,"Morphology development during sessile single droplet drying of mixed maltodextrin and whey protein solutions," Food Hydrocolloids, **75**, pp. 202–210.

[15] Walton D. E., and Mumford C. J., 1999,"Spray Dried Products—Characterization of Particle Morphology," Chemical Engineering Research and Design, **77**(1), pp. 21–38.

[16] Wu W. D., Liu W., Gengenbach T., Woo M. W., Selomulya C., Chen X. D., and Weeks M., 2014,"Towards spray drying of high solids dairy liquid: Effects of feed solid content on particle structure and functionality," Journal of Food Engineering, **123**, pp. 130–135.

[17] Hecht J. P., and King C. J., 2000,"Spray Drying: Influence of Developing Drop Morphology on Drying Rates and Retention of Volatile Substances. 1. Single-Drop Experiments," Ind. Eng. Chem. Res., **39**(6), pp. 1756–1765.

[18] Schutyser M. A. I., Both E. M., Siemons I., Vaessen E. M. J., and Zhang L., 2019,"Gaining insight on spray drying behavior of foods via single droplet drying analyses," Drying Technology, **37**(5), pp. 525–534.

[19] Fu N., Woo M. W., and Chen X. D., 2012,“Single Droplet Drying Technique to Study Drying Kinetics Measurement and Particle Functionality: A Review,” Drying Technology, **30**(15), pp. 1771–1785.

[20] Shamaei S., Kharaghani A., Seiiedlou S. S., Aghbashlo M., Sondej F., and Tsotsas E., 2016,“Drying behavior and locking point of single droplets containing functional oil,” Advanced Powder Technology, **27**(4), pp. 1750–1760.

[21] Wang Y., Che L., Selomulya C., and Chen X. D., 2014,“Droplet drying behaviour of docosahexaenoic acid (DHA)-containing emulsion,” Chemical Engineering Science, **106**, pp. 181–189.

[22] Malafronte L., Ahrné L., Schuster E., Innings F., and Rasmuson A., 2015,“Exploring drying kinetics and morphology of commercial dairy powders,” Journal of Food Engineering, **158**, pp. 58–65.

[23] Nuzzo M., Millqvist-Fureby A., Sloth J., and Bergenstahl B., 2015,“Surface Composition and Morphology of Particles Dried Individually and by Spray Drying,” Drying Technology, **33**(6), pp. 757–767.

[24] Al Zaitone B., 2009,“Drying of Multiphase Single Droplets in Ultrasonic Levitator,” Dissertation, Technische Universität Darmstadt, Darmstadt.

[25] Coumans W. J., 2000,“Models for drying kinetics based on drying curves of slabs,” Chemical Engineering and Processing: Process Intensification, **39**(1), pp. 53–68.

[26] Börnhorst T., Scharfer P., and Schabel W., 2021,“Drying Kinetics from Micrometer- to Nanometer-Scale Polymer Films: A Study on Solvent Diffusion, Polymer Relaxation, and Substrate Interaction Effects,” Langmuir the ACS journal of surfaces and colloids, **37**(19), pp. 6022–6031.

[27] Both E. M., Siemons I., Boom R. M., and Schutyser M., 2019,“The role of viscosity in morphology development during single droplet drying,” Food Hydrocolloids, **94**(303), pp. 510–518.

[28] Tran T. T. H., Terrazas-Velarde K., Avila-Acevedo J. G., and Tsotsas E., 2014, Particle morphology as a mean for investigating single droplet drying of dairy products, *IDS 2014: Proceedings of the 19th International Drying Symposium August 24-27, 2014, Lyon, France*, Andrieu J., Peczalski R., and Vessot S., eds., EDP Sciences, Les Ulis.

[29] Abdullahi H., Burcham C. L., and Vetter T., 2020,“A mechanistic model to predict droplet drying history and particle shell formation in multicomponent systems,” Chemical Engineering Science, **224**(9), 115713.

[30] Qin L., Yi R., and Yang L., 2018,“Theoretical breakup model in the planar liquid sheets exposed to high-speed gas and droplet size prediction,” International Journal of Multiphase Flow, **98**, pp. 158–167.

IFPRI

International Fine Particle
Research Institute

Research Project Brief

Numerical Modeling of Spray Droplet Formation

The International Fine Particle Research Institute (IFPRI) wishes to fund a research project on numerical modeling of droplet formation in atomization. Atomization is a critical process in many particle processes, and while the underlying physics of droplet formation is understood, quantitative simulation of atomizer performance is not yet possible. The objective of this project is to explore whether recent advances in simulation of complex fluid flows are sufficient to reproduce quantitatively the performance of commercial spray atomizers.

Specifically, the objective of this project is to develop an experimentally validated high-fidelity CFD model for spray atomization that captures both the near field behavior (sheet and filament formation and break up) and the ultimate far-field droplet size distribution. The model should be applicable to atomization of viscous liquids, aqueous and organic, with viscosity up to 1 Pa*s. Consideration of the behavior of non-Newtonian fluids (e.g., shear thinning) is a plus. The project should focus on pressure-driven atomizers (single or two fluid), however other atomizer types can be explored as a stretch goal.

High-Fidelity Modeling of Atomization from Nozzle Flow to Fully Developed Spray

---

Executive Summary

The objective of this research project is to demonstrate the ability of a recently-advanced high-fidelity modeling framework for spray formation to predict drop size and velocity distributions in high viscosity liquid atomization systems, such as found in spray drying applications. This framework, which has been developed by the PI's research group as part of an ongoing ONR MURI project on fuel spray control, hinges on several enabling components: (1) the large eddy simulation (LES) of the two-phase flow field, including the internal nozzle flow, in order to capture directly the large-scale flow dynamics critical to the liquid destabilization and break-up, (2) a fully conservative Eulerian interface tracking technique with the ability to capture subgrid scale liquid features such as thin films and thin ligaments, known to be of critical importance in the break-up of viscous fluids, and (3) a simple break-up model to convert these thin liquid features into spray droplets that can be tracked in a Lagrangian fashion.

In contrast to most existing atomization models, this framework has several key advantages: it is based on first principles instead of an assumed break-up phenomenology, it models an atomizer end-to-end, i.e., from its inlet to a fully dispersed spray, and it benefits from a much lower cost than brute-force direct numerical simulation (DNS). However, it has only been demonstrated on a two-fluid atomizer configuration with water and air so far. This project will explore the influence of higher viscosity and non-Newtonian behavior on the prediction of drop sizes. It is expected that thin liquid sheets and ligaments will dominate the atomization of higher viscosity fluids (e.g., in contrast to water), for which the ability to track subgrid scale interfacial features will prove invaluable. The work will begin by exploring the effect of increasing liquid viscosity on the predicted spray generated by an academic two-fluid atomizer for which extensive water-air data is available, but will seek reference data from IFPRI members and collaborators in order to validate the performance of the framework with high viscosity/non-Newtonian liquids.

1 Introduction

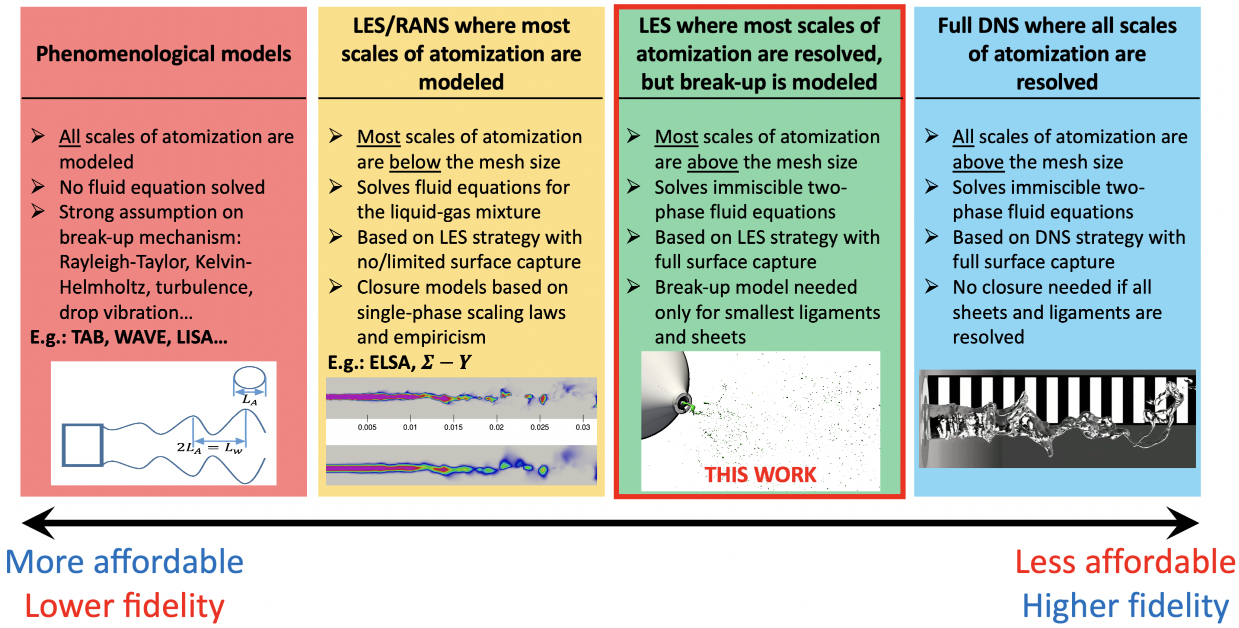
The reliable formation of a spray is a critical component of many engineering systems. In particular, producing powders often involves atomizing a liquid mixture into fine droplets, then drying them into solid particles. In this process known as spray drying, the quality of the powder hinges on the quality of the liquid atomization process, and as such, the droplet size distribution needs to be controlled. Yet, a well-controlled and predictable droplet size distribution is very challenging to achieve in practical applications, especially when considering that the liquids used in spray drying applications are often very viscous, potentially non-Newtonian slurries. Consequently, these systems are often designed and optimized through an expensive trial-and-error process instead of predictive modeling. **The main goal of this project is to bridge this gap by demonstrating that modern, high-fidelity CFD modeling of atomization can predict spray drop size and velocity distributions from first principles, thereby providing a critical modeling tool to engineers.**

Experimental studies of liquid atomization are needed to provide validation data for models and simulations. However, they present significant challenges: the liquid droplets effectively shield the liquid core and prevent optical access, making direct examination of the spray formation mechanisms difficult under realistic conditions. Velocity measurements in the gas phase cannot easily be obtained close to the liquid, so experiments are often limited to characterizing the size and velocity of droplets far downstream of the near-field spray formation region. Even when the atomizing flow is visible, light-scattering-based measurements require very careful analysis in order to extract quantitative data (e.g., see [1]). Recently, experimentalists have started using X-ray imaging techniques and other non-scattering methods in order to quantify liquid statistics in the near-field successfully [2]. For the first time, these new X-ray datasets are providing an opportunity to validate in details numerical simulations of atomization.

In a nutshell, all liquid atomizers follow the same principle: impart kinetic energy to the liquid-gas flow in such a way that as much of it as possible is converted into surface energy (i.e., more drops and smaller drops). The kinetic energy can be given to the liquid directly (using acoustic forcing for nebulizers, moving geometry for rotary disks, or pressurized tanks for pressure-driven atomizers), it may be given to the surrounding gas (using a pressurized gas in two-fluid atomizers), or a mixture of both (e.g., aerated injectors, jet-in-crossflow). Moreover, drop sizes can be selected by carefully choosing the topology of the liquid – in particular, the liquid is often flattened into a thin sheet (e.g., via prefilming or swirling flows). This wide range of atomization processes presents a fantastic challenge to modelers: they each display fundamentally different phenomenologies that, depending on operating conditions, can be dominated by turbulence, Kelvin–Helmholtz instabilities, Rayleigh–Taylor instabilities, flapping dynamics, ligament break-up, or bag bursting, to list just a few. Therefore, no single phenomenological reduced-order atomization model can be expected to capture accurately spray drop sizes over a range of injection strategies, flow conditions, and fluid properties. Nevertheless, the standard modeling strategy for atomization engineers today typically forgoes all details of the liquid injection process and break-up dynamics, instead representing the liquid stream as a series of large initial "blobs" that can be treated in a Lagrangian fashion and undergo break-up based on phenomenological processes such as surface instabilities [3–5], droplet shedding [6], and turbulence [7]. This approach is captured in the leftmost vignette in Fig. 1.

In contrast, first-principle higher-fidelity models based on the solution of the Navier-Stokes equations have the potential to capture all these phenomenologies appropriately, which is why they are the focus in this proposal. Of course, accurate simulations of multiphase turbulent systems in complex geometries are challenging to conduct, in part because of the wildly discontinuous densities and viscosities across the phases, as well as the singular surface tension force at the interface, and the wide range of length and time scales involved in these flows. Yet, numerical methods for complex atomizing multiphase flows have rapidly progressed in the recent years, and have reached a level of maturity that approaches that of single-phase flows. Given sufficient computational resources, it is possible to perform high-fidelity simulation of the early spray formation process, thereby providing direct access to droplet size and velocity in Eulerian frameworks such as level set and volume-of-fluid (VOF) methods. Note however that such simulations often require billions of degrees of freedom and thousands of computer cores over multiple weeks [8, 9], which limits their usefulness to purely academic studies in canonical configurations. This *full DNS strategy*, summarized in the rightmost vignette in Fig. 1, is not pursued in this project due to its inability to tackle atomization problems of industrial relevance.

Alternatively to DNS, **LES of two-phase atomizing flows is more promising for industrial applications**: instead of requiring all scales to be resolved, only the dynamically important



Phenomenological models

- All scales of atomization are modeled
- No fluid equation solved
- Strong assumption on break-up mechanism: Rayleigh-Taylor, Kelvin-Helmholtz, turbulence, drop vibration…

E.g.: TAB, WAVE, LISA…

LES/RANS where most scales of atomization are modeled

- Most scales of atomization are below the mesh size
- Solves fluid equations for the liquid-gas mixture
- Based on LES strategy with no/limited surface capture
- Closure models based on single-phase scaling laws and empiricism

E.g.: ELSA, $\Sigma - Y$

LES where most scales of atomization are resolved, but break-up is modeled

- Most scales of atomization are above the mesh size
- Solves immiscible two-phase fluid equations
- Based on LES strategy with full surface capture
- Break-up model needed only for smallest ligaments and sheets

Full DNS where all scales of atomization are resolved

- All scales of atomization are above the mesh size
- Solves immiscible two-phase fluid equations
- Based on DNS strategy with full surface capture
- No closure needed if all sheets and ligaments are resolved

Figure 1: Overview of various modeling strategies for liquid atomization, ranging from ad-hoc, phenomenological models on the left which are cheap but non-predictive, to full DNS on the right which is accurate but overly expensive. The proposed work corresponds to the third box from the left, where only the final stage of ligament and sheet break-up is modeled.

large scales are resolved on the mesh, while the more universal small scales are modeled. One possible LES strategy is to choose a mesh size such that almost all interfacial dynamics happen at the subgrid scale, as summarized on the second vignette from the left in Fig. 1. Then, the liquid-gas interface does not need to be carefully tracked, but the entirety of the break-up process needs to be modeled: the $\Sigma - Y$ and ELSA models [10–12] are the most well-known examples of such a strategy. The subgrid scale closures needed are numerous, complex, and often based on empiricism and parameter fitting. In fact, recent results reported using this type of models still rely heavily on coefficient tuning and show that more work is needed to improve predictions (e.g., see [13]).

The third vignette from the left in Fig. 1 presents the alternative strategy pursued in this work. Still in the context of a two-phase flow LES, we propose to perform detailed interface tracking so that **most scales of interfacial deformation are captured on the mesh**. However, requiring that the mesh size is sufficiently small to resolve properly all topology-change events leads to an exorbitant cost, as mentioned earlier. This is especially true for high viscosity liquids for which very elongated ligaments and very thin sheets are know to abound. Therefore, we propose instead to model the break-up of thin liquid features at the subgrid scale by first tracking the geometry of these thin features as they fall below the mesh size, then using a simple closure to convert these thin features into Lagrangian droplets. This approach leads to several orders of magnitude of reduction in computational cost compared to full DNS, but only relies on models for the final, most universal step of break-up, thereby preserving high fidelity predictions.

2 Prior Research

Predictive high-fidelity modeling of atomization with application to spray control has been the focus of a ONR-funded Multidisciplinary University Research Initiative led by Prof. Desjardins at Cornell in the past five years. That project has led to significant advances in both numerical techniques and modeling framework for spray atomization. In particular, we demonstrated the first detailed validation of atomization simulations against X-ray data, and we proposed and demonstrated a novel modeling paradigm for spray formation simulations which explicitly addresses the mesh-dependent nature of break-up in interface capturing simulations.

2.1 High-Fidelity Multiphase Flow Simulations with Experimental Validation

The effort to perform high-fidelity modeling of spray formation has led to several advances of techniques for accurate multiphase flow simulations. In particular, a new multiphase-ready stabilized traction boundary condition was developed that allows for droplets to seamlessly leave the computational domain and also prevents interface wave reflection [14]. Additionally, a dynamic contact line model was developed that accounts for subgrid scale surface tension forces at the triple contact line [15]. This model allows the interface to meander along the edge of the nozzle's liquid needle, a phenomenon that was identified and quantified using X-rays, and found to influence the downstream dynamics. With these advances, we were able to carefully validate simulations of the early destabilization of a two-phase planar shear layer against linear stability analysis and experiments [14,16], and simulations of a complete two-fluid annular airblast nozzle were validated against effective liquid path length (EPL) data obtained from X-ray measurements and against backlit imaging data (see Fig. 2).

2.2 Novel Modeling Framework for Mesh-Independent Break-up

Beyond improving the fidelity of the multiphase simulations of the very near-field region, we have focused on addressing head-on the issue of predictive break-up modeling. While level set and volume-of-fluid (VOF) methods provide visually pleasing interface topologies, it is important to understand that the droplet size distributions generated from classical interface capturing methods are *virtually always mesh-dependent*: this is due to the fact that the mesh size provides a minimal length scale for interface folding below which break-up is triggered. This is most obvious in the case of bag break-up, wherein a fast gas penetrates a liquid structure and inflates a thin liquid sheet into a large bag-like shape. From theory and experimental observations, the thin liquid sheet is expected to have a **sub-micron thickness** by the time the bag breaks. In contrast, in simulations, the bag always ruptures when the sheet reaches the mesh resolution. Simply put, it means that a true DNS of a flow with thin liquid bags would require a sub-micron mesh resolution, which is not affordable in most situations. To address this issue, we introduced a new approach that combines three elements: (i) the interface is reconstructed using R2P [17,18], a new computational interface model that allows multiple interfaces per grid cells, thereby allowing for arbitrarily thin interfacial features to be tracked at the subgrid scale, (ii) regions that are likely to undergo break-up momentarily are identified and classified as Lagrangian objects, i.e., sheets and ligaments are identified as such using a specially-designed Connected Component Labeling (CCL) scheme [19,20], and (iii) once a specified criterion has been reached, the sheet or ligament object is atomized through the use of a break-up model that creates droplets in a mass-conserving manner from physical arguments [21].

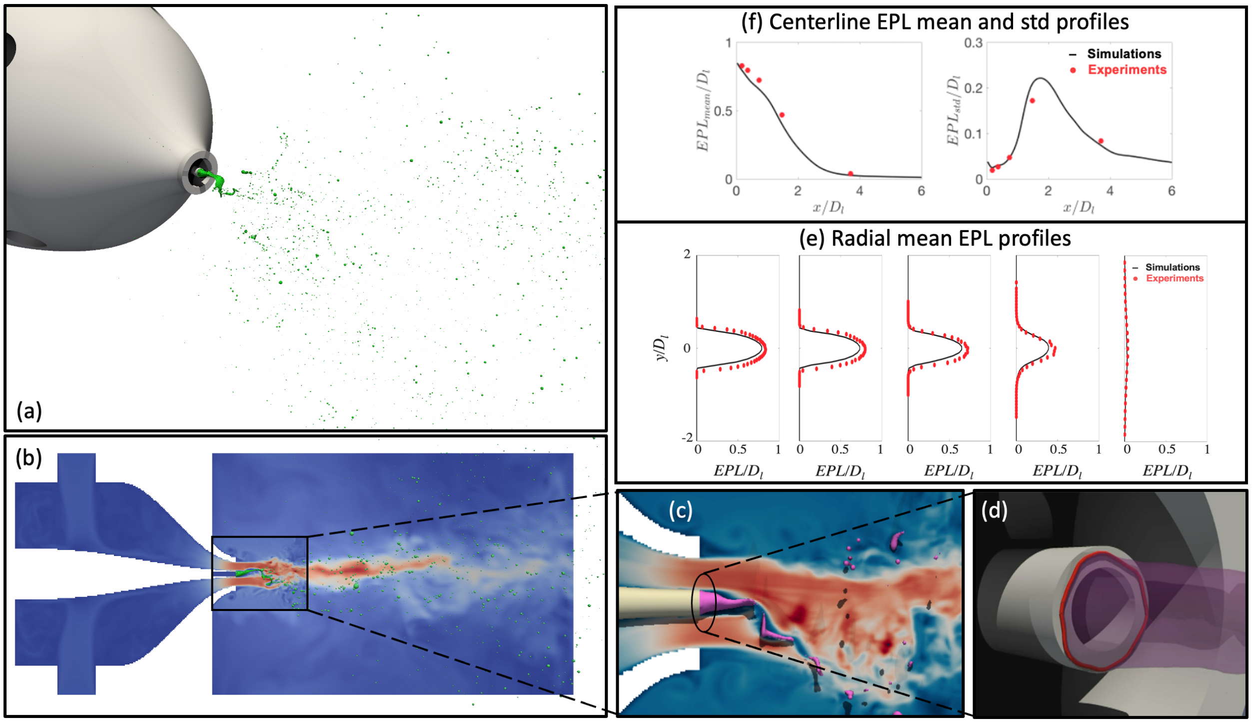


Figure 2: (a) Simulation of a complete annular airblast spray at a momentum flux ratio of 6, without swirl: the nozzle is visible on the top left in grey, and the liquid spray is shown in green. (b) Instantaneous velocity magnitude, showing the flow in the nozzle plenum, the near-field turbulence, and the turbulent spray dispersion downstream. (c) Zoom on the details of the liquid jet (shown in pink here) and the velocity field at the exit of the nozzle. (d) Zoom on the liquid needle, showing the dynamic anchoring of the liquid-gas interface. (e) and (f) show the comparison of the effective path length (i.e., line-of-sight integrated liquid length) obtained from X-ray measurements to the simulation data, along radial profiles and along the centerline.

This strategy is demonstrated in Fig. 3 with the classical problem of a droplet at a Weber number of approximately 20 undergoing bag break-up: a thin liquid sheet is formed, and bursts into $\mathcal{O}\left(10^4\right)$ droplets, while the rim forms a ligament that survives longer and undergoes a slower Rayleigh–Plateau break-up process. The classical VOF scheme, shown in green for a simulation with 13 cells across the droplet diameter, does not capture the formation of a bag and ultimately only generates a handful of large rim droplets. For such a VOF-based simulation to capture the correct drop size distribution via DNS, more than three orders of magnitude more grid cells would be needed. In contrast, the R2P+CCL+break-up model shown in pink at the same resolution of 13 cells per diameter generates a large bag which breaks into $\mathcal{O}\left(10^4\right)$ droplets as small as a few microns, in agreement with recent holographic measurements by Guildenbecher et al. [22]. Deployed in simulations of the canonical airblast nozzle studied mentioned above, this strategy enabled the end-to-end modeling of the atomization process shown in Fig. 2, a first of its kind. The drops generated by the break-up of the thin liquid structures are transferred to a Lagrangian representation, and their turbulent dispersion by the gas flow is computed downstream of the nozzle.

