IFPRI Project Brief (Max 6 pages)
Wetting of heterogeneous particles

Introduction:

The formulation of the scientific problem proposed for this brief is as follows, with the key elements highlighted in bold:

"*The process of dispersing a powder into a liquid involves many elementary processes with different kinetics that often occur simultaneously, such as* ***wetting, capillary imbibition, dissolution, swelling, particle erosion and fracture****, etc. The complex and often non-linear dependence of these processes on material and process variables hinders the development of a fundamental understanding of powder dispersion in liquids. When adding a powder to a liquid,* ***the first step*** *in dispersing the powder is* ***to move particles through the air-liquid interface*** *by gravitational force. We believe that developing a fundamental and quantitative understanding of this process for* ***individual complex particles****, e.g. ones with* ***complex shape****,* ***internal structure (porosity)****, and* ***complex surface chemistry****, is a good starting point for understanding the larger dispersion problem. This is the primary objective of this IFPRI project.*"

As mentioned above, the initial step of any dispersion of a dry powder into a liquid is the crossing of said powder through an air-liquid, typically water, interface. During this process, the three-phase contact line of the particle and fluid interfaces needs to move over the surface of the particle until the latter is fully immersed in the liquid. This process takes place spontaneously only if the surface of the particle is completely hydrophilic, i.e. if it is fully wetted by water. As many powders of industrial relevance do not meet this criterion, transfer to water does not happen spontaneously. Thermodynamically, particles with a different degree of hydrophilicity/hydrophobicity will spontaneously attain an intermediate position across the interface driven by the minimization of surface energy, and corresponding to an effective contact angle, but will not be fully transferred into the aqueous phase[1]. In order to ensure complete transfer, an external force needs to be applied to detach the particle from the interface, most commonly gravity or mechanical agitation.

The ratio of gravitational to interfacial forces is represented by the dimensionless Bond number, $Bo = \Delta\rho\ g\ R^2/\gamma$, where $\Delta\rho$ is the particle density relative to the liquid, g is the gravitational acceleration, R is the particle radius (i.e. a characteristic dimension of the particle) and γ is the air-liquid interfacial tension. For micrometric particles, $Bo \ll 1$, so that gravity may be neglected and mechanical agitation may be required to bring the particles through the interface. In the case where, $Bo \simeq 1$ then gravity may spontaneously move the particles through the interface.

In any case, both processes of partial wetting and detachment from the interface into the water phase require the free motion of the contact line over the surface of the particles. Even when this is thermodynamically and mechanically predicted, in practice surface heterogeneities leads to contact-line pinning over the particle surface, kinetically trapping the particle in metastable positions and preventing full wetting. The same process is observed in relation to the spreading of liquids onto solid surfaces and the differences and similarities between this latter case and the one of particles at fluid interfaces have been nicely reviewed by Stocco and Nobili [2].

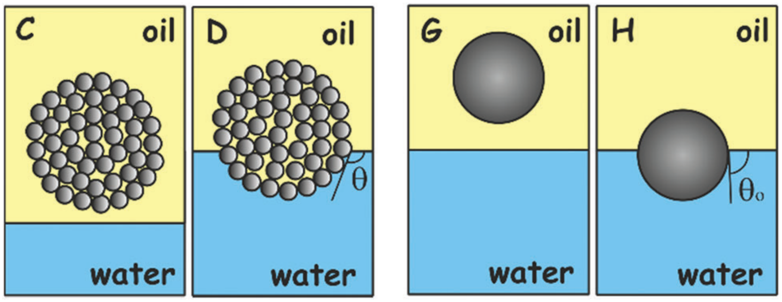
The case of solid particles has been extensively studied and the effect of both topographical (i.e. roughness and shape) and chemical (i.e. patchiness) heterogeneities have been widely studied[3].