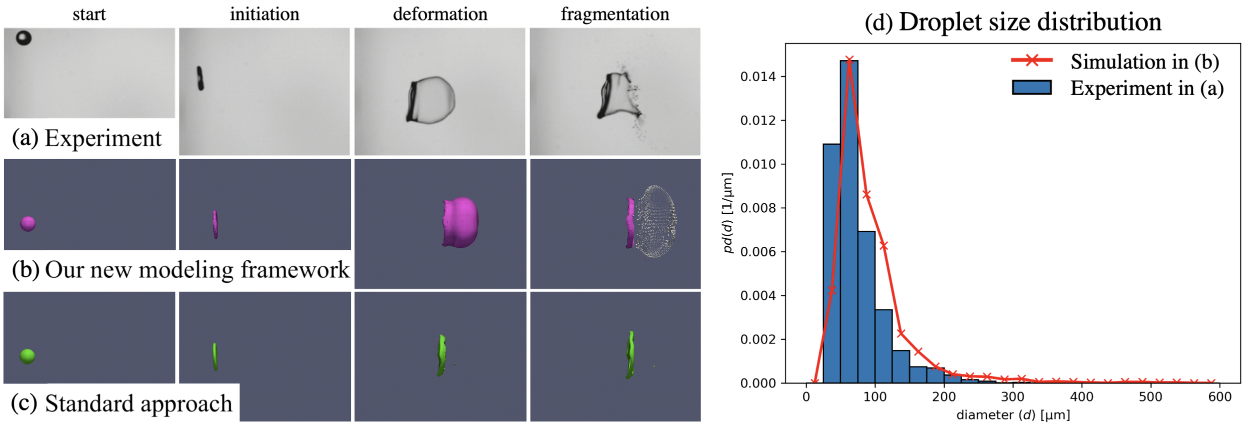


Figure 3: Bag break-up of a moderate Weber droplet: sequence of snapshots at four successive times from (a) experiments by Guildenbecher et al. [22], (b) a simulation using the new subgrid scale break-up model, and (c) a simulation using a standard volume of fluid strategy. The droplet size distributions generated by the bag break-up in (a) and (b) are compared in (d).

3 Proposed Work and Timeline

Several studies have elucidated the effect of increased viscosity on the performance of two-fluid airblast atomizers. For example, Mackrory [23] pointed out that ligaments that form during the primary break-up process are thinner and longer when the liquid is more viscous – and therefore more challenging to resolve numerically, which makes our approach that tracks these ligaments at the subgrid scale advantageous. Mackrory's study also reported a tendency of the more viscous liquids to pool at the nozzle lip, leading to large droplets being regularly released. Our ability to model accurately contact line physics will be important in capturing that effect. In general, the experimental consensus is that larger viscosities lead to larger droplets [24–27], although bimodal size distributions are not uncommon. These observations suggest that our spray modeling framework is already well-suited for predicting the atomization of high viscosity liquids without requiring significant changes, and as such we do not propose significant new development, instead focusing on assessing the performance of the framework, both in terms of computational cost and fidelity of predictions. Consequently, we propose the following work packages.

Work Package 1 – Exploring the Impact of Viscosity on Spray Formation

In WP1, we will investigate the impact of increasing liquid viscosity on the drop size and velocity distributions and on the atomization dynamics for the canonical two-fluid airblast atomizer that we developed as part of the ONR MURI project mentioned above. This atomizer, visible in Fig. 2 (a-c), captures the main features of externally mixed swirled two-fluid injectors, and has been extensively characterized using X-ray, backlit imaging, and PDPA for various swirl and momentum flux ratios using water and air, and as such it provides a validated starting point for our modeling effort. Increasing the viscosity presents no particular numerical challenge since our flow solver already treats the viscous terms fully implicitly, so we do not expect that we will have to drastically reduce the time step size to maintain stability, thereby keeping the cost of simulations low. We will compare the effect of increasing viscosity on the drop sizes to existing correlations, in particular the one proposed for high viscosity fluids by Aliseda et al. [27].

Timeline: Our ONR MURI airblast case will be studied with increasing liquid viscosity in year 1.

Work Package 2 – Detailed Validation of High Viscosity Liquid Spray Formation

In WP2, we will validate our detailed model predictions against experimental data. As a preliminary step during year 1, we will perform a review of the literature to identify the best reference data set for the purpose of validation. At the moment, we believe that the experimental work of Aliseda [27] might be optimal, especially given the close ongoing collaboration between the groups of Aliseda and Desjardins. We will also interact closely with IFPRI members and assess whether they can avail relevant pre-competitive data to augment our validation effort. Then, in year 2, we will study in details the experimental case (or potentially few cases) chosen in year 1 and compare our modeling predictions against spray measurements. We will draw conclusions regarding the computational performance of the method: in particular, we will characterize the impact of mesh resolution on the predictions, and the overall accuracy of our strategy.
Timeline: The best experimental dataset for validation will be identified in year 1, then the detailed comparison will be done in year 2.

Work Package 3 – Exploring the Atomization of Non-Newtonian Liquids

In WP3, we will first implement a simple non-Newtonian liquid model in our flow solver using a shear-dependent viscosity coefficient. While straightforward in an explicit flow solver, this will present some challenges in our time-implicit solver as the Jacobian of the viscous term will increase in complexity. We will test our implementation on well-known laminar flow solutions. We expect most of this work to be done within year 2, so we can then test the impact of non-Newtonian liquid dynamics on our model predictions in year 3. In particular, we expect that our current model closure for converting thin ligaments and sheets into droplets will need to be modified to reflect the non-Newtonian break-up dynamics of these simple topologies. The detailed study of the non-Newtonian Raleigh–Plateau instability for ligaments and of the Taylor–Culick instability for liquid sheets might be needed to elucidate how these fundamental break-up processes change for complex liquids.
Timeline: A simple non-Newtonian liquid with shear-dependent viscosity will be implemented in year 2, then will be used in atomization simulations in year 3 to better understand the capability of our approach for complex liquids. Subgrid scale modeling closures will be revisited for complex liquids.

4 Team Qualifications

Professor Desjardins is uniquely qualified to conduct this research. He has over fifteen years of experience working on high fidelity computational modeling of turbulent multiphase flows. He develops numerical methods and modeling strategies to investigate turbulent liquid-gas flows and particle-laden flows using large-scale computing resources. Specifically, he has focused on the prediction of turbulent liquid atomization, as well as the dynamics of dense disperse two-phase flows. He is the recipient of the National Science Foundation CAREER Award and the International Conference on Multiphase Flow Junior Award, and he is currently leading a $9 million ONR MURI project on spray control.

5 Budget

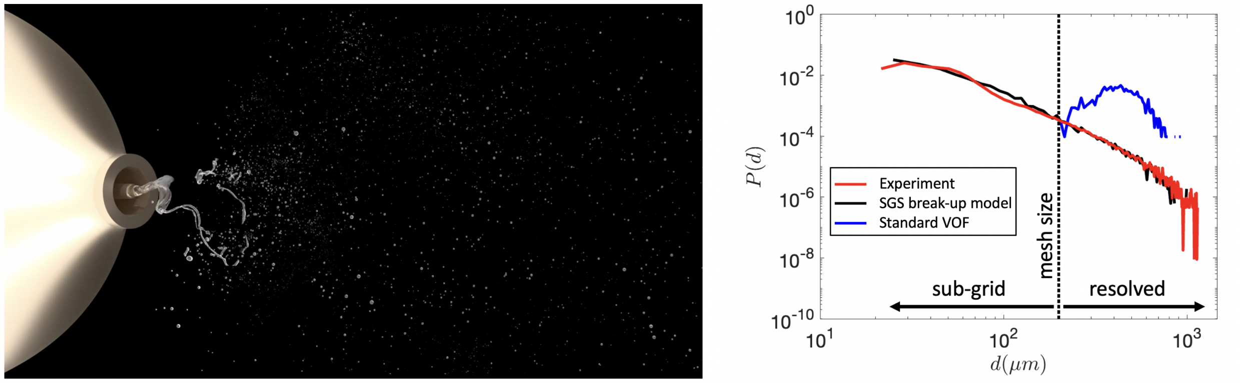
For the proposed work, \$40,000 per year for three years is requested. This amount accounts for one semester per year for a Cornell graduate student, some time for Prof. Desjardins, travel once a year internationally to the IFPRI general meeting, and limited funds for minor equipment. A detailed budget is included, along with a budget justification.

6 Response to Comments by IFPRI Members

In this section we respond directly to questions and comments by IFPRI members.

Members feel that proposal clearly meets the brief and are enthusiastic about approach:

We thank the members for the positive feedback on the proposal. In fact, since the original proposal was submitted last year, our group made significant progress on break-up modeling. In particular, we successfully compared our proposed R2P-CCL-break-up model strategy against experimental data in the realistic airblast configuration shown in Fig. 2. As can be seen in Fig. 4, our predicted droplet size distribution compares very favorably against experimental measurements. Contrary to standard VOF-based approaches that can only generate meaningful droplets larger than the mesh size, it can be seen that most droplets are well below the mesh resolution, confirming that our approach provides access to subgrid information at a fraction of the cost of full DNS.



(a) Visualization of airblast atomization simulation

(b) Comparison of droplet size distribution

Figure 4: End-to-end simulation of an annular airblast spray at a momentum flux ratio of 6, without swirl. Simulation encompasses the internal nozzle flow, followed by a near-field atomization region wherein subgrid liquid structures are tracked using R2P, detected using CCL, and atomized into droplets using a subgrid scale break-up model. Droplets are then tracked as Lagrangian objects as they undergo turbulent dispersion downstream. On the right, the droplet size distribution is compared against experimental measurements (in red). The drop size pdf is extracted at 9 nozzle diameters downstream, averaged over a transverse plane. In black our proposed simulation strategy is shown to agree well with experiments, while standard VOF-based approaches in blue are unable to capture the range of droplet sizes.

Details on the data used to validate model:

Simulations such as the one shown in Fig. 4 can be validated against any or all of the following experimental data:

- Liquid effective path length (EPL): using an X-ray beam passing through the multiphase flow, it is possible to measure accurately the *depth* of liquid along the line of sight, referred to as EPL. From instantaneous and pointwise EPL measurements, statistics of EPL can be formed and compared against simulation. So far, mean and standard deviation have been compared successfully. The main disadvantage of this technique is that it requires a very powerful X-ray source. We have used the Advanced Photon Source at the Argonne National Laboratory.
- Backlit image analysis: using a much simpler backlit imaging setup, it is possible to visualize an outline of the liquid jet and spray. Quantitative measures of the spray flow can be derived from backlit imaging data, in particular jet flapping frequency, intact core length distribution, and spray angle. We have successfully compared our simulations to flapping frequency and intact liquid core length distribution. It is also possible to extract the most unstable longitudinal and transverse wavelengths by performing careful imaging analysis, and we have used such measurements for the purpose of validation in past studies.
- Drop size distribution: these can be classically obtained from Phase Doppler Particle Analysis (PDPA) measurements, but can also be extracted from careful post-processing of backlit imaging data. We have successfully compared our predicted droplet size distribution against both, although for a single spray atomization case so far (shown in Fig. 4).
- Droplet velocity: PDPA can also readily provide access to droplet velocity information, which we are planning to use for validation of our simulations in the near future.

Note that the experimental work on non-Newtonian spray formation by Aliseda [27] provides backlit imaging data and droplet size measurement from PDPA.

Details on the timeline:

In year 1, WP1 will involve using the airblast configuration developed in our ONR MURI project in order to explore the effect of increasing liquid viscosity on our droplet size distribution. This computational configuration is ready to go, and as such it will be ideal to get a PhD student started on this project. Additionally, we will start WP2 by reviewing all available experimental datasets published in the literature for high-viscosity and non-Newtonian liquid atomization. We will also reach out to IFPRI members who may have relevant datasets that could be shared with us.

At the end of year 1, we expect to have identified one or two ideal datasets to use for validating our high-viscosity liquid atomization. In year 2, WP2 will focus on making numerical predictions of spray characteristics for these datasets, and validating against experiments. Adjustments to our modeling strategy will be made should shortcomings be identified. Moreover, in year 2 we will implement and verify a viscous stress model for non-Newtonian liquids.

In year 3, WP3 will switch focus to simulating non-Newtonian fluid atomization and comparing against experiments identified in year 1.

Could the code be made available to IFPRI members at the end of the project?

All developments will be made within the open-source code *nga2*, which can be downloaded from `https://github.com/desjardi/nga2`. Of course, Prof. Desjardins and the PhD student working on the project will be available to provide assistance to IFPRI members should they wish to use the code, especially as it pertains to the scope of the project. If necessary, further support for using *nga2* can be envisioned through various arrangements.

References

[1] N. Machicoane, G. Ricard, R. Osuna-Orozco, P. Huck, and A. Aliseda. Influence of steady and oscillating swirl on the near-field spray characteristics in a two-fluid coaxial atomizer. *International Journal of Multiphase Flow*, 129:103318, 2020.

[2] N. Machicoane, J. K. Bothell, D. Li, T. B. Morgan, T. J. Heindel, A. L. Kastengren, and A. Aliseda. Synchrotron radiography characterization of the liquid core dynamics in a canonical two-fluid coaxial atomizer. *International Journal of Multiphase Flow*, 115:1–8, 2019.

[3] Rolf D. Reitz. Modeling atomization processes in high-pressure vaporizing sprays. *Atomisation Spray Technology*, 3(4):309–337, January 1987.

[4] P.J. O'Rourke and A. A. Amsden. The TAB Method for Numerical Calculation of Spray Droplet Breakup. *SAE* Paper 872089, 1987.

[5] Jennifer C. Beale and Rolf D. Reitz. Modeling spray atomization with the kelvin-helmholtz/rayleigh-taylor hybrid model. *Atomization and Sprays*, 9(6):623–650, 1999.

[6] Rolf D. Reitz. Modeling the primary breakup of high-speed jets. *Atomization and Sprays*, 14(1), 2004.

[7] K. Y. Huh. A phenomenological model of diesel spray atomization. *Proc. of The International Conf. on Multiphase Flows '91-Tsukuba*, 1991.

[8] Y. Ling, D. Fuster, S. Zaleski, and G. Tryggvason. Spray formation in a quasi-planar gas-liquid mixing layer at moderate density ratios: A numerical closeup. *Phys. Rev. Fluids*, 2:014005, 2017.

[9] J. Carmona, N. Odier, O. Desjardins, B. Cuenot, A. Misdariis, and A. Cayre. A comparative study of direct numerical simulation and experimental results on a prefilming airblast atomization configuration. *Atomization and Sprays*, 31:9–32, 2021.

[10] A. Vallet and R. Borghi. Modélisation Eulerienne de L'Atomisation d'un Jet Liquide. *C. R. Acad. Sci. Paris Sér. II b*, 327:11015–10208, 1999.

[11] R. Lebas, T. Menard, P. A. Beau, A. Berlemont, and F. X. Demoulin. Numerical simulation of primary break-up and atomization: DNS and modelling study. *International Journal of Multiphase Flow*, 35:247–260, 2009.

[12] J. Chesnel, J. Reveillon, T. Menard, and F. X. Demoulin. Large eddy simulation of liquid jet atomization. *Atomization and Sprays*, 21:711–736, 2011.

[13] B. Wang, M. J. Cleary, and A. R. Masri. Coupling explicit volume diffusion with $\Sigma - Y$ model for LES of airblast atomisation. In *ICLASS 2021, 15th Triennial International Conference on Liquid Atomization and Spray Systems*, Edinburgh, UK, August 29 - September 2, 2021, 2021.

[14] Cyril Bozonnet. Primary wave of an air-water mixing layer: a numerical study. *Doctoral Dissertation, Grenoble Alpes University*, 2021.

[15] Sheng Wang and Olivier Desjardins. 3D numerical study of large-scale two-phase flows with contact lines and application to drop detachment from a horizontal fiber. *International Journal of Multiphase Flows*, 101:35–46, 2018.

[16] C. Bozonnet, J.-P. Matas, G. Balarac, and O. Desjardins. Stability of an air-water mixing layer: focus on the confinement effect. *Journal of Fluid Mechanics*, accepted, 2022.

[17] Robert Chiodi. Advancement of numerical methods for simulating primary atomization. *Doctoral Dissertation, Cornell University*, 2020.

[18] Robert Chiodi and Olivier Desjardins. General, robust, and efficient polyhedron intersection in the interface reconstruction library. *Journal of Computational Physics*, 449:110787, 2022.

[19] Kelli Hendrickson, Gabriel D. Weymouth, and Dick K.P. Yue. Informed component label algorithm for robust identification of connected components with volume-of-fluid method. *Computers and Fluids Fluids*, 197:104373, jan 2020.

[20] Austin Han and Olivier Desjardins. Liquid structure classification towards topology change modeling. In *ICLASS 2021, 15th Triennial International Conference on Liquid Atomization and Spray Systems*, Edinburgh, UK, August 29 - September 2, 2021, 2021.

[21] Austin Han and Olivier Desjardins. Liquid structure classification towards breakup and coalescence modeling. In *ILASS-Americas 31st Annual Conference on Liquid Atomization and Spray Systems*, Madison, WI, May 16-19, 2021, 2021.

[22] Daniel R. Guildenbecher, Jian Gao, Jun Chen, and Paul E. Sojka. Characterization of drop aerodynamic fragmentation in the bag and sheet-thinning regimes by crossed-beam, two-view, digital in-line holography. *International Journal of Multiphase Flows*, 94:107–122, 2017.

[23] A. J. Mackrory. Characterization of black liquor sprays for application to entrained-flow processes. *Doctoral Dissertation, Brigham Young University*, 2006.

[24] G. Ferreira, J. A. García, F. Barreras, A. Lozano, and E. Lincheta. Design optimization of twin-fluid atomizers with an internal mixing chamber for heavy fuel oils. *Fuel Process.Technol.*, 90:270–278, 2009.

[25] Z. H. Li, Y. X. Wu, C. R. Cai, H. Zhang, Y. L. Gong, and K. Takeno. Mixing and atomization characteristics in an internal-mixing twin-fluid atomizer. *Fuel*, 97:306–314, 2012.

[26] Z. H. Li, Y. X. Wu, H. Yang, C. R. Cai, H. Zhang, K. Hashiguchi, K. Takeno, and J. Lu. Effect of liquid viscosity on atomization in an internal-mixing twin-fluid atomizer. *Fuel*, 103:486–494, 2013.

[27] A. Aliseda, E. J. Hopfinger, J. C. Lasheras, D. M. Kremer, A. Berchielli, and 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*, 34(2):161–175, 2008.

Unveiling the Potential of CFD for Nozzle Spray Prediction

REVISIONS MADE TO THE PROPOSAL

Comments: The members feel that your proposal meets most of what is asked for in the brief, however they feel that it could be improved by providing more detail about the models you will use (e.g. turbulence models, droplet size distribution) …

***Response**: We will use the Large Eddy Simulation framework to capture the turbulence behavior of the flow. The droplet size distribution will not be empirically modelled, rather, it will be a results of the VOF-to-DPM framework implemented into model. We will be evaluating how different combinations of meshing strategies and VOF-to-DPM threshold settings affect the accuracy of the prediction. Building on top of the prediction on the primary atomization, we will also be evaluating the significance of secondary droplet breakup (using the Taylor analogy model) and coalescence (using the O'Rourke algorithm) on the overall droplet size prediction. One of our main goals will be to determine strategies to achieve a delicate balance between the level of complexity and the accuracy of the modelling framework.*

We have now updated the description above in the last paragraph of Work Package 2&4 on Page 6 of the proposal.

Comments: … and the experimental justification of the relevance of ANSYS-Fluent in producing closures with accurate predictions on realistic system size.

***Response**: There are numerous publications below lending evidence to the suitability of ANSYS-Fluent in capturing realistic atomization behavior for single fluid pressure swirl nozzles, which is the premise of this proposal.*

[24] Yu, H., Jin, Y.C., Cheng, W., Yang, X., Peng, X., Xie, Y. 2021. Multiscale simulation of atomization process and droplet particles diffusion of pressure-swirl nozzle. Powder Technology 379, 127-143.

[25] Sun, Y., Alkhedhair, A.M., Guan, Z., Hooman, K. 2018. Numerical and experimental study on the spray characteristics of full-cone pressure swirl atomizers. Energy 160, 678-692.

[26] Nihasigaye, P.B., Zhou, G., Yang, X. 2021. Modelling spray performance of alternative aviation fuel. Energy 224, 120086.

We have strong familiarity with the ANSYS Fluent CFD package and the ease-of-use of its interface will be attractive for subsequent industrial applications. Nevertheless, we will *interpret our results with emphasis on the fundamental theoretical model and the numerical strategy used, so that our recommendations are applicable even if a different CFD package or open-sourced framework is used.*

We have now revised the description of Work Package 1 on Page 5 of the proposal to include the above justification.

Comments: A significant amount of the work that you propose is experimental, while the brief specifies a computational project. Would it be possible to use published data to validate your model instead? This might allow you to include non-Newtonian systems in your project.

***Response**: We have undertaken an extensive search of the literature for suitable and reliable experimental data to complement our proposed simulation work. Experimental data from the two report below by Günter Brenn and co-workers will be adopted. Günter Brenn is the editor-in-chief (Europe) for the journal Atomization and Sprays. These sets of data cover Newtonian and non-Newtonian fluids. More interestingly is that they were generated in collaboration with Nestle under industry relevant conditions, suitable for this project.*

We have now significantly revise and included justification in selecting these two sets of experimental data for this project on Page 5 of the proposal in describing Work Package 2 & 4. We have also revised the Gantt Chart on Page 4.

[21] Tratnig, A., Brenn, G., Stricner, T., Fankhauser, P., Laubacher, N., Stranzinger, M. 2009. Characterization of spray formation from emulsions by pressure-swirl atomizers for spray drying. Journal of Food Engineering 95, 126-134.

[22] Tratnig, A., Brenn, G. 2010. Drop size spectra in sprays from pressure-swirl atomizers. International Journal of Multiphase Flow 36, 349-363.

Comments: Additionally, a number of members (representing most companies who use spray drying extensively) were disappointed that your plan doesn't include non-Newtonian fluids.

***Response**: We have now revised the proposal to include non-Newtonian fluids. Simulation work on the non-Newtonian fluids will be undertaken in Work Package 4. We will complement the simulation work with experimentally data from the report below. Two emulsion based non-Newtonian fluids with well characterized shear thinning behavior will be explored.*

[21] Tratnig, A., Brenn, G., Stricner, T., Fankhauser, P., Laubacher, N., Stranzinger, M. 2009. Characterization of spray formation from emulsions by pressure-swirl atomizers for spray drying. Journal of Food Engineering 95, 126-134.

Comments: Finally, your budget is front-end loaded, which is inconsistent with how IFPRI pays for projects (i.e., three annual $40,000 grants). Hopefully, this won't be a major inconvenience for you.

***Response**: The initial front-end loaded budget was mainly due to the experimental components in the initial proposal. We have now removed the experimental components and revised the proposal to use reported experimental data. Hence, the three annual $40,000 grant model will work for the project.*

We have now revised the budget on Page 6 of the proposal.

PROPOSAL TO:

International Fine Particle
Research Institute

PREPARED BY:

A/Prof. Meng Wai Woo

Unveiling the Potential of CFD for Nozzle Spray Prediction

27. April, 2022

(Revised)

EMAIL:
wai.woo@auckland.ac.nz

PHONE:
+642 1664 363

Unveiling the Potential of CFD for Nozzle Spray Prediction

EXECUTIVE SUMMARY

The state-of-the-art in using the Computational Fluids Dynamics (CFD) technique for spray prediction lies in the pursuit of a delicate balance between the computational requirements and the flexibility and accuracy of the prediction. We will investigate the potential of the VOF-DPM technique (volume of fluid-discrete particle modelling), which is a subset of CFD, to provide this delicate balance for routine engineering spray prediction. The scope of this numerical investigation will cover the pressure swirl atomization of *Newtonian* and *non-Newtonian* fluids. We will base the simulation exploration on experimental data from Günter Brenn and co-workers [21][22], undertaken and reported in collaboration with Nestle. Hence, the numerical exploration in this work will have strong industrial relevance. This project is in alignment with existing spray characterization facility in the University of Auckland. The main outcome from this project will be strategies in using the VOF-DPM technique for nozzle atomization prediction.

BACKGROUND

Commercially available swirl nozzles is commonly developed and characterized with water. This poses significant uncertainties in nozzle selection and operation for spray dryer or spray granulator operators, as the sprayed solutions are typically very different from water (eg. high viscosity binders, concentrated solution in spray drying, organic solvent-based solutions in the pharmaceutical industry). Contract manufacturers, in particular, will find these uncertainties even more challenging as they regularly deal with new product or binder formulations.

Direct measurement and characterization of nozzles in the industry is not routinely feasible due to manufacturing compliances and the cost associated in setting up the measurement facility onsite. Manufacturers work around these uncertainties by relying on guessing work and experiences with specific nozzles and settings. There are also a vast number of empirical correlations available in the literature to help guide manufacturers in nozzle selection and operation [1]. Due to the rapid development in nozzle design and the typically limited conditions in which these correlations are developed, the accuracy of these correlations adds another layer of uncertainty to the problem.

For these reasons, there is a need for a flexible toolbox to guide manufacturers in nozzle selection and operation. The flexible toolbox should overcome the current limitations and should be able to provide a reliable indication on the droplet size distribution and spray angle accounting for different nozzle constructions, product formulations and operating conditions.

This project will explore the use of the Computational Fluid Dynamics (CFD) simulation technique as a flexible atomization predictive toolbox.

STATE-OF-THE-ART IN CFD SPRAY PREDICTION

The atomization process from a pressure nozzle involves the initial formation of thin filaments. Primary breakup of the filaments forms the primary droplets, which undergoes further secondary breakup into finer droplets (also potential coalescence throughout the process). Figure 1 illustrates this process. Within the CFD simulation framework, the Volume-of-Fluid (VOF) technique (and its variant in meshing and surface detection algorithm), is the main method used to capture these various phenomenon composing the atomization process. Figure 2 summarizes the state-or-the-art in this area.

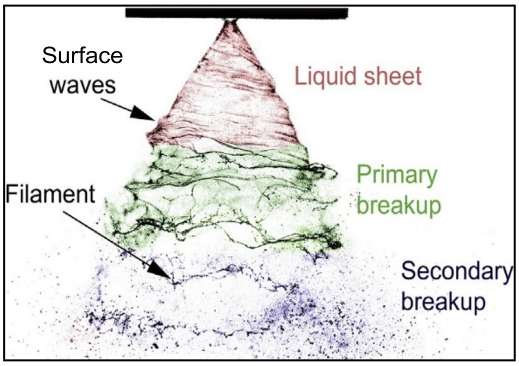


Figure 1. Breakdown of the atomization process [2]

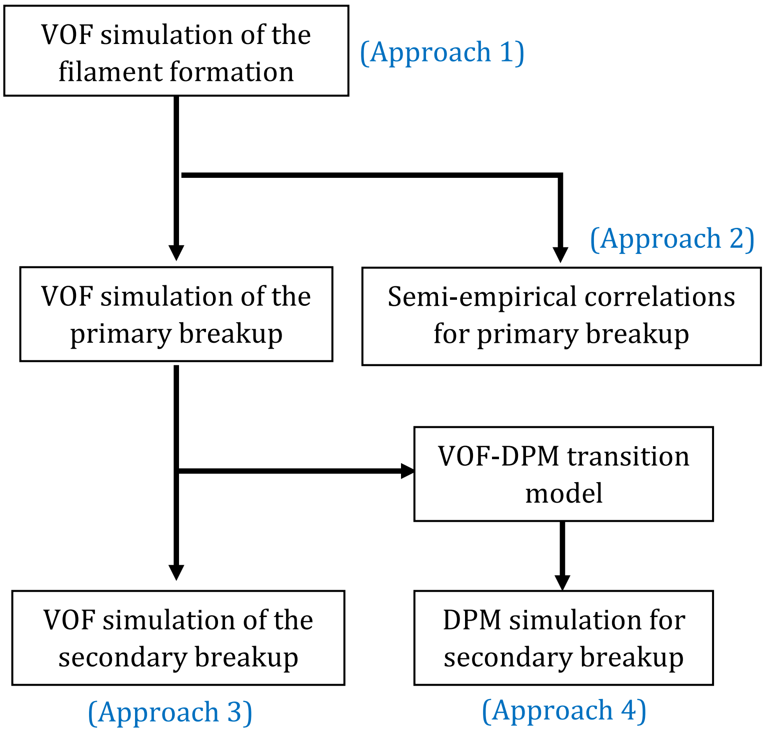


Figure 2. The state-of-the-art in CFD spray prediction

In essence, the VOF technique involves tracking the interface of the atomized fluid throughout the simulation domain. It is a very computationally expensive technique as excessively fine mesh is required to capture the characteristic length scale of the atomization process which stretches across several magnitudes: from centimeters (the nozzle size and the length scale of the whole spray), hundreds of microns (film formation), to tens of microns (primary and secondary droplets). The state-of-the-art in this area lies in the pursuit of a delicate balance between the computational requirements and the degree of flexibility and accuracy from the VOF simulation.

Most of the reported simulation work focuses on Approach 1 (Figure 2), as it provides a computationally inexpensive indication on the performance of the atomizer [3][4][5][6][7]. The application of just predicting the filament or cone formation is limited, because it does not provide a prediction of the final droplet size distribution. Some worker extended this approach by coupling the VOF predictions with empirical correlations linking the characteristics of the filament with the final droplet size distribution (Approach 2 in Figure 2) [8]. The empirical correlation developed so far, employed in the reported framework, was developed based only on an idealized primary breakup process [9][10][11]. While this approach may be low in computational cost, it is in essence empirical and there is significant random uncertainty in the accuracy of the prediction across a wide range of nozzle geometry and fluids [8].

At the other end of the spectrum, Approach 3 (Figure 2) utilizes the VOF technique to provide a full visualization of the atomization process, from the filament formation to the secondary breakup phenomenon [12][13][14][15][16]. The main drawback is that it requires very significant computational resources. Limiting the simulation to regions very close and adjacent to the nozzle may partly overcome this problem. However, this limits the predictive capability to capture the full effective characteristics of the spray. For this reason, this technique may not be useful for routine engineering application.

In the middle of the spectrum is Approach 4 (Figure 2), which involves the VOF-DPM technique [17][18][19]. This technique transforms the VOF predicted primary droplets and represents them as discrete points in the simulation (hence, DPM - Discrete Phase Modelling). This obviates the need for excessively high computational resources in modelling the secondary breakup of the primary droplets as imposed by Approach 3. This approach also does not have empirical limitations as imposed by Approach 2, because the VOF technique explicitly captures the primary breakup. Therefore, now, this technique provides the greatest potential for the application of CFD in atomization prediction for routine engineering applications; striking a balance between computational requirement and the level of details from the simulation. A survey of the literature on this approach revealed that there is currently limited systematic validation work for Approach 4. Most of the reported work focused on fuel injection atomization. There is currently no one single study systematically evaluating this approach across Newtonian and non-Newtonian fluids and across various nozzle sizes. It is uncertain how well the VOF-DPM technique predicts the atomized droplet sizes, capturing these parameters under industry relevant conditions. Most importantly, there is a need to ascertain suitable VOF-DPM numerical strategies for the different spray conditions. This project will fill these gaps in knowledge.

On this basis, the following are the objectives of this project:

Objective 1: To evaluate the VOF-DPM technique for Newtonian fluid pressure swirl atomization prediction

Objective 2: To evaluate the VOF-DPM technique for non-Newtonian fluid pressure swirl atomization prediction

EXPECTED PROJECT OUTCOMES

We will gain a deeper understanding on how the various numerical parameters of the VOF-DPM technique affect the accuracy and the computational requirements of the atomization prediction. We will provide recommendations on strategies to achieve a balance between accuracy and computational requirements from an industry perspective. In most cases (particularly for contract manufacturers), the capability to realistically cover a range of possible operating conditions may bring more benefits than achieving very high accuracy within a limited range. We will develop strategies for both Newtonian and non-Newtonian fluids. We envisage two publications from this project, one publication from each objective (Milestones #3 and #5 in the table below).

PROJECT PLAN

Work Packages		Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1	VOF-to-DPM modelling framework development	━	━	━									
2	VOF-to-DPM simulation (Newtonian fluid)				━	━	━	━					
3	Objective 1 completion							★					
4	VOF-to-DPM simulation (non-Newtonian fluid)								━	━	━	━	
5	Objective 2 completion											★	
6	Bi-quarterly project update			★		★		★		★		★	
7	PhD thesis completion												★
8	Project final report												★

Work Package 1: VOF-to-DPM modelling framework development

We have access to the New Zealand NESI high performance-computing cluster. We will develop the modelling framework locally using the ANSYS-Fluent package before integration with the NESI network. There are numerous publications lending evidence to the suitability of ANSYS-Fluent in capturing realistic atomization behavior for single fluid pressure swirl nozzles, which is the premise of this proposal [24][25][26]. We have strong familiarity with the ANSYS Fluent CFD package and the ease-of-use of its interface will be attractive for subsequent industrial applications. Nevertheless, we will interpret our results with emphasis on the fundamental theoretical model and the numerical strategy used, so that our recommendations are applicable even if a different CFD package or open-sourced framework is used.

Work Package 2 & 4: VOF-to DPM simulations

We have undertaken an extensive search of the literature for suitable experimental data to complement our proposed simulation work. Key criteria for the experimental data were:

1. Spray rates and droplet sizes relevant to industrial operation.
2. Sufficient atomizer geometry and spray operation data available for simulation.
3. Full set of fluid properties available for simulation.
4. Stretches across *Newtonian* and *non-Newtonian* fluids.
5. Atomized droplet size distribution data (not just data on the internal core and external film formation).
6. Reliable measurements from a reputable group.

Fulfilling the criteria above, we have decided to adopt the experimental data by Günter Brenn and co-workers (Graz University of Technology), published in two separate papers cited here [21][22]. These two sets of data were undertaken in collaboration with the Nestle Product Technology Centre and is of high relevance to the industry. In addition, both sets of data were generated using the same range of Delavan single-fluid swirl nozzles (with different housing and orifice plate combinations). This will allow us to systematically evaluate the capability of the model to capture various geometrical configurations and to systematically extend the evaluation across *Newtonian* and *non-Newtonian* fluids.

To be more specific, this work will cover the following range of fluid properties,

Newtonian fluids: Dynamics viscosity (8-166 mPas), density (1240-1315 kg/m^3), surface tension (51-72 mN/m)

Non-Newtonian fluids: Two shear thinning fluids (EM1 & EM2) with Carreau-Yasuda model fitted shear thinning characteristics

EM1 - solid contents (45.2 %wt), density (1110 kg/m^3), surface tension (0.0425 mN/m)

EM2 - solid contents (49.8 %wt), density (1090 kg/m^3), surface tension (0.0425 mN/m)

We will compare the film forming characteristics and droplet size distribution from the primary breakup of the film. We will be use the Large Eddy Simulation (LES) framework to capture the turbulence flow field of the atomization [23][24]. This has been reported as a suitable compromise, capturing sufficient turbulent characteristics for atomization prediction (compared to RANS and its variants) without excessive computational requirements (compared to DNS simulations). The droplet size distribution will not be empirically modelled, rather, it will be a results of the VOF-to-DPM framework implemented into model. We will be evaluating how different combinations of meshing strategies and VOF-to-DPM threshold settings affect the accuracy of the prediction. Building on top of the prediction of the primary atomization, we will also be evaluating the significance of secondary droplet breakup (using the Taylor analogy model) and coalescence (using the O'Rourke algorithm) on the overall droplet size prediction. One of our main goals will be to determine strategies to achieve a delicate balance between the level of complexity and the accuracy of the modelling framework.

PROJECT ALIGNMENT TO EXISTING FACILITIES

The project is in alignment with the following capabilities and facilities available to the team.

ANSYS Workbench access: We have access to the ANSYS Workbench academic license package. This package is also available in the NESI HPC Cluster that we will use for this project.

Access to NESI HPC Cluster: The University of Auckland is a partner of the NESI HPC cluster and we will have access to the cluster without any additional cost to the project.

BUDGET & JUSTIFICATION

Item	Year 1 ($NZD)	Year 2 ($NZD)	Year 3 ($NZD)
PhD Student:			
Stipend	28,500	28,500	28,500
Fees	9,540	9,540	9540
Equipment:			
Computer	4,000	-	-
TOTAL budget requested from IFPRI	**42,040**	**38,040**	**38,040**

PhD student stipend and fees: The amount requested is the standard three-year full scholarship provided to students in the University of Auckland.

Computer: The amount requested for a local workstation for the student in developing the model and to interface with the NESI HPC Cluster.

PERSONNEL

A/Prof. Meng Wai Woo has 15 years' experience in CFD simulations and have undertaken CFD projects with the spray drying, pharmaceutical and resource recovery industry. He will lead the project and will recruit a PhD student with strong CFD and CAD simulation background for the project. The student will be working on both objectives of the project.

REFERENCES

[1] Masters, K. 1991. Spray drying handbook. 5th Edition, Wiley, New York.

[2] Jedelsky, J., Maly, M., del Corral, N.P., Wigley, G., Janackova, L., Jicha, M. 2018. Air-liquid interactions in a pressure-swirl nozzle. International Journal of Heat and Mass Transfer, 121, 788-804.

[3] Laurila, E., Koivisto, S., Kankkunen, A., Saari, K., Maakala, V., Jarvinen, M., Vuorinen, V. 2020. Computational and experimental investigation of a swirl nozzle for viscous fluids. International Journal of Multiphase Flow, 128, 103278.

[4] Laurila, E., Roenby, J., Maakala, V., Peltonen, P., Kahila, H., Vuorinen, V. 2019. Analysis of viscous fluid flow in a pressure-swirl atomizer using large-eddy simulation. International Journal of Multiphase Flow, 113, 371-388.

[5] Dash, S.K., Halder, M.R., Peric, M., Som, S.K. 2001. Formation of Air Core in Nozzles With Tangential Entry. Journal of Fluids Engineering, 123, 829-835.

[6] Shao, C.X., Luo, K., Yang, Y., Fan, J.R. 2017. Detailed numerical simulation of swirling atomization using a mass conservation level set method. International Journal of Multiphase Flow, 89, 57-68.

[7] Renze, P., Heinen, K., Schonherr, M. 2011. Experimental and Numerical Investigation of Pressure Swirl Atomizers. Chemical Engineering & Technology, 34, 1191-1198.

[8] Liao, Y., Sakman, A.T., Jeng, S.M., Jog, M.A., Benjamin, M.A. 1999. A comprehensive model to predict simplex atomizer performance. Journal of Engineering for Gas Turbines and Powder, 121, 285-294.

[9] Drombowski, N., Johns, W.R. 1963. The Aerodynamic Instability and Disintegration of Viscous Liquid Sheets. Chemical Engineering Science, 18, 203-214.

[10] Wang, X.F., Lefebvre, A.H. 1987. Mean drop sizes from pressure-swirl nozzles. Journal of Propulsion, 3, 11-18.

[11] Suyari, M., Lefebvre, A.H. 1986. Film thickness measurements in a simplex swirl atomizer. Journal of Propulsion, 2, 528-533.

[12] Galbiati, C., Tonini, S., Conti, P., Cossali, G.E. 2016. Numerical Simulations of Internal Flow in an Aircraft Engine Pressure Swirl Atomizer. Journal of Propulsion and Power, 32, 1433-1441.

[13] Fuster, D., Bague, A., Boeck, T., Le Moyne, L., Leboissetier, A., Popinet, S., Ray, P., Scardovelli, R., Zaleski, S. 2009. Simulation of the primary atomization with an octree adaptive mesh refinement and VOF method. International Journal of Multiphase Flow, 35, 550-565.

[14] Ding, J.W., Li, G.X., Yu, Y.S., Li, H.M. 2016. Numerical Investigation on Primary Atomization Mechanism of Hollow Cone Swirling Sprays. International Journal of Rotating Machinery, 1201497.

[15] Pairetti, C., Damian, S.M., Nigro, N., Popinet, S., Zaleski, S. 2020. Mesh resolution effects on VOF simulations of primary atomization. Atomization and Sprays, 30, 913-935.

[16] Zheng, G., Nie, W., Feng, S., Wu G. 2015. Numerical Simulation of the Atomization Process of a Like-doublet Impinging Rocket Injector. Procedia Engineering, 99, 930-938.

[17] Kumar, A.B., Kumar, V., Nakod, P., Rajan, A., Schutze, J. 2020. Multiscale modelling of a doublet injector using hybrid VOF-DPM method. Proceedings from the AIAA SciTech Forum, 6-10 January, Orlando, Florida.

[18] Herrmann, M. 2010. A parallel Eulerian interface tracking/Lagrangian point particle multi-scale coupling procedure. Journal of Computational Physics, 229, 745-759.

[19] Ul Haq, M., Latif, R., Shafi, I., Javaid, A. 2018. Modelling Primary Atomization and its effects on spray Characteristics under Heavy Duty Diesel Engine Condition. Proceedings from the 21st Australasian Fluids Mechanics Conference, Adelaide, Australia, 10-13 December.

[20] Mandato, S., Rondet, E., Delaplace, G., Barkouti, A., Galet, L., Accart, P., Ruiz, T., Cuq, B. 2012. Liquids' atomization with two different nozzles: Modeling of the effects of some processing and formulation conditions by dimensional analysis. Powder Technology 224, 323-330.

[21] Tratnig, A., Brenn, G., Stricner, T., Fankhauser, P., Laubacher, N., STranzinger, M. 2009. Characterization of spray formation from emulsions by pressure-swirl atomizers for spray drying. Journal of Food Engineering 95, 126-134.

[22] Tratnig, A., Brenn, G. 2010. Drop size spectra in sprays from pressure-swirl atomizers. International Journal of Multiphase Flow 36, 349-363.

[23] Chen, Y., Chen, S., Chen, W., Hu, J., Jiang, J. 2021. An Atomization Model of Air Spraying Using the Volume-of-Fluid Method and Large Eddy Simulation. Coatings 11, 1400.

[24] Yu, H., Jin, Y.C., Cheng, W., Yang, X., Peng, X., Xie, Y. 2021. Multiscale simulation of atomization process and droplet particles diffusion of pressure-swirl nozzle. Powder Technology 379, 127-143.

[25] Sun, Y., Alkhedhair, A.M., Guan, Z., Hooman, K. 2018. Numerical and experimental study on the spray characteristics of full-cone pressure swirl atomizers. Energy 160, 678-692.

[26] Nihasigaye, P.B., Zhou, G., Yang, X. 2021. Modelling spray performance of alternative aviation fuel. Energy 224, 120086.

IFPRI

International Fine Particle
Research Institute

Research Project Brief

Computational Modeling of Particle Suspensions

The International Fine Particle Research Institute (IFPRI) wishes to fund a research project on computational modeling of particle suspensions. IFPRI has a long history of supporting research in the rheology of Brownian and non-Brownian suspensions, however the last project that we funded focused on simulation of suspension behavior was John Brady's project on Stokesian dynamics which ended in 2004. With this project, we hope to fill this gap in IFPRI's "wet systems" portfolio.

New state-of-the-art simulations incorporate hydrodynamic interactions to generate large-scale (10^6 or more) particle simulations that quantitatively capture macroscopic properties, including sedimentation/stability, processability, dispersibility, flowability) and microstructural changes over time and in flows. With two excellent experimental projects currently in the wet systems portfolio (Jan Vermant, "Simulated Industrial Formulations"; Erin Koos, "Slurries and Pastes"), maximum benefit can be extracted from that work with computational support to give further insights to properties that cannot be disentangled experimentally.

Simulations with different particle shapes, sizes, chemical heterogeneities and at high loadings are now increasingly feasible, allowing the model to closely approach the complexity of real product formulations in the SIFs and Slurries and Paste projects.

The goal of this project is to bring insights to failure modes that can be experimentally observed but not understood (for example delayed collapse of particle networks) and provide detailed particle-level mechanistic details so that strategies to prevent or predict failure can be developed. Work can also guide formulation decisions, increase the applicability and relevance of the experimental projects by identifying key mechanisms that are difficult or impossible to access experimentally (e.g., role of friction, particle shape and dispersity). A long-term goal of this work is towards computer simulations that can be used to guide formulation design and explore large design spaces as the complexity of systems increases through the incorporation of multiple aspects of shape, roughness, polydispersity, heterogeneity, etc. Specific objectives include:

- Provide insight, and ultimately access, to current wet system modeling tools.
- Reflect the state of the art of modeling to predict flow phenomena in industrial systems to understand the gap and define the steps needed to improve the models.
- Develop and validate simulations against benchmark literature studies, such as shear rheology (e.g., viscosity, viscoelasticity, yielding), delayed consolidation, and microstructural transitions on shearing (e.g. as measured by scattering).

- Work with the experimental SIFs and Slurry and Pastes project groups to perform coordinated characterization of structure, rheology, and interactions.
- Advance simulations to combine with experiments for model suspension development.

Computational and Theoretical Modeling of Complex Particulate Suspensions

Prof. Roseanna N. Zia
Department of Chemical Engineering
Stanford University

Overview

The objective of this work is to advance computational modeling capabilities for colloidal and non-colloidal particulate suspensions that more accurately and efficiently represent the complexity of real product formulations. The long-term goal is construction of models that incorporate new algorithms for higher-fidelity representation of sophisticated chemical and physical interactions including patchy interactions (physical valency), size and shape polydispersity, chemical reactions, bumpy surface topography, and temperature-, salt-, or pH-sensitive attractive or repulsive forces that impact material phase transitions and flow behavior. **The nearer-term focus of this proposal focuses on representing size polydispersity, detailed matching of interactions between particles to experimental systems, and modeling bumpy particle shapes.** Long-range many-body hydrodynamic and lubrication interactions are important in some industrial suspensions and unimportant in others; to address both regimes, the stated objectives will be carried out in our two primary simulation platforms. For suspensions in which particles experience strong hydrodynamic interactions, we will implement the new algorithms into our Parallel Accelerated Stokesian Dynamics with Brownian Motion (PASD-B). For freely-draining systems, we will implement the new algorithms into our adaptation of the LAMMPS algorithm. In both platforms, massive parallelization provide high computational efficiency. Microscopic particle and interaction detail will be connected to macroscopic material behavior and will provide a tool for iterative refinement of particle formulation and material performance, using our existing suite of post-processing codes. The advanced tools developed in the proposed research will be used to model and further the understanding of the impacts of size and shape polydispersity as well as sophisticated surface attraction and repulsion on suspension flow, gelation and vitrification, with options to study impact on gravitational collapse of colloidal gels. This work aims to synergize with the experimental investigations of Professor Jan Vermant (ETH) and Matthew Helgeson (UCSB). The outcome of this work will be an expansion of computational modeling capabilities available to industrial scientists for understanding and engineering particle interactions to control the flow of particulate suspensions, gels, and glasses.

Science Background

Colloidal gels, glasses, and suspensions form the vast majority of industrial-coating materials, most pharmaceutical fluids, over 95% of biological fluids, and are ubiquitous across personal-care and agricultural formulations. Despite the pervasiveness of these fluid-suspended, microscopically small particles (colloids), many of the behaviors of these materials have long defied explanation – such as the sudden collapse of colloidal gels, vitrification that thwarts crystallization, aggregation of therapeutic antibodies which can either destroy or enhance function, and discontinuous changes in viscosity as a few examples. A primary goal in the study of these materials is direct predictive relationships between micro-particle formulation, suspension preparation, and macroscopic material performance. Progress in the last several decades has been substantial including:

1. Advances in theoretical understanding of microscopic forces (electrostatic, hydrodynamic, Brownian, for example) and how these underlie dramatic changes in suspension behavior;
2. Development of model experimental systems; and
3. Modern computational algorithms and processors that enabled study of individual particles and their interactions, as a complement to experimental studies.

These developments answered many open questions in the behavior of dilute to moderately concentrated suspensions of spherical colloids – such as the origin of shear thinning, shear thickening, normal stress differences, and more recently, discontinuous shear thickening. In simple colloidal fluids for example, a competition between Brownian relaxation and imposed flow can produce pronounced shear thinning, and hydrodynamic forces can induce shear thickening [1,2] central to the flow behavior of foodstuffs such as mayonnaise [3–5] or industrial fluids such as polymeric solutions used for enhanced oil recovery [6]. Changes in concentration can increase viscosity and amplifies overall non-Newtonian shear-thickening and shear-thinning behavior. Increased interparticle repulsion can dramatically reduce hydrodynamic shear thickening [7] but direct frictional contact can lead to discontinuous shear thickening [8,9]. Thermodynamic phase change can also be triggered, such as crystallization by increasing colloid concentration [10], but even within one thermodynamic phase, changes in the interactions between particles can produce dramatically different microstructures and in turn, mechanical behaviors.

Phase/property relations are extensively exploited in the processing of food and industrial products. A familiar example is milk, a special colloidal suspension that comprises fat droplets suspended in water, which forms an oil-in-water nano-emulsion. Processing techniques such as heating, acidification, and enzyme treatment control the size and interactions between the droplets to produce dairy products such as cream and yoghurt or imbue unique textures to cheese. Another broad colloidal material class is industrial coatings, which leverage particle attractions and phase transitions for curing and development of color and electronic properties. For example, phases of colloidal laponite [11,12], pigment [13,14], or metal oxide particles [15,16] can be fine-tuned to create colloidal films that impart corrosion resistant glazes, color, and magnetic properties for storage. Techniques such as attraction-driven self-assembly or evaporation-driven convective assembly that sculpt crystalline, glassy, or bi-continuous network structures have been developed for manufacturing paint [13,14], ceramics [17,18], magnetic storage [15,16], and biomedical devices [19,20]. Despite the sophistication of structural and rheological characterization methods, techniques for fine tuning structure and rheology of novel materials such as vegan dairy and meat products to mimic their traditional counterparts or industrial coatings with any color and desired selective permeability are typically empirical, because computational models lack much of the details of particle attributes in these more complex but very common systems.

Modeling Challenges

Hard-sphere colloids have been the workhorse model system for colloidal phase behavior, where two parameters determine the thermo-dynamic/equilibrium state of the system: particle-scale interactions and colloid concentration. The potential of interaction between colloids in suspension can be modulated to trigger equilibrium phase transitions and formation of non-equilibrium "states" such as gels. However, as noted above, most industrial suspensions involve colloidal particles that are irregular in shape, polydisperse in size distribution, squishy, soft, or porous, and which experience short- and long-range attractions and repulsions that can shift with changing temperature or other environmental triggers, and thus dramatically alter flow rheology, phase behavior, curing, and long-term stability. Predictive modeling of such behavior in dynamic simulation requires advances in algorithms to accurately mimic particle interactions and the impact of real processing conditions. While molecular-dynamics simulations is capable of representing such detailed interactions between pairs of particles, predictive models of entire suspension behavior requires representation of these interactions between hundreds of thousands of particles in large-scale models — and such large-scale modeling capability lags far behind.

Advancement requires multi-scale connection between molecular-scale modeling (which can explicitly represent individual solvent and other molecules that give rise to interactions between colloids, but are severely limited in duration and system size owing to the extremely high resolution of molecular modeling) and meso-scale modeling such as Stokesian dynamics or Brownian dynamics, which can simulate very large suspensions but coarse-grains particle interactions. In addition, verification that a computational model produces the same material behavior as the experimental system (effective viscosity, viscoelastic moduli, osmotic pressure, phase and gel lines) is essential, and this requires algorithms to iteratively refine computational models to experimental systems. Together, these three — molecular-scale modeling, colloidal-scale modeling, and experiment are the three legs required to support a comprehensive modeling effort.

Dynamic Simulation of Colloidal Systems

Colloids are microscopically small particles suspended in a continuum fluid. Colloids range in size from a few nanometers to a few microns can be spherical, rod-like, or irregularly shaped; they can be slippery, sticky, squishy, porous, or solid; and can exist in dilute conditions like a gas of particles, dense liquid-like suspensions, or concentrated enough to form crystals or glasses. Continuum mechanics describe the flow of the suspending medium, but because colloids are Brownian, their motion and distribution are stochastic. The competition between Brownian, hydrodynamic, and external forces that determines the arrangement of particles in space, which in turn affects the bulk material properties. There are three primary ingredients required to model colloidal suspensions[21]: detailed models of the microscopic forces between the colloids; a systematic way to connect these forces to the distribution of particles in space and time; and statistical models to predict bulk suspension properties as volume or configuration averages over all phases. Of these, the representation of microscopic forces is the center of advancement in modeling suspensions.

Mature computational techniques: hydrodynamic interactions. In dilute suspensions, robust theory exists to explain the fundamental physics of hydrodynamic interactions and Brownian motion, and how their interplay under various flow conditions leads to non-Newtonian rheology and phase transitions. However, many-body interactions become important in moderately concentrated and dense suspensions, requiring the computational solution of the detailed momentum balance on either the fluid or on each individual colloidal particle. In contrast to Molecular Dynamics modeling, most meso-scale modeling approaches (like Stokesian dynamics, Brownian dynamics, and Immersed Boundary Methods, among others) represent the suspending fluid implicitly, treating it as a continuum solvent with specified viscosity ad density. Dissipative Particle Dynamics (DPD) straddles both limits. The continuum approach makes it possible to follow suspension behavior over seconds, minutes, even hours or days – as compared with nano-seconds in MD approaches.**There are two primary approaches for mesoscale computational modeling colloidal suspensions: those in which the Navier-Stokes equations are solved, subject to boundary conditions on each particle; and those in which detailed solution of fluid motion are bypassed and instead the microhydrodynamics are encoded into mobility and resistance tensors that dictate how particles move.** Each approach has its strengths and weaknesses. Approaches such as Immersed Boundary Methods are powerful for representing complex flow and container geometries, as well as non-Newtonian suspending solvents, but are challenging beyond a small number of particles. Approaches such as Fast Multipole Methods (FMM) and Stokesian Dynamics (SD) bypass solution of the Navier-Stokes equations, but must overcome two key challenges: representing lubrication interactions between nearly-contacting colloids, which are singular; and representing many-body interactions for other particles. Stokesian Dynamics overcomes both challenges using an efficient and accurate superposition technique[22–25].

The Stokesian dynamics algorithm changed the landscape of the study of low-Re number particulate flows by making accessible the study of real systems where many-body effects and lubrication forces (e.g dense suspensions) play a role[23]. It established dynamic simulation as an important complement to experiments, free of many of the assumptions made in dilute theories. The ability to monitor detailed particle positions and trajectories provided crucial insight inaccessible to experimentalists until decades later when microscopy methods advanced. This produced mechanistic understanding of key non-Newtonian behaviors of flowing Brownian suspensions, including the role of hydrodynamic interactions in shear thickening and verification that weakening Brownian motion, rather than a disorder-to-order structural transition produces shear thinning[26,27]. Stokesian Dynamics also provided a verification of theoretical models and insight into many other suspension phenomena[24,28,29]. More recent expansion of the Stokesian Dynamics algorithm includes modeling confined suspensions[30–32].

The primary limitations of Stokesian dynamics center on matrix operations where, for a system of N particles, required initially $O(N^3)$ operations and limited early simulations to fewer than 30 particles. However, several algorithmic advances in the last 20 years have resulted in dramatic efficient gains. The $O(N \log N)$ scaling of Accelerated Stokesian Dynamics (ASD) changed the game dramatically and enabled the accurate and fast study of $O(100)$ particles systems with many-body hydrodynamic interactions, by operating matrix free and thus bypassing the expense associated with matrix inversions. Despite this progress, computation of far-field coupling due to Brownian disturbance flows remained an Achilles' heel of Stokesian dynamics. The computations involved in Brownian motion were not accelerated in the version of ASD with Brownian motion[33]; an approximation used as a workaround sufficed for many years of study of flowing suspensions but can introduce questionable error into study of phase behavior, where Brownian motion is a central factor in system dynamics. Until recently, the far-field Brownian force has been computed either with a Chebychev approximation[33] or other techniques[30,32,34].

Moreover, serial versus parallel implementation can enhance performance significantly: serial computation is limited to $O(100)$ particles[35]. Recently Stokesian Dynamics was implemented on a single GPU on a shared memory architecture and is able to simulate from $O(10,000)$[34] to $O(100,000)$ particles[36], where efficient algorithms were designed to account for the GPU architecture, along with implementations of new methods to efficiently handle the complexities of Brownian disturbance flows. We recently developed a suite of scalable algorithms to simulate large-scale colloidal systems amenable for modeling dense colloidal suspensions, glasses and gels with full hydrodynamics[37]. To handle the large number of particles and consequent many-body interactions present in such systems, we developed a novel parallel implementation of Accelerated Stokesian Dynamics (ASD) a distributed memory architecture. We demonstrated good scaling for a million particles distributed over tens of thousands of processors. In addition, we developed a novel algorithm to efficiently simulate correlated Brownian motion with hydrodynamic interactions. Our straightforward and flexible approach reduces the computational time of the Brownian far- field force construction from $O(N \log N) + |\alpha|$ to $O(N \log N)$[37]. More recently, we have implemented an interparticle interactions algorithm that represents a basic isotropic attraction and repulsion between particles, and demonstrated phase separation, gelation, and vitrification behavior. **Overall, representation of strong hydrodynamic interactions and Brownian forces in large suspensions is now robust.**

Opportunities in computational techniques: complex interparticle forces. Progress in the last several years in the computational modeling of of interparticle forces in suspensions has shed light on several long-standing open questions in industrial colloidal materials. For example, recent efforts to represent frictional forces in computational models now recovers discontinuous shear

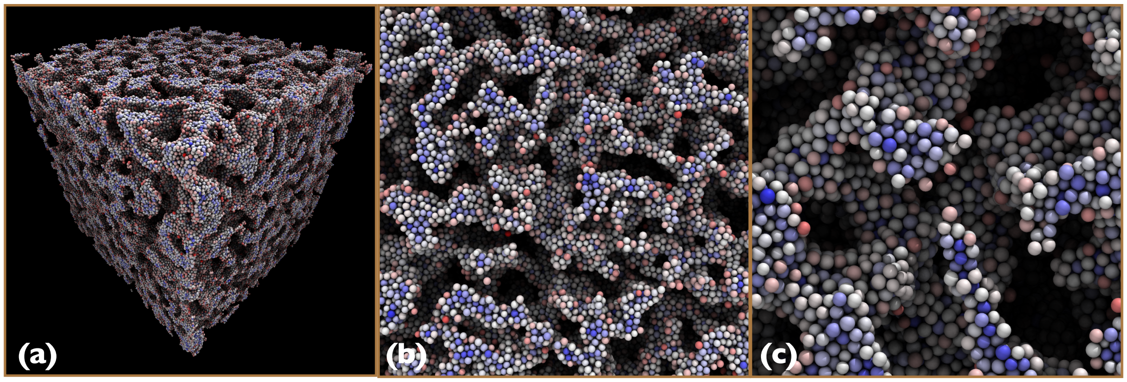


Figure 1: Snapshots of a colloidal gel from dynamic simulation. (a) One periodic cell. (b) 2x magnification. (c) 4x magnification. Number of contacts per particle indicated by color, ranging from red (few) to blue (many). [40] Cross sections of gel strands reveal high-contact number interior particles and glassy interior morphology.

thickening long observed in industrial suspensions but was the subject of contentious disagreement until theoretical and computational modeling interrogated the detailed influence of surface friction and contact. Another example is the representation of reversible attractive physico-chemical forces in colloids that led to the first studies of age-evolution of structure and rheology in colloidal gels, which led in turn to explaining the origins of gravitational collapse and delayed shear yield. Vitrification is another area of progress in computational study, where recent work has been able to interrogate particle dynamics deep into the glassy region inaccessible to experiments. **While these advances provide fundamental mechanistic insight and particle/structure/property relationships for general phase and non-Newtonian behavior, current models are still relatively simple in terms of particle attributes and interactions.**

One of the key requirements for constructing computational models that accurately represent the real laboratory material is a means by which to match particle-scale interactions between colloids *in silico* to those in the experimental system. The typical approach in simulations is to select one of several standard analytical potentials with a nominal strength and range that matches those reported in the experimental literature. However, the experimental measurements typically rely on indirectly inferring the pair-level interparticle potential using a combination of measurements of microstructure – in dilute suspensions obtained via scattering techniques such as small angle x-ray or neutron scattering (SAXS or SANS). These techniques require diluteness and equilibrium conditions to avoid complex data analysis of measured scattering data[38]. Thus, it is typically assumed that the interparticle potential in dilute conditions is sufficient to describe interactions for dense samples, and that measurements of equilibrium structure alone can be utilized to construct a potential model that can accurately represent attractive forces between particles in simulation. However, these assumptions fail when the attractive forces are long-ranged and potentials developed from these techniques fail to accurately predict equilibrium and non-equilibrium phase boundaries as the detailed interaction profile influence the location of such boundaries[39]. As a result, current computational methods cannot accurately *match* interparticle potentials to laboratory systems that predict gelation, vitrification, and percolation lines except in very simple cases.

Our progress in simulating laboratory conditions for particle interactions. We recently developed a new algorithm that combines experiments and simulations that accurately predicts not only equilibrium phase transitions in colloids, but also gelation, vitrification, and self-assembly into complex structures[40–43]. We expanded the existing LAMMPS software package to implement time-dependent adjustment of pairwise-interaction forces that can mimic laboratory "quenches" in temperature, pH, or concentrations that change interparticle interactions over time. The novel

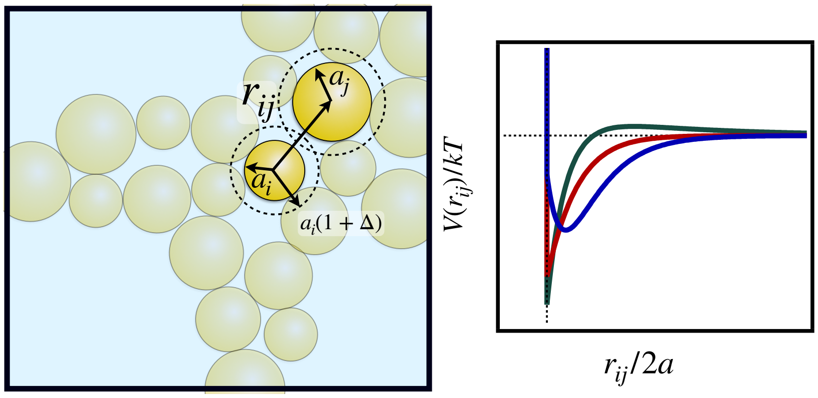


Figure 2: Our algorithm can predict experimentally-derived particle interactions that mimic equilibrium and non-equilibrium phase transitions in laboratory samples.[44] The computational model constructed in our expanded LAMMPS can represent this interparticle interaction, that can take any range or detailed shape.

framework includes an iterative process for analyzing scattering measurements data to construct an interparticle potential. The framework is agnostic to the size, shape, or topology (e.g. patchy interactions) of particles and interactions and is thus suitable for a wide range of particulate systems found in natural, biological, and industrial samples. To streamline the analysis of large simulation outputs, our group also developed a suite of post-processing code that can quickly assess the microscopic and macroscopic structure, rheology, and tortuosity of suspensions and solids formed in our simulations. Thus, our framework for extracting potentials, simulation tools, and post-processing code can be pipelined to interrogate in vitro samples to construct a computational model that can be subjected to simulations that replicate laboratory samples. In our current work, we demonstrated an application of our tools to extract an interparticle potential from a laboratory model thermoresponsive nanoemulsion system and implement it simulation. The resultant simulations produce a close match in equilibrium and non-equilibrium phase transitions.

Proposed Work

We propose to advance the modeling of industrially-relevant complex particle systems by expanding our current models beyond smooth hard-sphere colloids. To do so, we propose to systematically incorporate a set of physico-chemical surface conditions into our models, interacting with experiments and molecular-dynamics simulations to refine the detailed representation of interactions. We can then optionally apply our models to the study of three important problems in colloidal systems: colloidal gelation; gravitational collapse of colloidal gels; and flow-dependent rheology of dense suspensions.

Aim 1. We will develop new potential interactions via collaboration with experimentalists and molecular dynamics simulations towards detailed matching of interactions between particles to experimental systems.
Specific Objective 1: Develop the bumpy-surface model. We will utilize two approaches for building the ‘raspberry’ particle model as defined by the Vermant group at ETH. First we will construct the algorithm in our LAMMPS model using valency model recently developed in our group. We will explore the impact of the bumpy shape on diffusion, viscosity, osmotic pressure, and packing. We will then conduct an evaluation of how this portion of the algorithm can be incorporated into our Accelerated Stokesian dynamics model.
Specific Objective 2: Match to molecular dynamics simulations. Insight from MD simulations will be leveraged model the details of contour interactions, to determine if the colloidal-scale model can be simplified for efficiency, and to provide a baseline for refinement during experimental matching.

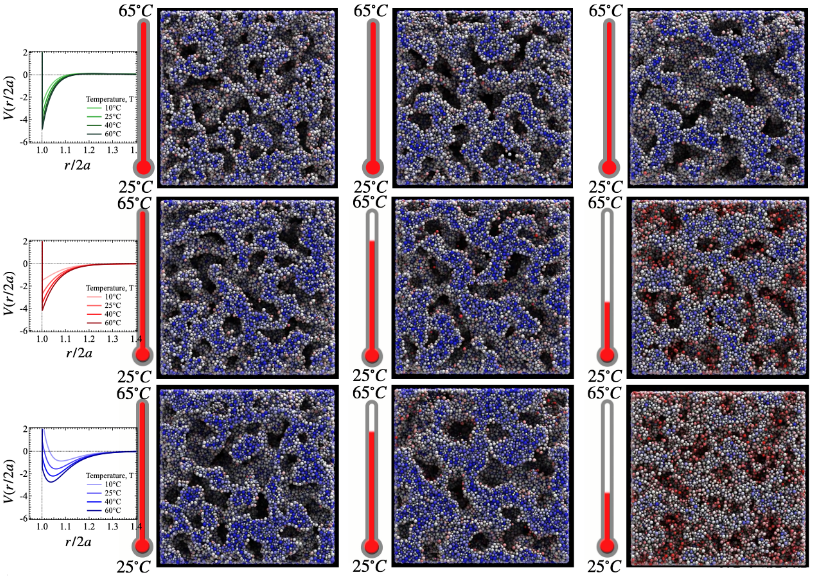


Figure 3: Our interactive algorithm accurately predicts qualitative changes in gelation and vitrification when attractive forces that are identical at equilibrium are involved in phase arrest.[44] In the proposed work, we can expand this model for other laboratory conditions besides temperature changes, or other particle surface conditions.

Specific Objective 3: Match to experiments. We recently developed an algorithm for detailed matching of the interactive potential of an experimental system to both equilibrium and non-equilibrium phase transitions and complex self-assembly [Figure 3][44,45]. We will expand this algorithm with additional models of the interactive potential to simulate the bumpy-surface 'raspberry' particles synthesized in the research laboratories of Prof. Dr. Jan Vermant and Prof. Dr. Lucio Isa at ETH. We will then carry out the matching process via iterative refinement with experiments to select best representative potential.

Aim 2. Incorporate the new particle interaction algorithms and size polydispersity into our Parallelized ASD model.

Specific Objective 1: Represent size polydispersity in ASD. Representing size polydispersity in the ASD environment requires adapting new spectral methods into the domain discretization. We will incorporate these changes into our model during the first two years of the project. This will involve merging spectral or other methods for distributing size into our parallel computing platform. This work can occur alongside Aim 1.

Specific Objective 2: Validation testing. In collaboration with experimentalists, we will verify the impact of size polydispersity on packing, diffusion, osmotic pressure, and vitrification.

References

[1] G. K. Batchelor, "Transport properties of two-phase materials with random structure," *Annual Review of Fluid Mechanics*, vol. 6, no. 1, pp. 227–255, 1974.

[2] G. Batchelor, "The effect of brownian motion on the bulk stress in a suspension of spherical particles," *Journal of fluid mechanics*, vol. 83, no. 1, pp. 97–117, 1977.

[3] M. Marcotte, A. R. T. Hoshahili, and H. Ramaswamy, "Rheological properties of selected hydrocolloids as a function of concentration and temperature," *Food Research International*, vol. 34, no. 8, pp. 695–703, 2001.

[4] M. A. Rao, S. S. Rizvi, A. K. Datta, and J. Ahmed, *Engineering properties of foods*. CRC press, 2014.

[5] Z. Ma and J. I. Boye, "Advances in the design and production of reduced-fat and reduced-cholesterol salad dressing and mayonnaise: a review," *Food and Bioprocess Technology*, vol. 6, no. 3, pp. 648–670, 2013.

[6] K. C. Taylor and H. A. Nasr-El-Din, "Water-soluble hydrophobically associating polymers for improved oil recovery: A literature review," *Journal of Petroleum Science and Engineering*, vol. 19, no. 3-4, pp. 265–280, 1998.

[7] B. J. Maranzano and N. J. Wagner, "The effects of interparticle interactions and particle size on reversible shear thickening: Hard-sphere colloidal dispersions," *Journal of Rheology*, vol. 45, no. 5, pp. 1205–1222, 2001.

[8] H. Barnes, "Shear-thickening ("dilatancy") in suspensions of nonaggregating solid particles dispersed in newtonian liquids," *Journal of Rheology*, vol. 33, no. 2, pp. 329–366, 1989.

[9] R. Seto, R. Mari, J. F. Morris, and M. M. Denn, "Discontinuous shear thickening of frictional hard-sphere suspensions," *Physical review letters*, vol. 111, no. 21, p. 218301, 2013.

[10] J. L. Digaum, J. J. Pazos, J. Chiles, J. D'Archangel, G. Padilla, A. Tatulian, R. C. Rumpf, S. Fathpour, G. D. Boreman, and S. M. Kuebler, "Tight control of light beams in photonic crystals with spatially-variant lattice orientation," *Optics express*, vol. 22, no. 21, pp. 25788–25804, 2014.

[11] H. Z. Cummins, "Liquid, glass, gel: The phases of colloidal laponite," *Journal of Non-Crystalline Solids*, vol. 353, no. 41-43, pp. 3891–3905, 2007.

[12] B. Ruzicka and E. Zaccarelli, "A fresh look at the laponite phase diagram," *Soft Matter*, vol. 7, no. 4, pp. 1268–1286, 2011.

[13] J. E. Wijnhoven and W. L. Vos, "Preparation of photonic crystals made of air spheres in titania," *Science*, vol. 281, no. 5378, pp. 802–804, 1998.

[14] J. F. Galisteo-López, M. Ibisate, R. Sapienza, L. S. Froufe-Pérez, Á. Blanco, and C. López, "Self-assembled photonic structures," *Advanced Materials*, vol. 23, no. 1, pp. 30–69, 2011.

[15] Z. Yu, C.-F. Wang, L. Ling, L. Chen, and S. Chen, "Triphase microfluidic-directed self-assembly: Anisotropic colloidal photonic crystal supraparticles and multicolor patterns made easy," *Angewandte Chemie*, vol. 124, no. 10, pp. 2425–2428, 2012.

[16] J. Wang, Y. Hu, R. Deng, R. Liang, W. Li, S. Liu, and J. Zhu, "Multiresponsive hydrogel photonic crystal microparticles with inverse-opal structure," *Langmuir*, vol. 29, no. 28, pp. 8825–8834, 2013.

[17] L. Gauckler, T. Graule, and F. Baader, "Ceramic forming using enzyme catalyzed reactions," *Materials chemistry and physics*, vol. 61, no. 1, pp. 78–102, 1999.

[18] J. A. Lewis, "Colloidal processing of ceramics," *Journal of the American Ceramic Society*, vol. 83, no. 10, pp. 2341–2359, 2000.

[19] G. Bonacucina, M. Cespi, M. Misici-Falzi, and G. F. Palmieri, "Colloidal soft matter as drug delivery system," *Journal of pharmaceutical sciences*, vol. 98, no. 1, pp. 1–42, 2009.

[20] M. C. Koetting, J. T. Peters, S. D. Steichen, and N. A. Peppas, "Stimulus-responsive hydrogels: Theory, modern advances, and applications," *Materials Science and Engineering: R: Reports*, vol. 93, pp. 1–49, 2015.

[21] W. B. Russel, "The Huggins coefficient as a means for characterizing suspended particles," *J. Chem. Soc., Faraday Trans. 2*, vol. 80, no. 1, pp. 31–41, 1984.

[22] J. F. Brady and G. Bossis, "The rheology of concentrated suspensions of spheres in simple shear flow by numerical simulation," *Journal of Fluid Mechanics*, vol. 155, pp. 105–129, 1985.

[23] L. Durlofsky, J. F. Brady, and G. Bossis, "Dynamic simulation of hydrodynamically interacting particles," *Journal of fluid mechanics*, vol. 180, pp. 21–49, 1987.

[24] G. Bossis and J. F. Brady, "Self-diffusion of brownian particles in concentrated suspensions under shear," *The Journal of chemical physics*, vol. 87, no. 9, pp. 5437–5448, 1987.

[25] J. F. Brady and G. Bossis, "Stokesian dynamics," *Annual review of fluid mechanics*, vol. 20, no. 1, pp. 111–157, 1988.

[26] G. Bossis and J. Brady, "The rheology of brownian suspensions," *The Journal of chemical physics*, vol. 91, no. 3, pp. 1866–1874, 1989.

[27] D. R. Foss and J. F. Brady, "Brownian dynamics simulation of hard-sphere colloidal dispersions," *Journal of Rheology*, vol. 44, no. 3, pp. 629–651, 2000.

[28] T. N. Phung, J. F. Brady, and G. Bossis, "Stokesian dynamics simulation of brownian suspensions," *Journal of Fluid Mechanics*, vol. 313, pp. 181–207, 1996.

[29] D. R. Foss and J. F. Brady, "Self-diffusion in sheared suspensions by dynamic simulation," *Journal of fluid mechanics*, vol. 401, pp. 243–274, 1999.

[30] J. W. Swan and J. F. Brady, "The hydrodynamics of confined dispersions," *Journal of Fluid Mechanics*, vol. 687, pp. 254–299, 2011.

[31] C. Aponte-Rivera and R. N. Zia, "Simulation of hydrodynamically interacting particles confined by a spherical cavity," *Physical Review Fluids*, vol. 1, no. 2, p. 023301, 2016.

[32] C. Aponte-Rivera, Y. Su, and R. N. Zia, "Equilibrium structure and diffusion in concentrated hydrodynamically interacting suspensions confined by a spherical cavity," *Journal of Fluid Mechanics*, vol. 836, pp. 413–450, 2018.

[33] A. J. Banchio and J. F. Brady, “Accelerated stokesian dynamics: Brownian motion,” *The Journal of chemical physics*, vol. 118, no. 22, pp. 10323–10332, 2003.

[34] M. Wang and J. F. Brady, “Spectral ewald acceleration of stokesian dynamics for polydisperse suspensions,” *Journal of Computational Physics*, vol. 306, pp. 443–477, 2016.

[35] A. Sierou and J. F. Brady, “Accelerated stokesian dynamics simulations,” *Journal of fluid mechanics*, vol. 448, pp. 115–146, 2001.

[36] A. M. Fiore and J. W. Swan, “Fast stokesian dynamics,” *Journal of Fluid Mechanics*, vol. 878, pp. 544–597, 2019.

[37] G. Y. Ouaknin, Y. Su, and R. N. Zia, “Parallel accelerated stokesian dynamics with brownian motion,” *Journal of Computational Physics*, p. 110447, 2021.

[38] J. t. Schelten and W. Schmatz, “Multiple-scattering treatment for small-angle scattering problems,” *Journal of Applied Crystallography*, vol. 13, no. 4, pp. 385–390, 1980.

[39] M. G. Noro and D. Frenkel, “Extended corresponding-states behavior for particles with variable range attractions,” *The Journal of Chemical Physics*, vol. 113, no. 8, pp. 2941–2944, 2000.

[40] R. N. Zia, B. J. Landrum, and W. B. Russel, “A micro-mechanical study of coarsening and rheology of colloidal gels: Cage building, cage hopping, and smoluchowski’s ratchet,” *Journal of Rheology*, vol. 58, no. 5, pp. 1121–1157, 2014.

[41] P. Padmanabhan and R. Zia, “Gravitational collapse of colloidal gels: Non-equilibrium phase separation driven by osmotic pressure,” *Soft Matter*, vol. 14, no. 17, pp. 3265–3287, 2018.

[42] X. Peng, J. G. Wang, Q. Li, D. Chen, R. N. Zia, and G. B. McKenna, “Exploring the validity of time-concentration superposition in glassy colloids: Experiments and simulations,” *Physical Review E*, vol. 98, no. 6, p. 062602, 2018.

[43] J. G. Wang, Q. Li, X. Peng, G. B. McKenna, and R. N. Zia, ““dense diffusion” in colloidal glasses: short-ranged long-time self-diffusion as a mechanistic model for relaxation dynamics,” *Soft matter*, vol. 16, no. 31, pp. 7370–7389, 2020.

[44] B. K. Ryu, S. M. Fenton, T. T. D. Nguyen, M. E. Helgeson, and R. N. Zia, “Incorporating non-equilibrium phenomena in the modeling of colloidal interactions with application to thermoresponsive gelation.” Provisionally accepted, the Journal of Chemical Physics., 2022.

[45] S. Fenton, B. K. Ryu, P. Padmanabhan, T. Nguyen, R. N. Zia, and M. E. Helgeson, “Intersection of percolation, phase separation and glassy behavior sets minimal conditions for gelation of colloidal systems.” In preparation, for submission to PNAS., 2022.

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

Continuation Proposal

2021

Primary Investigator: Nasser Ashgriz
PhD Students: Isaac Jackiw & Siyu (Jerry) Chen
Institution: University of Toronto, Canada

IFPRI
International Fine Particle Research Institute

University of Toronto | Department of Mechanical and Industrial Engineering

Abstract

This proposal is a continuation of our current IFPRI research on the atomization process by swirl and twin-fluid nozzles. The current research is on homogenous viscous fluids, and the present proposal extends it to slurries and fluids with suspensions. We will measure the droplet size distributions from sprays of suspensions with different particle types and sizes, and solutions with elongational viscosity, surface tension, and molecular weight. Both pressure-swirl and twin-fluid nozzles will be studied. We will develop physical models for the atomization of these fluids. This will be achieved by performing breakup studies on droplets and ligaments of fluids with suspension. Breakup process of a droplet or a ligament will also allow for a quantitative determination of the effect of the cross-flow temperature on the breakup process.

Summary of the Current IFPRI Project

A detailed description of the project was submitted in our final report to IFPRI. Here, only a brief discussion of our previous project is provided.

We performed experiments on the sprays generated by swirl and twin fluid nozzles and measured droplet size distributions and obtained near-nozzle images of the atomization process for these nozzles. Glycerin/water and CMC/water solutions were used as test fluids. Mass flow rate, spray angle and liquid sheet breakup lengths were measured for each case.

1. Liquid Sheet Breakup Based Model for Swirl Nozzles

The droplet size distribution of high viscosity and polymeric fluids can have a bimodal distribution, with a minor and a major peaks (modes). A mixture of two lognormal distributions fit the volume distribution of all testing conditions. The minor peak (mode) of the size distribution represents the long tail of the volume distribution and it corresponds to droplets of less than 10 µm. These small droplets are mainly generated by the breakup of thin and stretched ligaments generated by the breakup of the swirling liquid sheet. The transition from minor to major peak is smoother for polymeric fluids. The thin ligaments are stretched into a wide range of sizes in the polymeric cases, while they rapidly breakup in glycerin solutions.

A distribution function of the following form was developed that fits the data well: $f_3(d) = k_v f_{3,1}(d; \hat{\mu}_1, \hat{\sigma}_1) + (1 - k_v) f_{3,2}(d; \hat{\mu}_2, \hat{\sigma}_2)$. Here, k_v represents the volume ratio between the major mode for large droplets ($f_{3,1}$) and the minor mode for small droplets ($f_{3,2}$). Based on our model, the droplet size distribution can be predicted using the following steps:

1) Determine the fluid properties including density ρ, kinematic viscosity ν, surface tension σ and the operating conditions, including the injection pressure P and the swirl nozzle orifice diameter d_o. Measure the mass flow rate $\dot{m}$ and the spray angle θ.
2) Calculate the sheet velocity u using $u = k_d\sqrt{2P/\rho}$, where $k_d$is the discharge coefficient of the nozzle.
3) Solve for the sheet thickness, t_{or}, from $\dot{m} = (\rho u \cos\theta)\, \pi t_{or}(d_o - t_{or})$.
4) Solve for the dominant wavenumber k_{max} using the dispersion equation

$$\omega = -2\nu k^2 + (4\nu^2 k^4 + \rho_r u^2 k^2 - (\sigma k^3/\rho_l\,)^{\,0.5},$$

where ω is the growth rate and k is the wavenumer.

5) Calculate the dominant wavelength λ_{KH} using $\lambda_{KH} = 2\pi/k_{max}$.
6) Calculate the parameters in the distribution equation using

$$\hat{\mu}_1 = 1.96\lambda_{KH}^{0.589} \;\; and \;\; \hat{\sigma}_1 = 0.065t_{or}^{0.517}.$$

7) The volume distribution is given by $f_3(d) = f(d; \hat{\mu}_1, \hat{\sigma}_1)$, where f is a lognormal distribution:

$$f(d) = \frac{1}{d\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{ln(d/\hat{\mu})}{\hat{\sigma}}\right)^2\right).$$

SMD and other averages can be determined from the above distribution function. In addition, the following correlation is developed for the Sauter Mean Diameter (SMD) of sprays formed by a swirl nozzle and for high viscosity fluids.

$$\frac{d_{32}}{d_o} = 42.52\, Re_p^{-0.151}\, We_p^{-0.519}$$

High resolution closeup imaging of the swirl nozzles revealed that the liquid sheet perforation process in the dominate mechanism for the atomization process. In order to quantify this process, experiments on the atomization of flat sheets of liquid is currently being performed. A flat sheet of liquid, as in fan sprays, eliminates the sheet curvature, and allow for better imaging. Figure 1 shows some typical images of a 60% glycerin-water solution at different injection pressure. At 600 psi injection pressure, the sheet is smooth. As the pressure increases to 700 psi, the liquid inside the nozzle becomes turbulent. Increasing the pressure to 800 psi and then to 900 psi, increases the turbulent intensity, and makes the sheet more perturbed right at the exit of the nozzle. These perturbations expedite the breakup of the sheet. Therefore, laminar sheet breakup models overpredict sheet breakup length. The size of the these turbulent structures are at the scale of Taylor microscale. We are currently developing a turbulent based model for this process.

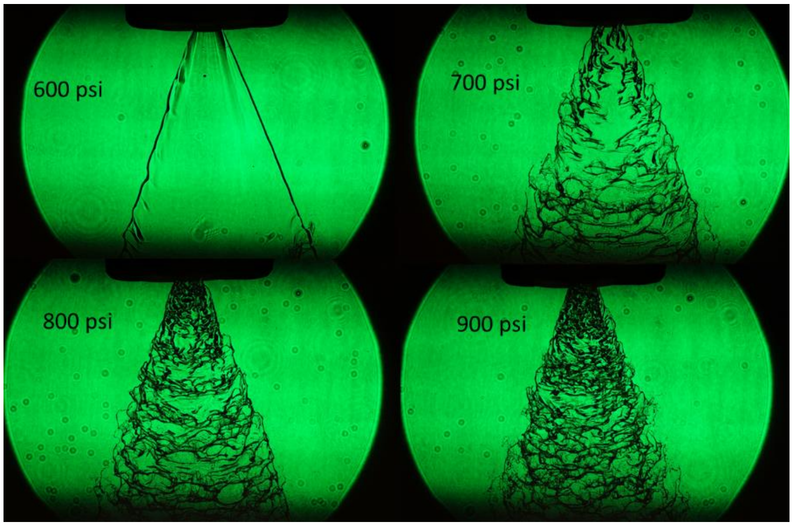


Figure 1. Atomization of 60% glycerin-water solution in a flat fan nozzle at different injection pressures.

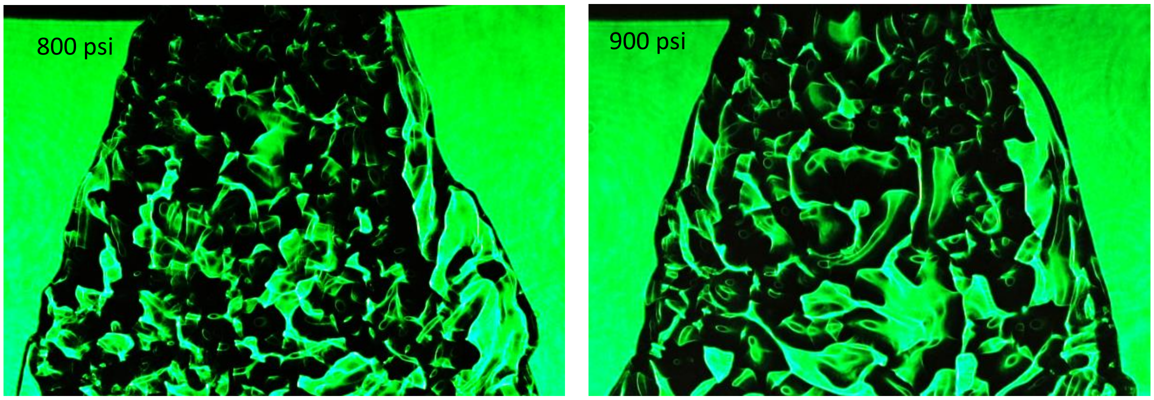


Figure 2. Turbulent structures right at the exit of the nozzle.

2. Droplets Breakup Based Model for Twin Fluid Nozzles

For twin fluid nozzles, a new phenomenological model was developed that predicts the size distribution from the primary and secondary atomization. The details of the experience and the model are present in the final report and two journal articles[1,2]. The model is outlined as follows: Starting from an initial characteristic size and relative velocity, the formation of the ligaments (i.e., the rims) is predicted via the droplet deformation rate. The characteristic size can be obtained from the KH wavelength, the liquid jet diameter, or the drop diameter. Three modes of ligament breakup are modeled. Several mechanisms contribute to the breakup of each. Taking the mean and standard deviation of the predictions for each mechanism, the distribution resulting from each mode is predicted. Combining the distributions of the modes, the multimodal distribution of the spray is predicted. In cases where modes overlap considerably, a weighted mean and standard deviation can be used to predict the overall distribution of the constituent modes.

This model is applied to the atomization of twin fluid nozzles, by using the oscillation characteristic of a liquid jet exiting the nozzle (figure 3). The Kelvin Helmholtz wave is used as the size of the droplet that goes through bag breakup. Then, the droplet sizes from this breakup are used to determine the droplet size distribution in the spray as depicted in figure 4. The results of the predictions are compared with the experimental data in figure 5, which shows a good prediction.

---

[1] Jackiw, I., and Ashgriz, N., "On aerodynamic droplet breakup," Journal of Fluids Mechanics, Volume 913, 25 April 2021, A33.

[2] Jackiw, I., and Ashgriz, N., "Prediction of the droplet size distribution in aerodynamic droplet breakup," Journal of Fluids Mechanics, (2022), vol. 940.

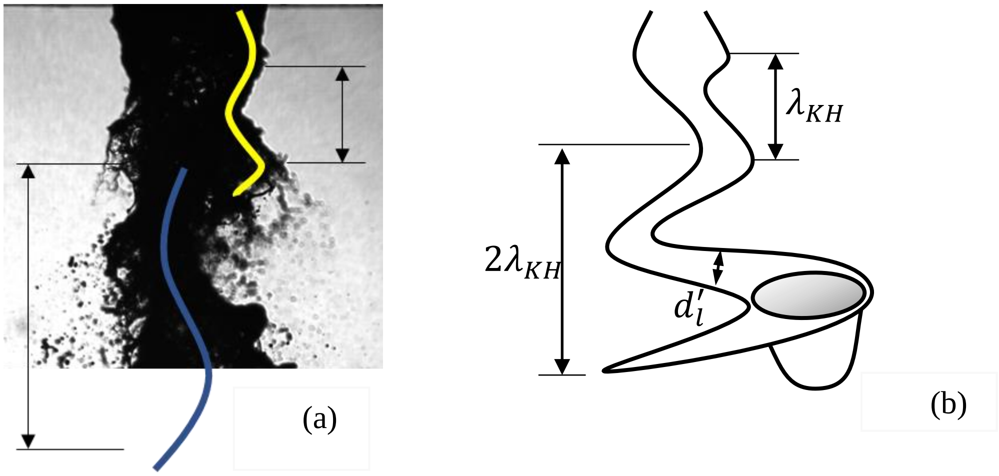


Figure 3. (a) In a twin fluid atomization process, the waves on the liquid grow to an extent that the high velocity air breaks them into small droplets. (b) This is modeled through a bag breakup process.

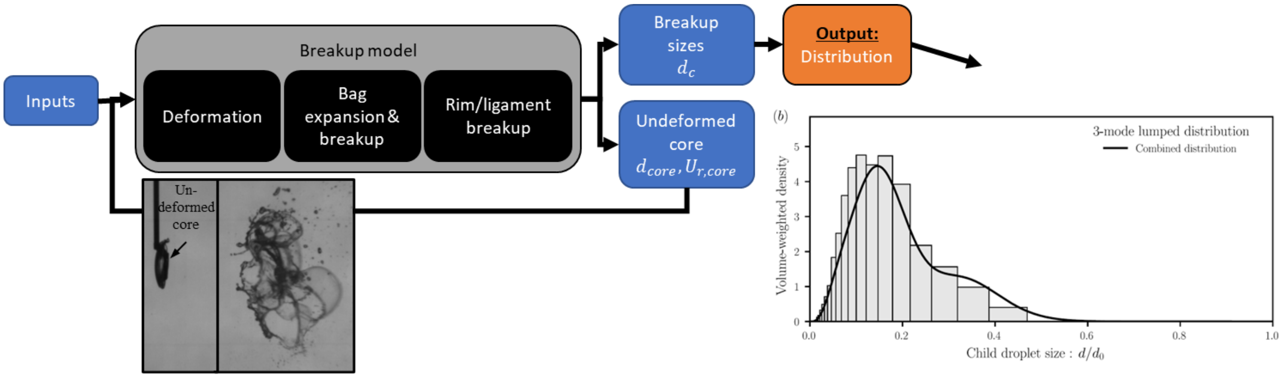


Figure 4. Using droplet breakup model to predict the droplet size distribution in a twin fluid spray.

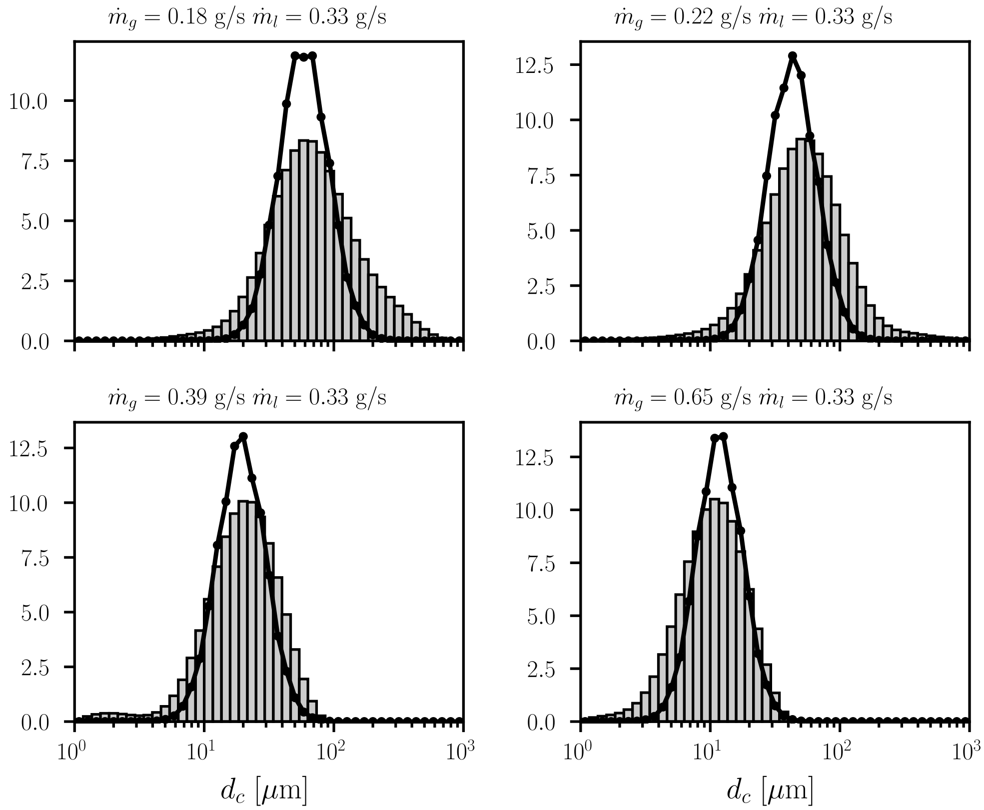


Figure 5. Comparison of our atomization model with the experimental measurements for droplet size distribution for four different flow conditions of a twin fluid nozzle.

Literature review on the atomization of slurries

The prior studies on the atomization of liquids with suspensions have identified the followings: The influence of the particles suspension on the atomization intimately relates to the particle size and concentration. No change in the spray droplet sizes was found when atomizing slurries with 4 to 16 µm particle sizes and concentrations of 0 to 30 weight percent.[3] However, solid particles of larger than 20 µm separate from water droplets with 70% weight percentage of solid suspension.[4,5] Several studies have shown bimodal distributions for slurry sprays.[6] On the other hand, unimodal size distributions were reported for slurries with mean particles sizes of less than 50 µm, and bimodal distribution for larger than 50 µm. One peak corresponded to the solid particle diameter in the suspension, and the other peak represented pure liquid spray size. At low injection pressures, the peak of the liquid droplet diameter was controlled by the solid particle size. Suspension with relatively fine solid particles result in a smaller diameter peak than the suspension with relatively large solid particles. At high injection pressures, this diameter peak is

---

[3] Isenschmid, T., 1992 Diss. ETH Nr. 9609.

[4] Glaser, H. W., 1989 VDI Düsseldorf.

[5] Mulhem, B. Fritsching, U. Schulte, G. and Bauckhage, “Characterisation of Twin-Fluid Atomisation for Suspensions,” 2001 ILASS-2001 Zurich.

controlled by the gas velocity. Atomization of lime particle slurries using a pressure-swirl nozzle has shown that SMD increases with increasing solid percentages of lime slurry.[6]

Generally, the shear thinning behaviour of the suspension viscosity, which increases with increasing solid concentration and decreasing solid particle size, makes the influence of the viscosity on the suspension break-up within a twin-fluid atomizer less important with increasing velocity of the atomizing gas[7].

Based on the current state of knowledge on the slurry atomization, the following issues are raised:

1- How does a solid particle separate from the solution? It is not clear whether the liquid is sheared off the solid particle or the particle separates during the breakup of the mixture.
2- Is there a correlation between the particle separation from the solution with respect to its size, the suspension concentration, and other solution rheological properties?
3- Does the SMD of the spray increase with an increase in solid particle size? There are conflicting results on this, as some show no increase, whereas some show an increase in SMD with particle size.
4- At what conditions does the unimodal size distribution turns into a bimodal size distribution? Clearly this is a pressure and nozzle dependent conditions. However, we aim to determine the physical conditions that may result in this. We will develop a correlation for a critical suspension parameter, at which point the size distribution becomes bimodal.
5- What are the differences between the suspension fluid atomization in pressure-swirl and twin-fluid atomization? In pressure-swirl atomization, a solution is converted into a thin sheet, which is then atomized into droplets, whereas in a twin-fluid atomization, a high gas velocity tears the solutions into droplets and ligaments. The influence of particles in each of these processes can be different. For instance, particles in a sheet may expedite preformation and breakup, whereas particles may not break off the core liquid in shearing process of twin-fluid atomization.

The present proposal is designed to address these questions.

---

[6] Yan, Y., Zhang, L., Pan, W., and Pu, G., Experimental Investigation of Atomizing Performance of Low Pressure Swirl Nozzle, Advances in Mechanical Engineering, Volume 2014, Article ID 782064, 10 pages.

[7] Mulhem, B., Schulte, G., Fritsching, U., "Solid–liquid separation in suspension atomization," Chemical Engineering Science 61 (2006) 2582 – 2589.

Objectives of the current Proposal

1. Spray droplet size measurement of liquids with solid suspension.
2. Development of correlations for droplet size distribution for slurries using swirl and twin fluid nozzles.
3. Secondary breakup of ligaments of fluids with suspensions.
4. Development of a perforation-based model for slurry atomization by swirl nozzles.
5. Development of a droplet breakup-based model for slurry atomization by twin fluid nozzles.

Proposed Research

1. Spray Characterization of Liquids with Solid Suspension

There have been several requests from IFPRI members to perform tests with slurry fluids, as well as considering the effects of other rheological properties on the atomization. We propose to investigate the effect of the following specific properties on the atomization: **slurries with different particle types and sizes** to determine how the atomization is affected; **fluids having significant elongational viscosity**, which influences the breakup of the ligaments during the secondary atomization; **surface tension**, which was not specifically studied in the previous work; and **molecular weight**, which was also not studied in the previous work. We will use both pressure-swirl and twin-fluid nozzles in this study.

The objective of this part of the research is to measure droplet size distributions generated by different slurries. There are numerous studies on the coal-slurry particles[8,9]. However, there are very limited systematic studies on other types of suspension. The non-Newtonian rheological properties of the suspension play an important role in their disintegration process. We will measure the droplet size distribution for a range of suspension fluids. We plan to use glass and zeolite particles in our study (other suspension fluids of interest to IFPRI members can be considered if suggested). The solubility effect can also be studies using zeolite with a surrogate fluid. The maximum concentration of the particles to be tested depends on the sizes of the particles. For large particle sizes, higher pressures may be needed to push high particle concentration through the nozzle orifice. Therefore, the particle concentration will be increased to as high as our pumping facility will allow.

We have been using Mavlern Spraytec Dropsizer to characterize our sprays. We also use high resolution imaging instruments to obtain close-up images of the atomization process. The same instruments will be used in the proposed study.

---

[8] Tsai, S.C., Ghazimorad, K., and Viers, B., "Airblast atomization of micronized coal slurries using a twin-fluid jet atomizer," FUEL, 1991, Vol 70, *483.*

[9] Andreussi, P., Tognotti, L., Graziadio, M., and De Michele, G., "Atomization of Coal-Water Fuels by a Pneumatic Nozzle: Characteristics of the Spray," Aerosol Science and Technology, 13, pp 35-46 (1990).

2. Correlations for Droplet Size Distribution

Malvern Dropsizer generates volume percentages of droplet size distribution. Figure 6 shows typical histograms generated by Malvern for water and glycerin-water solutions at three different operating pressures. For almost all the test cases, the histograms have one peak with a long tail on the left corresponding to the smaller droplets of less than 10 µm. The results show that as the injection pressure increases, the volume percentage of large droplets decreases and that of smaller droplets increases (e.g., the peaks move to the left).

The volume percentage is converted to the volume distribution by dividing the height of each bin by the corresponding bin width. Figure 7 shows the volume distributions corresponding to the volume percentage of figure 6. The volume distribution amplifies the changes in the effect of droplet size on volume. Therefore, Fig. 7 shows bimodal distributions for the unimodal distribution of Fig. 6. The small tail in Fig. 6, results in the first peak in volume distribution curves. In order to find a size distributions corresponding to a volume distribution, we first guess a size distribution, and then calculate the volume distribution based on that and compare it with the experimental results. The parameters of the size distribution are then changed to match the experimental data. This procedure is simple for unimodal distributions, but more complex for bimodal distributions.

We will performed similar work for slurry sprays and will develop correlations for both the SMD and also for the droplet size distributions. The PDF of the size distribution provides much more information than just the SMD.

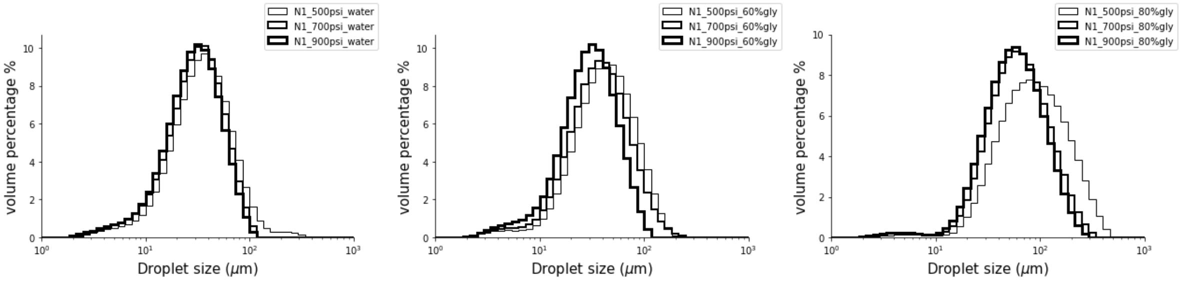


Figure 6: Volume percentage of each testing cases.

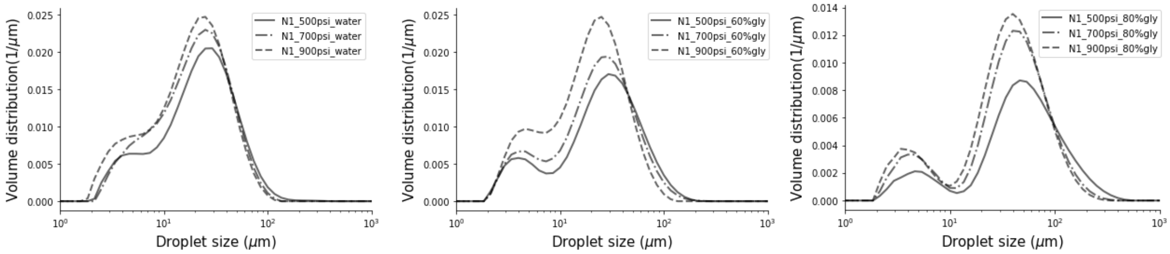
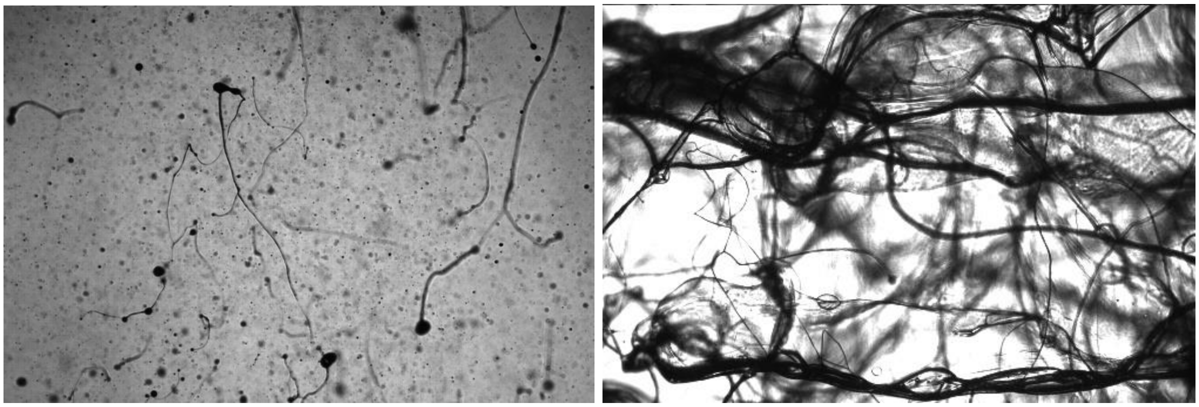


Figure 7: Volume distributions for all testing cases.

3. Secondary Breakup of Ligaments of fluids with suspensions

The atomization process for high viscosity fluids is a two step process: primary atomization generating relatively large droplets and ligaments, and secondary atomization further breaking the droplets and ligaments into smaller ones.

Our current near nozzle images of high viscosity liquids show the existence of long ligaments that may persist far downstream of the primary atomization region. This indicates a shortcoming in the traditional definitions of the atomization regions. Typically, the primary atomization results in the formation of droplets, while the secondary atomization is the breakup of those droplets. However, for viscous liquids, rather than only droplets being formed in the primary atomization region, ligaments are also produced that may undergo secondary breakup. Figure 8 shows images downstream of the nozzle where large ligaments still exist.



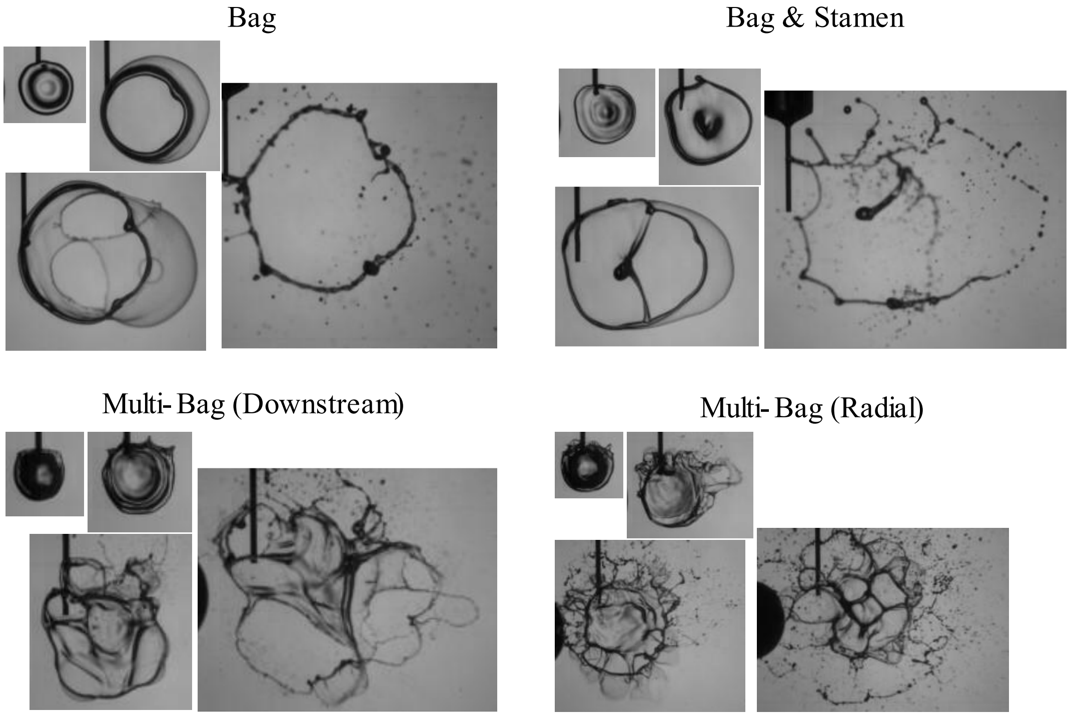
(11) (b)

Figure 8: Image of (a) a 0.5% CMC spray at 20-25mm, and (b) 80% Glycerin-water spray at 10mm downstream of the nozzle, showing the persistence of ligaments far downstream of the primary atomization region.

Although the secondary breakup of droplets has been studied extensively in the literature, the secondary breakup of ligaments has not. The question of the secondary breakup of the ligaments poses a few interesting problems, the most relevant of which is “do the ligaments break into small droplets or collapse into large droplets, and does this process occur over the timescales of spray drying?” If the timescale of the ligament secondary breakup is shorter than the drying process, then the resulting powder will have mainly spherical particles. However, if the ligaments do not break within the drying time, then the powder may have long, fibrous particles that decrease the quality of the powder. A better understanding of the secondary atomization of the ligaments will provide a basis for designing sprays to ensure that the ligaments do break within the drying time.

As we have found in our previous work, analyzing these ligaments based on commercial nozzle sprays is highly challenging. Due to the crowding of the images, ligament characterization and temporal tracking become difficult. Furthermore, it is difficult to create controlled experiments of the ligament dynamics, as they are generated somewhat chaotically. By focusing on the fundamental aspect of the secondary breakup of single ligaments, we aim to provide models and understanding of the secondary breakup of ligaments that can be used as a basis for analyzing the complex ligament networks in commercial sprays more effectively.

We propose to study the fundamental behaviours of the secondary breakup of droplets and ligaments. The study of the breakup of droplets will be a direct continuation of our previous IFPRI term,[11] which sought to understand and model the processes that lead to ligament formation and breakup. Some of the images that resulted from this study are shown in Fig. 9.


Bag

Bag & Stamen

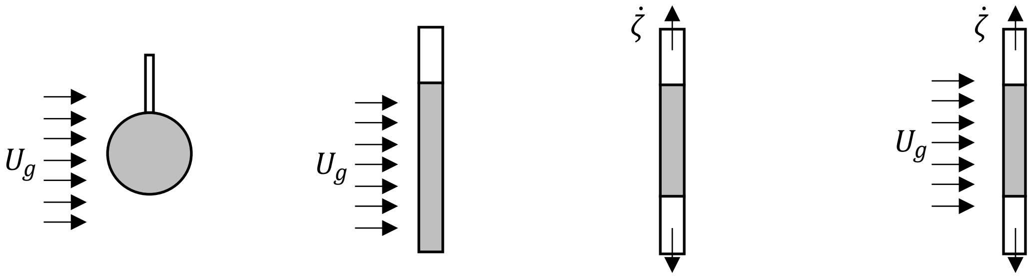
Multi-Bag (Downstream)

Multi-Bag (Radial)

Figure 9: Images of droplet breakup for various morphologies showing the formation of ligaments.

To study the breakup of ligaments, we will generate small diameter ligaments of viscous, polymeric, and slurry fluids that we will expose to a variety of conditions such as a gaseous cross flow to study their breakup. We will use both an elongated liquid bridge and also inject a liquid jet into a gaseous cross flow. These methods are illustrated in Figure 10. The dynamics of the ligaments will be captured using high-speed video so that the temporal behaviour of the ligaments can be resolved. Key factors to be determined in these experiments are the effects of the extensional viscosity on the breakup and the timescales of the ligament breakup in addition to the sizes generated. These factors are expected to be related by the critical conditions required for the ligament breakup or collapse, thus, we will aim to determine what the critical conditions are and what parameters affect or determine them.

In these experiments, we may also study the effects of elevated ambient temperatures. Since the primary atomization occurs rapidly for two-fluid nozzles, there is no significant heat transfer to the fluid during the primary atomization. However, since the ligaments in viscous sprays persist for a long time after they are formed, their dynamics may be affected by the elevated temperatures, either in the changing of the liquid properties due to heating or by the evaporation of the solvents in the liquid.



(a) Droplet in airflow (b) Jetted ligament in crossflow (c) Ligament bridge in extension (d) Ligament bridge in extension and airflow

Figure 10: Illustrations of experimental setups for study of droplet and ligament breakup

4. Perforation Based Model for Pressure-Swirl Nozzles

Based on studying the near nozzle images, we have developed a new atomization model for the pressure-swirl nozzles. The new model is based on a combination of a Kelvin-Helmholtz wave (KH) and a sheet perforation. In order to extend this model to fluids with suspensions, we need to determine the breakup length of the swirling sheet of such fluids, characterize the diameter of the ligaments formed, and determine the number and frequency of the perforations on the sheet. These are planned for the proposed period.

A perforation-based atomization model as depicted in Fig. 12 is proposed. The liquid sheet breaks up into droplets in the following steps:

1. As the high-speed swirling conical liquid sheet exits the orifice, surface waves are generated due to the Kelvin-Helmholtz (KH) instability.
2. As the liquid sheet moves downstream, the amplitude of wave crests become larger, and eventually break the sheet into segments.
3. Each segment is perforated based turbulent structures.
4. The perforation process results in a set of rectangular cells, that have span-wise and stream-wise sides.
5. The cells eventually breakup forming span-wise and stream-wise ligament with different diameters, which eventually breakup to result in droplet with different diameters.

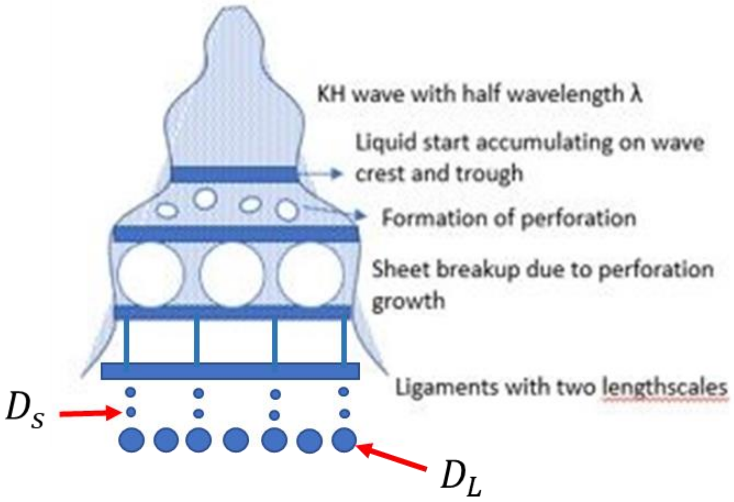


Figure 12. A schematic of the perforation-based atomization model

This breakup model provides two different length scales, which take up different weight percentages: One based on the thickness of the thin sheet between the crests and troughs of the waves (D_S) with a total mass of m_S, and one based on the diameters of the crests and troughs (D_L) with a total mass of m_L and these can be given as

$$D_L = \sqrt{\frac{4m_c}{\pi^2 D_b}}, D_s = \sqrt{\frac{4(m - m_c)}{\pi n \lambda}}$$

where D_b is the breakup length, n is the number of perforations on the thin sheet and λ is the distance between the wave crests.

We will model the spray size distribution using two size distribution (PDF) each for one of the spray length scales. In order to complete this model, we need to determine correlations for the characteristic sizes of both the spanwise and the streamwise ligaments, in terms of the fluid properties and the operating conditions. In order to develop a correlation that can be generalized to a wider range of fluids and operating conditions, the following tasks are planned

- Determine the frequency of perforations on the thin sheets with fluids with suspensions.
- Determine how much mass is accumulated at the wave crest
- Develop a theory for how long the sheet can stretch in Newtonian case
- Determine the breakup length of the fluids sheets with suspensions

Theses data will be combined with the ligament breakup model (Rayleigh-Plateau instability) for non-Newtonian fluids to generate a model for droplet size distribution. More detailed information on the testing cases and their results including droplet size distribution and near nozzle images are provided in the final report.

6. Physics Based Model for Twin-Fluid Nozzles

Two key advantages to the atomization models that we developed for twin-fluid nozzles in our previous project term are the ability to relate the rate of the deformation to the breakup and to predict the formation of ligaments in the spray. This allows for the opportunity to directly include rheological effects such as extensional viscosity in our models and to support their development by using what we learn in our experiments on the breakup dynamics of the ligaments and the spray characterization. Our previously developed model for the atomization of twin-fluid nozzles is comprised of the following processes: KH waves form on the jet that exits a nozzle and cause small droplets to break off its surface; the liquid core in the jet (the liquid left behind after KH droplets break off) goes through flapping instability, forming larger droplets with length scale of the flapping wavelength, and the secondary atomization process breaks the large droplets to smaller droplets. The breakup model is related to the rate of deformation of the waves. The advantages of modelling the spray in this way is the isolation of the slow wave growth from the fast wave breakup and the prediction of ligaments in the breakup, which previous models do not consider. While the development of the KH and flapping instabilities will be somewhat affected by the rheological fluids, the greater effect is expected to be on their breakup, especially when the extensional viscosity is high. We aim to extend our existing models to include these effects.

Our currently developed model for the atomization of the twin-fluid nozzles comprises of the following processes:

- High-speed gas flow over the liquid breaks off small droplets from the surface of the liquid jet issuing from the nozzle based on Kelvin-Helmholtz (KH) instability. The droplet sizes are related to the wavelength of the fastest growing KH waves.
- The liquid core in the jet (the liquid left behind after KH droplet break offs) goes through flapping instability, forming larger droplets with length scale of the flapping wavelength.
- The secondary atomization process breaks the large droplets to smaller droplets. The following secondary atomization model is developed: The high-speed gas flow deforms the front of the droplet into a disk shape. The volume-fraction in the frontal disk determines the breakup morphology:
    - A model is developed that can predict the following morphologies: single bag and multibag breakup, as well as bag and stamen breakups. The breakup is related to the rate of deformation of the droplet.
    - Each disk shape droplet forms a bag with a relatively thick rim. The bag grows and eventually breaks forming small droplets, and the rim breaks forming larger droplets.
    - Rims are analogous to the ligaments seen in high-viscosity spray breakup.
- The final spray droplet size distribution is predicted based on the primary and the secondary atomization models.

The advantages of modelling the spray in this way is the isolation of the slow wave growth from the fast wave breakup and the prediction of ligaments in the breakup, which previous models do not consider. While the development of the KH and flapping instabilities will be somewhat affected by the rheological fluids, the greater effect is expected to be on their breakup, especially when the extensional viscosity is high. Using what we learn about the breakup dynamics of the ligaments, we aim to extend our existing models to include these effects. Further details on the developed twin-fluid nozzle is given in the final report.

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.

IFPRI Research project - ExPowSE

Exploring food powder surface under controlled environment

LIBio – Laboratoire d'Ingenierie des Biomolecules (Université de Lorraine, France)
Jennifer Burgain – Stéphane Desobry - Claire Gaiani

I. Proposal context, positioning and objective(s)

I.A. Objectives and research hypothesis

The current inability of most consumers to achieve the recommended daily intake of fruits and vegetables triggers food research toward the generation of new and improved fruit- and vegetable-based products and ingredients. The World Health Organization (WHO) recommends consuming at least 400 g each day to reap their health and nutrition benefits. In 2017, some 3.9 million deaths worldwide were attributable to the lack of fruit and vegetables in the diet (**WHO, 2019**). Actions are needed to **increase the production and consumption of fruit and vegetables and make them more economically accessible to consumers, while generating economic, social and environmental benefits in line with the Sustainable Development Goals**. In declaring 2021 as the international year of fruits and vegetables, the United Nations (UN) general assembly aims to raise awareness of the nutritional and health benefits of fruit and vegetables and their contribution to a balanced and healthy diet and lifestyle (**FAO, 2020**). The diverse range and characteristics of fresh fruit and vegetables and their inherently perishable nature warrants the deployment of conservation techniques in order to: (1) **guarantee their accessibility** throughout the year and in particular outside production periods, (2) **deliver stable products** in non-producing regions by exportation, (3) **reduce food waste** due to seasonality and report the consumption by using drying and powdering methods. However, these operation units govern powder structure and functional properties and it is of paramount importance to master them.

The overall scientific objectives of ExPowSE are:

- Preserving product stability and quality.
- Bringing knowledge in the technofunctionality of food powders using a multiscale approach with a focus on the particle surface. Even if the powder surface is one of the main players during the reconstitution or transport (powder flowability), it has been poorly studied in the literature for fruit and vegetables powders.
- Elucidating physical mechanisms occurring when materials reach the glass transition by increasing temperature and/or relative humidity (RH). Until now, only hypotheses were proposed as the techniques were not able to probe the progressive evolution. Atomic Force Microscopy (AFM) is the technique of choice to gather physicochemical and nanomechanical data during the glass transition phase.

A profound understanding of the **process–structure–function relations** to tailor the **functional properties** of fruits and vegetables powders is then required. A schematic representation of the key concept of the ExPowSE project is displayed in **Figure 1**.

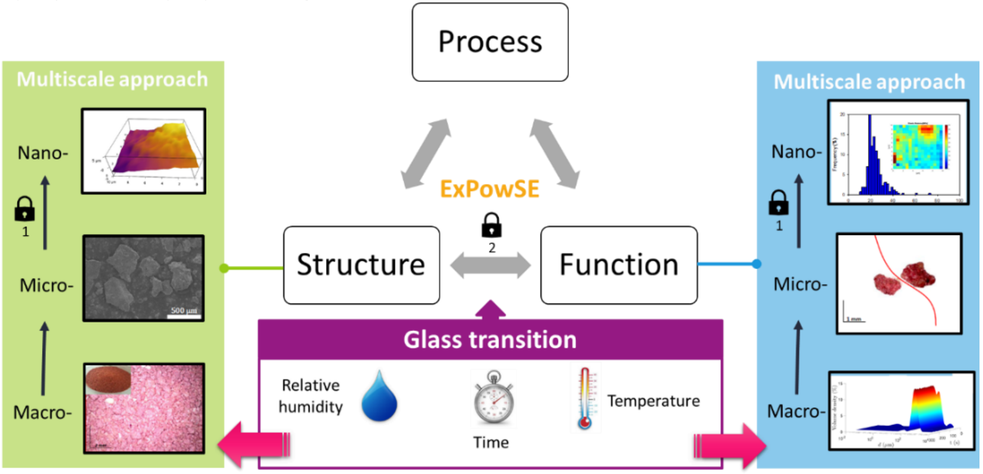


Figure 1: Schematic overview of the ExPowSE project: process–structure–function relations with a multiscale approach.

Research on this project will be performed at a nanoscopic, microscopic, and macroscopic level entailing particle surface investigations with the aim to answer to the following questions:

- How surface modification (topography, chemistry, nanomechanics) can impact the macroscopic behaviour (reconstituability and flowability) of the powder?
- What are the phenomena occurring at particle surface during the glass transition phase?
- How to improve powder stability and quality during shelf-life?

I.B. State of the art

Many types of fruit and vegetables are processed to increase their shelf-life, year-round availability, or to increase their value, which integrates structure-enabling and preservation techniques. Minimal processing includes drying and/or grinding (powdering process) of fruits and vegetables and guarantee that such foods are as nutritious as the food in its unprocessed form (**Fitzpatrick and Ahrné, 2005**). However, fruits and vegetables powders contain a high quantity of low molar mass sugars with low glass transition temperature (T_g) (**Fang and Bhandari, 2011**). The direct consequence is that fruit powders are highly hygroscopic and sticky at high temperatures but also at ambient temperature if the water content is not well mastered. This feature causes the powder adhesion to surfaces and powder caking during the storage, which affects the quality of the final product. **The T_g is one of the most important parameters to consider during powder storage.** Indeed, the phenomenon of glass transition is the gradual and reversible transition of amorphous materials from a hard and "glassy" state into a viscous and rubbery state as the temperature and/or the moisture content is increased. The glass transition is also linked to the water activity and water as a strong plasticizer decreases the T_g. Also, the glass transition temperature depends on the molecular mass as the T_g of monosaccharides, disaccharides, oligosaccharides and polysaccharides increases with increasing their molecular mass (**Roos, 2002**). If the glass transition is reached during powder storage, unexpected phenomena can happen that affect powder functionality such as reconstitution ability.

An important structure-determining component in this context is the particle surface. It should be noted that particle surfaces, in the case of fruits and vegetables powders, are essentially constituted by broken structures. Because of various origins, their particle size and shape distributions, chemical composition, surface composition, and physical properties are highly variable. Therefore, more than one analytical technique is often required to obtain a full set of information about a given scientific question (**Burgain et al., 2017**). Among these questions, the powders flowability and reconstitution are of upmost importance for the industry considering that most powdered ingredients are transported and dissolved or infused before use. For the past few years, numerous powder surface analysis techniques were used to further understand the role of powder surface on functionalities impairments. For example, microscopy techniques such as Scanning Electron Microscopy (SEM), Confocal Laser Scanning Microscopy (CLSM) or even chemical composition techniques such as X-ray Photoelectron Spectroscopy (XPS) are already widely used (**Burgain et al., 2017**). However, **AFM is currently a rising star in the food powder surface analysis field**, mainly for its resolutive capacity. AFM is a versatile tool compared to other surface analysis techniques. For example, AFM allows to study particle surface topography and roughness, surface chemistry and nanomechanics.

In a previous project, we were able to have a better understanding of surface modification after high temperature storage of whey protein isolate and micellar casein powders (**Burgain et al., 2016a, 2016b**). Surface hardening with the development of a poorly dispersible skin layer composed of aggregated micelles was evidenced to be the phenomenon responsible for the reconstitution impairment. However only punctual analyses were possible and the development of an environmental chamber around the AFM will allow for continuous measurements at nanometer scale. **By controlling the temperature and RH, their variation during time in the neighbouring of the sample will provide new insight in the elucidation of mechanisms occurring during powders storage or transport under unfavourable conditions, in particular when they reach the glass transition.** Even if AFM was already applied to dairy powder, application to fruits and vegetables powders is still missing while there is an important industrial stake with the growth of the plant products market and the development of vegetable formulations.

First experiments on fruits and vegetables powders provided hopeful results showing that when approaching glass transition, patches at the surface were crystallising by nucleation and the rest of the matrix presented a decreased elasticity (**Figure 2**). The glass transition event is accompanied by a physical change at the powder surface (modified topography) with a change in the Young modulus (modified nanomechanical properties) (**Palzer, 2007).** Moreover, powder caking related to glass transition is promoted by moisture adsorption which create liquid bridges between hydrophilic groups at particle surface (modified physicochemical properties). **The strength of the technique is that it is now possible to follow the evolution of the same area during dynamic variation of temperature and RH**. These observations confirm the fact that a focus at particle surface is undeniably required to better understand macroscopic phenomenon such as powder flowability, caking or reconstitution. This is particularly true for fruit powders that are highly hygroscopic materials with low glass transition temperature and as a consequence easily affected by ambient temperature and RH. In a recent work, we evidenced that above T_g, a viscous layer around the particle limits water entrance and is the limiting step in the global reconstitution process (**Gaudel et al., 2022**). With AFM, surface structure and chemical properties will be correlated thanks to the combination of surface topography analysis and force measurements.

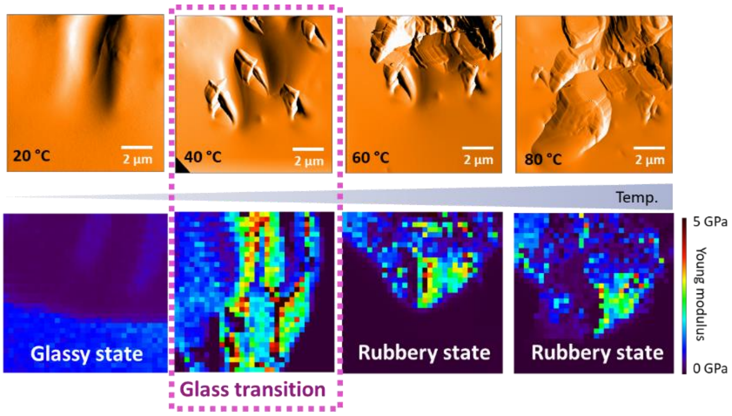


Figure 2: Use of AFM on maltodextrin powders with progressive temperature increase. The same area was analysed in situ during temperature increased (unpublished results from the team).

I.C. Project methodology

The project will be divided into three Work Packages (WP).

WP1: Fruits and vegetables powders screening (months: 0 – 12). The powder functional properties will be investigated at the macroscale by the evaluation of hygroscopicity, flowability and reconstituability. Powder thermal properties will also be determined and linked to powder proximate composition. In this WP, powders will be grouped as a function of their origin, T_g, solubility index, flowability index and only few powders of each group will be investigated in the WP2.

WP2: Probing surface physicochemical and nanomechanical properties by AFM-CE (months: 6 – 30). In this WP, a newly designed Controlled Environmental chamber around the AFM (AFM-CE where temperature and RH can be managed) will be employed. AFM-CE will be employed for the determination of particle surface topography and roughness and for the estimation of nanomechanics and adhesion forces. Even if process parameters define powder surface structure and functional properties, they can be impacted by environmental conditions. The technical and scientific challenge in the ExPowSE project will be to observe and quantify surface evolution during temperature and RH modulation (**Figure 1 - Locker 1**). In fact, the design of the environmental chamber was done in a way to recreate thermal and hygroscopic conditions that can be encountered by powders during transport and storage, but it is also possible to reach higher conditions in order to exceed the glass transition region. However, mechanical features of the AFM tip can evolve with increasing temperature or water droplet can deposit on the tip. All of these technical issues must be mastered to produce reliable data.

WP3: Modelling the process–structure–function relations (months: 24 – 36). Using mechanistic and statistical models, data will be processed in order to establish the process–structure–function relations and describe mechanisms at the basis of surface evolution (as a function of temperature and RH) and impacting powder reconstitution and/ or flowability. The second scientific challenge here will be to link powder surface structure with powder function and to get enough data to model the phenomena occurring and elucidate the underlying mechanisms (**Figure 1 - Locker 2**).

II. Team and link’s with the actual IFPRI project

The work packages outlined above will be carried out by a dedicated full time PhD student 100 % funded by the IFPRI Consortium. Materials and consumables will be covered by the LIBio. This project can be leveraged to obtain local funds from the Grand Est region and the University of Lorraine Impact “Biomolecules” program leaded by a LIBio professor. These organizations provide 2-to-1 support for industrial cash grant. The PhD student will be embedded in the LIBio laboratory under the direct supervision of Prof. Claire GAIANI and Jennifer BURGAIN. They received more than of 2 000 k€ funding for projects on which they were principal investigators. Among other important activities, they successfully managed fundamental competitive programs including the French ANR and European projects. They also participated in international collaborations. Finally, they managed many industrial partnerships with leading international food companies (including Nestlé, Lactalis, Bel, Arla Food, and CNIEL).

Nowadays, their research thematic deals with the establishment of links between surface and functional properties of food powders. The objective will be to further develop, the work that was recently initiated into the IFPRI project managed by Claire GAIANI (more particularly in the WP2). The idea is to loop the approach process-structure-function and the development of AFM in controlled environmental.

The ExPowSE team will be managed by Claire GAIANI and Jennifer BURGAIN and composed of one PhD student, one technician (working mainly on the AFM technique) and a specialist of food glass transition (Pr Stephane DESOBRY). Therefore, four permanent staffs will be involved in the team plus one PhD student (IFPRI funds). The complementarity of the team members is clearly an asset for this project.

Finally, this project will be in close collaboration with the IFPRI members with regular meetings and reports. We will test powders of interest for the industry and if possible directly from the industrial partners.

III. References related to the project

Burgain, J., Scher, J., Petit, J., Francius, G., Gaiani, C., (2016a). Links between particle surface hardening and rehydration impairment during micellar casein powder storage. Food Hydrocolloids, 61, 277-285. DOI 10.1016/j.foodhyd.2016.05.021

Burgain, J., El Zein, R., Scher, J., Petit, J., Norwood, E.A., Francius, G., Gaiani, C., (2016b). Local modification of whey protein isolate powder surface during high temperature storage. Journal of Food Engineering, 178, 39-46. DOI 10.1016/j.jfoodeng.2016.01.005

Burgain, J., Petit, J., Scher, J., Rasch, R., Bhandari, B., Gaiani, C., (2017). Surface chemistry and microscopy of food powders. Progress in Surface Science, 92, 4, 409-429.

FAO. 2020. Fruit and vegetables – your dietary essentials. The International Year of Fruits and Vegetables, 2021, background paper. Rome. https://doi.org/10.4060/cb2395en

Fang, Z., Bhandari, B., 2011. Effect of spray drying and storage on the stability of bayberry polyphenols. Food Chem. 129, 1139–1147.

Fitzpatrick, J. J., & Ahrné, L. (2005). Food powder handling and processing: Industry problems, knowledge barriers and research opportunities. Chemical Engineering and Processing: Process Intensification, 44(2), 209-214.

Gaudel, N., Gaiani, C., Harshe, Y. M., Kammerhofer, J., Pouzot, M., Desobry, S., & Burgain, J. (2022). Reconstitution of fruit powders: A process–structure–function approach. Journal of Food Engineering, 315, 110800.

Palzer, S., (2007). Agglomeration of Dehydrated Consumer Foods, Granulation, 592-671. DOI 10.1016/S0167-3785(07)80048-0

Roos, Y.H., 2002. Importance of glass transition and water activity to spray drying and stability of dairy powders.

WHO, World Health Organization, 2019, Increasing fruit and vegetable consumption to reduce the risk of noncommunicable diseases.

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.).

IFPRI Project renewal: Erin Koos

1. State of the art

The structural properties of suspensions and other multiphase systems are vital to overall processability, functionality and acceptance among consumers. Therefore, it is crucial to understand the intrinsic connection between the microstructure of a material and the resulting rheological properties. In the previous portion of the project, we demonstrated how the transitions in the microstructural conformations can be quantified and correlated to rheological measurements. We found semi-local parameters from graph theory, the mathematical study of networks, to be useful in linking structure and rheology. Our results, using capillary suspensions as a model system, show that the use of the clustering coefficient, in combination with the coordination number, is able to capture not only the agglomeration of particles, but also measures the formation of groups [1]. A recent review paper outlines the various wetting-induced changes that occur in capillary suspensions [2].

1.1. Methodology

Capillary suspensions consisting of silica particles fluorescently labeled with rhodamine B isothiocyanate in a mixture of 1,2-cyclohexane dicarboxylic acid diisononyl ester (Hexamoll DINCH) and n-dodecane, with added aqueous glycerol. The three components are all index matched and the silica contact angle can be modified [3]. The attractive interaction strength can be modified by tuning the contact angle and fraction of secondary liquid. This lets us access both granular-like systems with weak interactions and strong attractive gels using the same model system. During the project, we switched from using porous silica particles to nonporous particles as there were problems noted with adsorption of the secondary liquid into the pores. This simplified the particle detection algorithm now includes a graphical user interface for both local detection and manual addition or removal of missing or misdetected particles improve the final detection efficiency.

Our initial goal of the project was to track microstructural changes in the network in response to external shear applied via a linear shear cell. These structural changes were correlated with the rheological response of the material. Application of external shear via the linear shear cell, however, was unsuitable. Due to the very low yield strain in capillary suspensions, the applied shear was often above the flow point and specific changes during yielding could not be adequately captured. Furthermore, the present setup only allowed for the deformation profile to be captured in one shear plane. While this has provided valuable information, proving that capillary suspensions tend to undergo solid-body movement, where the rotation of particles around their respective bridges is resisted through both the structure of the network and the extra torque provided by the contact angle pinning and/or the contact angle hysteresis, full 3D tracking is necessary. Therefore, a rheometer has now been mounted onto a high-speed confocal microscope. The improved setup will allow us to directly compare bulk, rheological changes with local, microscopic changes to the clusters and network.

1.2. Project results

Semi-local measurements capture rheological changes: Using both the coordination number and the clustering coefficient (Figure 1), we could rationalize the transitions in the structure and tie these changes to the rheological properties of the material. For instance, the transition from a pendular network, where particles are connected by binary bridges, to the funicular state, where larger clusters are formed, occurs at $\phi_{\mathrm{sec}}/\phi_{\mathrm{solid}} = 0.09$. This point corresponds to a peak in the coordination number and beginning of a plateau in clustering coefficient. While there is a slight shift in the distribution of coordination numbers, there is a large shift in the distribution of clustering. The number of particles with zero clustering drops significantly while there is an increase in intermediate and high clustering. These results are published in the journal Soft Matter [1].

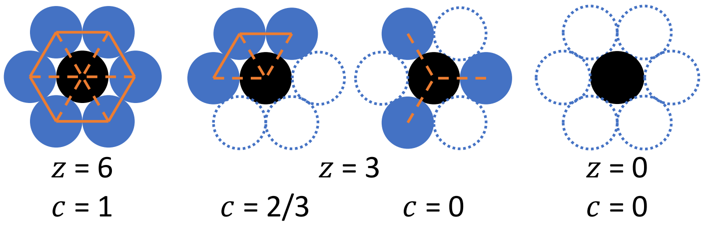


Figure 1: Difference between the coordination number z, the number of bonds per particle (dashed lines), and the clustering coefficient c. The clustering coefficient is defined as $c = \frac{2e}{z(z-1)}$, where the number of bonds between neighbors (solid lines) is e.

Particle volume fraction: Samples with particle volume fractions $\phi = 0.1 - 0.3$ were examined. Below $\phi = 0.15$, the flocs not fully percolated. The intracluster structure of all capillary suspensions was the same ($z \approx 5$ and $c = 0.33$), but the system becomes more dense with increasing particle volume fraction. This can be interpreted as a growing floc size with constant intrafloc structure. The microstructure after compression was examined for the higher particle volume fractions. The samples were compressed to a gap around 1 mm, equal to the measurement gap that was applied on the rheometer. The coordination number before and after compression remained constant, increasing at most by $z = 0.5$ for the $\phi = 0.3$ sample. The clustering coefficient was unchanged for all three samples.

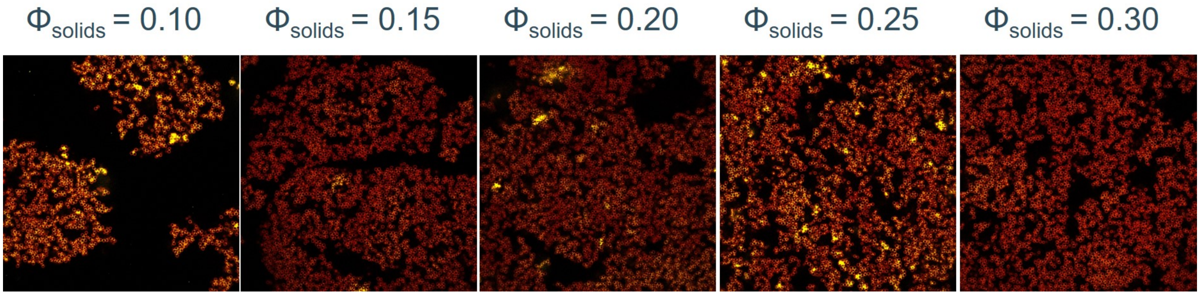


Figure 2: Confocal images of capillary suspensions with increasing particle volume fraction using non-porous particles.

Particle size: Samples with particles with sizes 3, 10 and 50 µm were prepared. The volume fractions are kept constant as is the contact angle and the mixing conditions. While it is expected that the particle size R should have an influence on the structure through the balance between the capillary and gravitational forces (Eötvös or Bond number),

$$\mathrm{E\ddot{o}} = \frac{\text{Capillary force}}{\text{Particle weight}} \approx \frac{2\pi R\Gamma\cos\theta}{\frac{4}{3}\pi R^3\rho} \sim \frac{1}{R^2}$$

no densification of the structure was observed. Changes to the bridge shape and distribution account for this relatively constant structure. In all three samples, a distribution of bridge sizes, ranging from large, coalesced bridges connecting three or more particles, binary bridges connecting two particles, and very small drops and bridges between particle asperities are observed. These small bridges or patches of secondary fluid appear as a “uniform” film on the small particles whereas they form patches (with an apparent contact angle near 90°) on the particle surface of the large particles. This implies an influence of the particle roughness. Comparing the yielding behavior, we see that the stress at the end of the linear viscoelastic region increases with decreasing particle size, as would be predicted from $\sigma_y \sim F_c/R^2 \sim 1/R$. The flow point, on the other hand, is nearly identical for the small 3 µm particles as the large 50 µm particles and highest for the 10 µm. This change may be due to the changes in the bridge volumes and network structure of this sample.

Particle polydispersity: Adding a small percentage of larger 10 µm particles to the small 3 µm particles shows some influence on the network strength. The storage modulus shows no change with 1% 10 µm particles but does increase slightly with the addition 5% 10 µm particles. This increases G' towards the value with 100% 10 µm particles. The loss modulus shows no clear trend and the data for 100% 10 µm remains higher. We do not see a dramatic in the meniscus size that would be expected from large-large interactions. Instead, the structure is dominated by the interactions between the small particles with some small-large interactions. Preliminary image detection shows that the average network structure is the same with only local changes around the large particles. The large particles have a larger coordination number, owing to their larger size. We also see region, particularly around the large particles, where there are dense flocs consisting of many coalesced bridges. This may imply some change in the mixing conditions caused by the large particles.

Particle roughness (raspberry particles): To directly test the influence of particle roughness on our system, silica nanoparticles are electrostatically adsorbed onto the surface of the larger microparticles and then smoothed with a Stöber silica layer [4]. By attaching differently sized NPs, we can form raspberry particles with tunable roughness. For samples with a constant secondary fluid volume, the increase in roughness results in several changes. First, for the attachment of 40 nm particles to the 3 µm primary particles, the storage modulus remains unchanged, but the loss modulus increases, shifting the yielding region and the flow point shifts to higher strain. With further increases in the roughness (attachment of 100 nm and 200 nm particles), a transition to asperity wetting – with corresponding decrease in the storage modulus – is observed. By adjusting the secondary fluid volume, the storage modulus in all samples can be matched. There remains, however, an increase in the yield strain and decreasing trend in z and c (Figure 3).

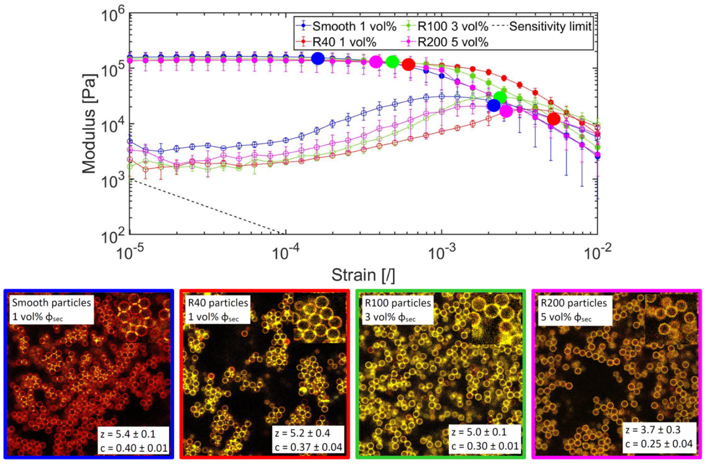


Figure 3: Influence of particle roughness for samples with secondary fluid volume adjusted to match the storage moduli. Increasing roughness increases the yield strain with very little effect on the flow point. The structure becomes less dense (decreasing both the coordination number and clustering coefficient) as the roughness increases.

The influence of particle roughness was further examined using information obtained from the medium amplitude (or asymptotically nonlinear) oscillatory shear regime. Previous research has shown that the third harmonic is non-integer and non-cubic [5] and the scaling of the third harmonic is sensitive to particle collisions [6]. The strength of the Hertzian contact is decreases with roughness as the samples transition from bridge to asperity wetting demonstrating the sensitivity of this rheological measure to the particle contact strength. The ratio of the elastic to viscous scaling is tied to the nature of the frictional contact and a transition from adhesion- to load-controlled friction may occur in these samples, but additional measurements must be conducted.

2. Proposed work

After discussion with project liaisons, we have decided to concentrate on the rheo-microscope in the project renewal. This will allow us to better connect the changes in the microstructure with the dynamics. The initial focus will be on the changes in the asymptotically nonlinear region to study both the bridging dynamics and yielding of the network. This will be supplemented by better detection of the bridge shape to determine changes to particle clustering and bridged contacts. A generalization of the particle detection algorithm will also allow us to investigate the influence of particle shape, integrating changes to the particle orientation and contact type (e.g. edge-edge or corner-edge).

While we will examine intermediate particle volume fraction in the renewal project up to $\phi_{solid} = 0.3$, the study of concentrated systems with $\phi_{solid} > 0.5$ is not envisaged. First, the strong attraction provided by the secondary fluid bridges means that the mixing becomes much more difficult at higher volume fractions leading to inhomogeneous samples. While we can use the squeeze flow caused by lowering the rheometer plates to expel some of the bulk fluid (thereby concentrating the particles and bridges), this is not a repeatable procedure. Second, concentrated systems, especially those exhibiting shear thickening, are also being investigated in the project of Jan Vermant. We are able to use similar particles (our rough particles follow the same procedure albeit usually with larger particle sizes) which should allow us to compare results.

2.1. Specific work packages

WP1: Yielding of capillary suspensions

We have now built a combined rheometer-confocal microscope setup that can be used to provide more accurate shear profiles while directly obtaining the resultant rheological properties. This new setup will allow us to better investigate the local, cluster-level changes to the structure and determine if yielding is the result of bond-breaking between a few, critical bridges or if general restructuring occurs. By tracking the individual particle deformation and that of the neighboring particles, we can correlate the motion of individual particles to the local clustering and local bridge strength. Of particular interest is the development of the coordination and clustering coefficient during shear.

To investigate the yielding dynamics, we will employ both oscillatory and step shear profiles. Our previous experiments showed how oscillatory shear in the asymptotically nonlinear regime is sensitive to particle collisions with little influence on the re-arrangement of the particles (resulting in network coarsening or compaction). Step shear profiles, however, can result in more pronounced re-arrangement and allow us to investigate the difference between inter- and intra-cluster bonds. We will also be able to directly track the different shear layers to investigate the influence of slip and shear banding. Such effects are expected to be more pronounced with the higher volume fraction samples.

WP2: Bridge sizes and asperity wetting

Previous experiments with both varying particle sizes and particle roughness have shown the importance of bridge size and size distribution on the structure and rheological properties. The transition between asperity wetting to particle bridging is associated with an increase in the storage modulus and decrease in the coordination number and clustering. This clustering can be highly inhomogeneous, however, as demonstrated for the mixtures of large and small particles. There, mixing conditions leads to a local change in the bridge size near the added large particles. Changes in the local displacement of particles both close to and far away from these inclusions should be further investigated. The previous experiments using large and small particle mixtures should further be expanded to investigate intermediate to high fractions and larger differences between the sizes. With the bimodal distributions, the mixing order (and particle wetting) is expected to play a larger role.

The experiments with rough particles also showed changes to the frictional contacts in the system with increased roughness. Despite matching the plateau storage modulus, the rougher particles had a lower clustering. There was scatter in the data between samples demonstrating adhesion- and load-controlled friction. This change should better be correlated to the local structure and the deformation of the particles. By modifying the particle hydrophobicity, we can include variations in the wetting to further investigate these changes.

WP3: Particle aspect ratio and cubic particles

The investigation of particles with a varying aspect ratio and/or angular shape is also viewed as of interest. Such particles can be printed using a Nanoscribe or particle stretcher. The strength of capillary suspensions varies with particle shape [7] and higher fractions of secondary fluid can induce changes from edge-edge contacts with high connectivity to hedgehog-like clusters formed through corner-corner contacts with low connectivity [8]. While these systems have been investigated rheologically, their structure remains largely unknown and of industrial interest. The local structure and aggregate behavior will be monitored as a function of the applied shear.

2.2. Gantt chart

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

3. Leverage opportunities

I have already started to investigate the structure of capillary suspensions using these confocal microscopy techniques both within and outside of the present project. The project will also benefit from expertise added by a current doctoral student who is modeling capillary suspensions using the coarse-grained MD code ESPResSo. We recently improved the simulation methods so that pseudo-rheological experiments, mimicking the conditions present in the rheometer without the need for a biased shear, could be performed [9]. This can be further supplemented by the project “Computational Modeling of Particle Suspensions” currently in proposal stage.

I am also participating in a Marie Skłodowska-Curie Innovative Training Network “Dynamics of dense nanosuspensions: a pathway to novel functional materials” combining expertise from several European universities and companies to study the influence of combination of particles of different sizes and wettabilities as well as the properties of the liquid phases on the network structure and rheology of capillary nanosuspensions (capillary suspensions with nanoparticles both as the primary particles and with nanoparticles incorporated into the bridges). The aim of this project is to fabricate and characterize porous bodies from capillary suspensions containing particles of at least two different wettabilities and nanoparticles.

The industrial expertise of the IFPRI members has also been 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.

4. References

1. Bindgen, S., Bossler, F., Allard, J., Koos, E. (2020). Connecting particle clustering and rheology in attractive particle networks. *Soft Matter*, *16* (36), 8380–8393.
2. Bindgen, S., Allard, J., Koos, E. (2021). The behavior of capillary suspensions at diverse length scales: from single capillary bridges to bulk. *arXiv*, 2107.14714.
3. Bossler, F., Koos, E. (2016). Structure of Particle Networks in Capillary Suspensions with Wetting and Nonwetting Fluids. *Langmuir*, *32* (6), 1489–1501.
4. Hsu, C. P., Ramakrishna, S. N., Zanini, M., Spencer, N. D., Isa, L. (2018). Roughness-dependent tribology effects on discontinuous shear thickening. *Proceedings of the*

National Academy of Sciences of the United States of America, *115* (20), 5117–5122.

5. Natalia, I., Ewoldt, R. H., Koos, E. (2020). Questioning a fundamental assumption of rheology: Observation of noninteger power expansions. *Journal of Rheology*, *64* (3), 625–635.
6. Natalia, I., Ewoldt, R. H., Koos, E. (2021). Particle contact dynamics as the origin for non-integer power expansion rheology in attractive suspension networks. *arXiv*, 2104.05678.
7. Maurath, J., Bitsch, B., Schwegler, Y., Willenbacher, N. (2016). Influence of particle shape on the rheological behavior of three-phase non-brownian suspensions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *497*, 316–326.
8. Sun, H., Zhang, X., Yuen, M. M. F. (2016). Enhanced conductivity induced by attractive capillary force in ternary conductive adhesive. *Composites Science and Technology*, *137*, 109–117.
9. Bindgen, S., Weik, F., Weeber, R., Koos, E., de Buyl, P. (2021). Lees–Edwards boundary conditions for translation invariant shear flow: Implementation and transport properties. *Physics of Fluids*, *33* (8), 083615.

IFPRI Project renewal: Erin Koos

1. State of the art

The structural properties of suspensions and other multiphase systems are vital to overall processability, functionality and acceptance among consumers. Therefore, it is crucial to understand the intrinsic connection between the microstructure of a material and the resulting rheological properties. In the previous portion of the project, we demonstrated how the transitions in the microstructural conformations can be quantified and correlated to rheological measurements. We found semi-local parameters from graph theory, the mathematical study of networks, to be useful in linking structure and rheology. Our results, using capillary suspensions as a model system, show that the use of the clustering coefficient, in combination with the coordination number, is able to capture not only the agglomeration of particles, but also measures the formation of groups [1]. A recent review paper outlines the various wetting-induced changes that occur in capillary suspensions [2].

1.1. Methodology

Capillary suspensions consisting of silica particles fluorescently labeled with rhodamine B isothiocyanate in a mixture of 1,2-cyclohexane dicarboxylic acid diisononyl ester (Hexamoll DINCH) and n-dodecane, with added aqueous glycerol. The three components are all index matched and the silica contact angle can be modified [3]. The attractive interaction strength can be modified by tuning the contact angle and fraction of secondary liquid. This lets us access both granular-like systems with weak interactions and strong attractive gels using the same model system. During the project, we switched from using porous silica particles to nonporous particles as there were problems noted with adsorption of the secondary liquid into the pores. This simplified the particle detection algorithm now includes a graphical user interface for both local detection and manual addition or removal of missing or misdetected particles improve the final detection efficiency.

Our initial goal of the project was to track microstructural changes in the network in response to external shear applied via a linear shear cell. These structural changes were correlated with the rheological response of the material. Application of external shear via the linear shear cell, however, was unsuitable. Due to the very low yield strain in capillary suspensions, the applied shear was often above the flow point and specific changes during yielding could not be adequately captured. Furthermore, the present setup only allowed for the deformation profile to be captured in one shear plane. While this has provided valuable information, proving that capillary suspensions tend to undergo solid-body movement, where the rotation of particles around their respective bridges is resisted through both the structure of the network and the extra torque provided by the contact angle pinning and/or the contact angle hysteresis, full 3D tracking is necessary. Therefore, a rheometer has now been mounted onto a high-speed confocal microscope. The improved setup will allow us to directly compare bulk, rheological changes with local, microscopic changes to the clusters and network.

1.2. Project results

Semi-local measurements capture rheological changes: Using both the coordination number and the clustering coefficient (Figure 1), we could rationalize the transitions in the structure and tie these changes to the rheological properties of the material. For instance, the transition from a pendular network, where particles are connected by binary bridges, to the funicular state, where larger clusters are formed, occurs at $\phi_{\mathrm{sec}}/\phi_{\mathrm{solid}} = 0.09$. This point corresponds to a peak in the coordination number and beginning of a plateau in clustering coefficient. While there is a slight shift in the distribution of coordination numbers, there is a large shift in the distribution of clustering. The number of particles with zero clustering drops significantly while there is an increase in intermediate and high clustering. These results are published in the journal Soft Matter [1].

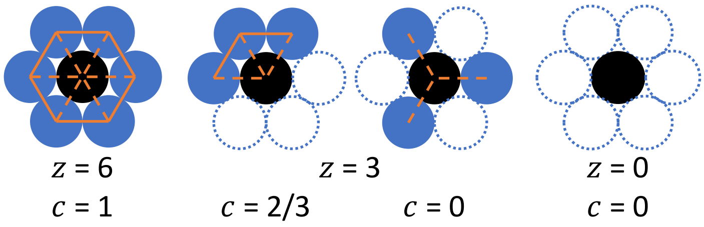


Figure 1: Difference between the coordination number z, the number of bonds per particle (dashed lines), and the clustering coefficient c. The clustering coefficient is defined as $c = \frac{2e}{z(z-1)}$, where the number of bonds between neighbors (solid lines) is e.

Particle volume fraction: Samples with particle volume fractions $\phi = 0.1 - 0.3$ were examined. Below $\phi = 0.15$, the flocs not fully percolated. The intracluster structure of all capillary suspensions was the same ($z \approx 5$ and $c = 0.33$), but the system becomes more dense with increasing particle volume fraction. This can be interpreted as a growing floc size with constant intrafloc structure. The microstructure after compression was examined for the higher particle volume fractions. The samples were compressed to a gap around 1 mm, equal to the measurement gap that was applied on the rheometer. The coordination number before and after compression remained constant, increasing at most by $z = 0.5$ for the $\phi = 0.3$ sample. The clustering coefficient was unchanged for all three samples.

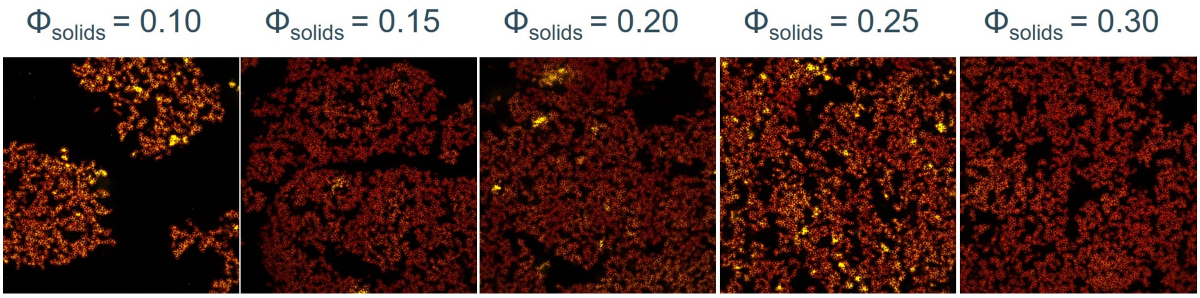


Figure 2: Confocal images of capillary suspensions with increasing particle volume fraction using non-porous particles.

Particle size: Samples with particles with sizes 3, 10 and 50 µm were prepared. The volume fractions are kept constant as is the contact angle and the mixing conditions. While it is expected that the particle size R should have an influence on the structure through the balance between the capillary and gravitational forces (Eötvös or Bond number),

$$\text{Eö} = \frac{\text{Capillary force}}{\text{Particle weight}} \approx \frac{2\pi R\Gamma\cos\theta}{\frac{4}{3}\pi R^3\rho} \sim \frac{1}{R^2}$$

no densification of the structure was observed. Changes to the bridge shape and distribution account for this relatively constant structure. In all three samples, a distribution of bridge sizes, ranging from large, coalesced bridges connecting three or more particles, binary bridges connecting two particles, and very small drops and bridges between particle asperities are observed. These small bridges or patches of secondary fluid appear as a “uniform” film on the small particles whereas they form patches (with an apparent contact angle near 90°) on the particle surface of the large particles. This implies an influence of the particle roughness. Comparing the yielding behavior, we see that the stress at the end of the linear viscoelastic region increases with decreasing particle size, as would be predicted from $\sigma_y \sim F_c/R^2 \sim 1/R$. The flow point, on the other hand, is nearly identical for the small 3 µm particles as the large 50 µm particles and highest for the 10 µm. This change may be due to the changes in the bridge volumes and network structure of this sample.

Particle polydispersity: Adding a small percentage of larger 10 µm particles to the small 3 µm particles shows some influence on the network strength. The storage modulus shows no change with 1% 10 µm particles but does increase slightly with the addition 5% 10 µm particles. This increases G' towards the value with 100% 10 µm particles. The loss modulus shows no clear trend and the data for 100% 10 µm remains higher. We do not see a dramatic in the meniscus size that would be expected from large-large interactions. Instead, the structure is dominated by the interactions between the small particles with some small-large interactions. Preliminary image detection shows that the average network structure is the same with only local changes around the large particles. The large particles have a larger coordination number, owing to their larger size. We also see region, particularly around the large particles, where there are dense flocs consisting of many coalesced bridges. This may imply some change in the mixing conditions caused by the large particles.

Particle roughness (raspberry particles): To directly test the influence of particle roughness on our system, silica nanoparticles are electrostatically adsorbed onto the surface of the larger microparticles and then smoothed with a Stöber silica layer [4]. By attaching differently sized NPs, we can form raspberry particles with tunable roughness. For samples with a constant secondary fluid volume, the increase in roughness results in several changes. First, for the attachment of 40 nm particles to the 3 µm primary particles, the storage modulus remains unchanged, but the loss modulus increases, shifting the yielding region and the flow point shifts to higher strain. With further increases in the roughness (attachment of 100 nm and 200 nm particles), a transition to asperity wetting – with corresponding decrease in the storage modulus – is observed. By adjusting the secondary fluid volume, the storage modulus in all samples can be matched. There remains, however, an increase in the yield strain and decreasing trend in z and c (Figure 3).

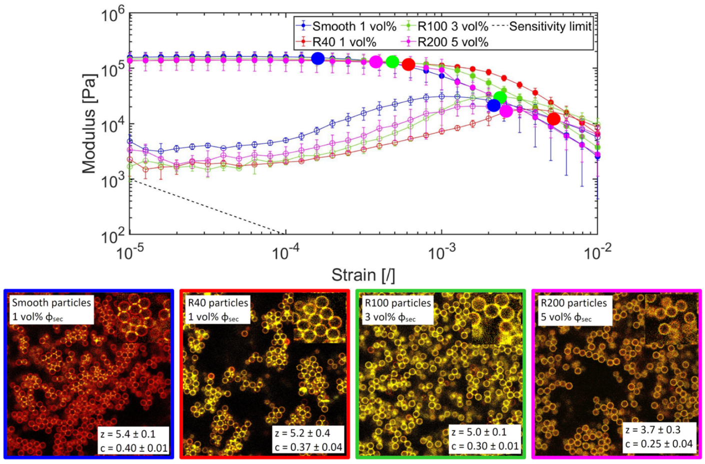


Figure 3: Influence of particle roughness for samples with secondary fluid volume adjusted to match the storage moduli. Increasing roughness increases the yield strain with very little effect on the flow point. The structure becomes less dense (decreasing both the coordination number and clustering coefficient) as the roughness increases.

The influence of particle roughness was further examined using information obtained from the medium amplitude (or asymptotically nonlinear) oscillatory shear regime. Previous research has shown that the third harmonic is non-integer and non-cubic [5] and the scaling of the third harmonic is sensitive to particle collisions [6]. The strength of the Hertzian contact is decreases with roughness as the samples transition from bridge to asperity wetting demonstrating the sensitivity of this rheological measure to the particle contact strength. The ratio of the elastic to viscous scaling is tied to the nature of the frictional contact and a transition from adhesion- to load-controlled friction may occur in these samples, but additional measurements must be conducted.

2. Proposed work

After discussion with project liaisons, we have decided to concentrate on the rheo-microscope in the project renewal. This will allow us to better connect the changes in the microstructure with the dynamics. The initial focus will be on the changes in the asymptotically nonlinear region to study both the bridging dynamics and yielding of the network. This will be supplemented by better detection of the bridge shape to determine changes to particle clustering and bridged contacts. A generalization of the particle detection algorithm will also allow us to investigate the influence of particle shape, integrating changes to the particle orientation and contact type (e.g. edge-edge or corner-edge).

While we will examine intermediate particle volume fraction in the renewal project up to $\phi_{solid} = 0.3$, the study of concentrated systems with $\phi_{solid} > 0.5$ is not envisaged. First, the strong attraction provided by the secondary fluid bridges means that the mixing becomes much more difficult at higher volume fractions leading to inhomogeneous samples. While we can use the squeeze flow caused by lowering the rheometer plates to expel some of the bulk fluid (thereby concentrating the particles and bridges), this is not a repeatable procedure. Second, concentrated systems, especially those exhibiting shear thickening, are also being investigated in the project of Jan Vermant. We are able to use similar particles (our rough particles follow the same procedure albeit usually with larger particle sizes) which should allow us to compare results.

2.1. Specific work packages

WP1: Yielding of capillary suspensions

We have now built a combined rheometer-confocal microscope setup that can be used to provide more accurate shear profiles while directly obtaining the resultant rheological properties. This new setup will allow us to better investigate the local, cluster-level changes to the structure and determine if yielding is the result of bond-breaking between a few, critical bridges or if general restructuring occurs. By tracking the individual particle deformation and that of the neighboring particles, we can correlate the motion of individual particles to the local clustering and local bridge strength. Of particular interest is the development of the coordination and clustering coefficient during shear.

To investigate the yielding dynamics, we will employ both oscillatory and step shear profiles. Our previous experiments showed how oscillatory shear in the asymptotically nonlinear regime is sensitive to particle collisions with little influence on the re-arrangement of the particles (resulting in network coarsening or compaction). Step shear profiles, however, can result in more pronounced re-arrangement and allow us to investigate the difference between inter- and intra-cluster bonds. We will also be able to directly track the different shear layers to investigate the influence of slip and shear banding. Such effects are expected to be more pronounced with the higher volume fraction samples.

WP2: Bridge sizes and asperity wetting

Previous experiments with both varying particle sizes and particle roughness have shown the importance of bridge size and size distribution on the structure and rheological properties. The transition between asperity wetting to particle bridging is associated with an increase in the storage modulus and decrease in the coordination number and clustering. This clustering can be highly inhomogeneous, however, as demonstrated for the mixtures of large and small particles. There, mixing conditions leads to a local change in the bridge size near the added large particles. Changes in the local displacement of particles both close to and far away from these inclusions should be further investigated. The previous experiments using large and small particle mixtures should further be expanded to investigate intermediate to high fractions and larger differences between the sizes. With the bimodal distributions, the mixing order (and particle wetting) is expected to play a larger role.

The experiments with rough particles also showed changes to the frictional contacts in the system with increased roughness. Despite matching the plateau storage modulus, the rougher particles had a lower clustering. There was scatter in the data between samples demonstrating adhesion- and load-controlled friction. This change should better be correlated to the local structure and the deformation of the particles. By modifying the particle hydrophobicity, we can include variations in the wetting to further investigate these changes.

WP3: Particle aspect ratio and cubic particles

The investigation of particles with a varying aspect ratio and/or angular shape is also viewed as of interest. Such particles can be printed using a Nanoscribe or particle stretcher. The strength of capillary suspensions varies with particle shape [7] and higher fractions of secondary fluid can induce changes from edge-edge contacts with high connectivity to hedgehog-like clusters formed through corner-corner contacts with low connectivity [8]. While these systems have been investigated rheologically, their structure remains largely unknown and of industrial interest. The local structure and aggregate behavior will be monitored as a function of the applied shear.

2.2. Gantt chart

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

3. Leverage opportunities

I have already started to investigate the structure of capillary suspensions using these confocal microscopy techniques both within and outside of the present project. The project will also benefit from expertise added by a current doctoral student who is modeling capillary suspensions using the coarse-grained MD code ESPResSo. We recently improved the simulation methods so that pseudo-rheological experiments, mimicking the conditions present in the rheometer without the need for a biased shear, could be performed [9]. This can be further supplemented by the project “Computational Modeling of Particle Suspensions” currently in proposal stage.

I am also participating in a Marie Skłodowska-Curie Innovative Training Network “Dynamics of dense nanosuspensions: a pathway to novel functional materials” combining expertise from several European universities and companies to study the influence of combination of particles of different sizes and wettabilities as well as the properties of the liquid phases on the network structure and rheology of capillary nanosuspensions (capillary suspensions with nanoparticles both as the primary particles and with nanoparticles incorporated into the bridges). The aim of this project is to fabricate and characterize porous bodies from capillary suspensions containing particles of at least two different wettabilities and nanoparticles.

The industrial expertise of the IFPRI members has also been 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.

4. References

1. Bindgen, S., Bossler, F., Allard, J., Koos, E. (2020). Connecting particle clustering and rheology in attractive particle networks. *Soft Matter*, *16* (36), 8380–8393.
2. Bindgen, S., Allard, J., Koos, E. (2021). The behavior of capillary suspensions at diverse length scales: from single capillary bridges to bulk. *arXiv*, 2107.14714.
3. Bossler, F., Koos, E. (2016). Structure of Particle Networks in Capillary Suspensions with Wetting and Nonwetting Fluids. *Langmuir*, *32* (6), 1489–1501.
4. Hsu, C. P., Ramakrishna, S. N., Zanini, M., Spencer, N. D., Isa, L. (2018). Roughness-dependent tribology effects on discontinuous shear thickening. *Proceedings of the*

National Academy of Sciences of the United States of America, *115* (20), 5117–5122.

5. Natalia, I., Ewoldt, R. H., Koos, E. (2020). Questioning a fundamental assumption of rheology: Observation of noninteger power expansions. *Journal of Rheology*, *64* (3), 625–635.
6. Natalia, I., Ewoldt, R. H., Koos, E. (2021). Particle contact dynamics as the origin for non-integer power expansion rheology in attractive suspension networks. *arXiv*, 2104.05678.
7. Maurath, J., Bitsch, B., Schwegler, Y., Willenbacher, N. (2016). Influence of particle shape on the rheological behavior of three-phase non-brownian suspensions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *497*, 316–326.
8. Sun, H., Zhang, X., Yuen, M. M. F. (2016). Enhanced conductivity induced by attractive capillary force in ternary conductive adhesive. *Composites Science and Technology*, *137*, 109–117.
9. Bindgen, S., Weik, F., Weeber, R., Koos, E., de Buyl, P. (2021). Lees–Edwards boundary conditions for translation invariant shear flow: Implementation and transport properties. *Physics of Fluids*, *33* (8), 083615.