Therefore, little room for innovation is left other than employing strategies to reduce interfacial tension, promote particle wettability and inject energy, e.g. in the form of mechanical vibration or shaking to aid dispersion. An area that remains far less explored is the one of porous particles, or particle agglomerates, which as described in the brief proposal *"... are in scope, particularly loosely bound ones that can represent the "lumps" of powder that often persist at the air-liquid interface during dispersion preparation.*"

In this project, we would like to focus on the fabrication of model particle aggregates in the form of porous supraparticles, of which we can tune dimensions and chemical composition, both changing the wettability of the primary particles in homogeneous supraparticles and by combining different primary particles to obtain heterogeneous aggregates. We will then focus on the characterization of the wetting of those aggregates at an air-water interface as a function of their compositional parameters by a set of complementary techniques that enable the simultaneous visualization of the interface and its deformation, and the direct measurement of the forces experienced by the aggregate during wetting. Finally, we will compare the cases where the aggregates are loosely bound and examine the synergy between wetting and dissolution. While the primary focus will be on model particle aggregates synthesized in our lab, we will be very excited to test the same experiments on powders of direct industrial interest from IFPRI members.

Before describing the detailed work plan, we concisely review some of the prior art that constitutes the starting point of our working hypothesis for the project.

State of the art



As opposed to the case of solid particles, the wetting of composite particle aggregates, often called supraparticles in the literature, has received little attention. A fundamental contribution comes from the work of Panuov et al., who derived an expression for the contact angle of a spherical supraparticle as a function of the contact angle of the primary particles forming it and on its porosity (see figure above)[4,5]. For supraparticles adsorbing to the water phase from a non-polar phase, e.g. oil or air, they derived an expression for a critical value of the primary particles' contact angle $\theta_0$that ensures full, spontaneous transfer to the water phase as $cos\theta \ = \eta_s(1 + cos\theta_0)^2 - 1$, where η_s the packing fraction at the surface of the supraparticle. When $cos\theta$ becomes equal to 1, the supraparticle is spontaneously transferred to the water phase. In particular, for hexagonal packings of spheres, θ_0 is around 60 degrees. Their theoretical calculations were then supported by experiments, which used NMR to follow the imbibition of water into the porous particles.

However, many open questions remain and the constitute the starting point of the proposed work:

1) The primary particles used in this work were more hydrophobic than the critical contact angle, so spontaneous transfer was never observed. This leaves immediate opportunities to test the predictions with more hydrophilic materials.

2) The composition of the supraparticles was homogeneous. Having primary particles of different wettability is completely open and lends itself to a modification of the theory to investigate the fraction of hydrophilic particles needed to ensure full transfer. This observation has very high potential for new formulations where a fraction of hydrophilic particles, to be considered as additives, may promote transfer to the aqueous phase.
3) The kinetics of the process and the role of contact line pinning were not considered/followed (in fact these authors used mechanical vibration to allow the supraparticles to attain their equilibrium contact angles). The extension of models previously developed to describe the effect of capillary pressure on water impalement through arrays of obstacles[6] to the case of supraparticles is highly interesting and can lead to new promising directions for particle design, i.e. to tune porosity.
4) Supraparticle dissolution was not considered but is central to the industrial applications.

Resources

In this proposal, we will systematically address all these issues, starting from carefully designed systematic experiments complemented by simple models. The proposed work aligns directly with many existing programs in which our group is engaged, in particular:

1) *Particle synthesis*:

Our group has developed robust strategies to synthesize and engineer the surface of heterogeneous colloids (from 600 nm to 15 µm) based on heteroaggregation processes [7],[8]. We have also recently demonstrated evaporation-induced, emulsion-based strategies to produce tailored supraparticles with a broad range of initial primary particles[9,10]. We have used both bulk emulsification to obtain large, sub-mm supraparticles and microfluidics-based emulsification to produce supraparticles with highly monodispersed sizes and controlled compositions. Both strategies are highly versatile and serve as the basis of the proposed synthesis.

2) *Wetting of complex particles*:

Our group has extensively investigated the wetting of colloidal particles at fluid interfaces using a suite of complementary tools across scales [11], [12], [13] including optical, cryo-electron and atomic force microscopy (AFM). Additionally, we have also carried out direct force measurements during wetting for different particle sizes and chemistries by AFM[14,15] and with larger scale force sensors.

Currently the group has 1 AFM technician, 1 Senior Scientist with strong expertise in wetting phenomena, one PhD student working directly on wetting of complex particles. Several group members are involved in particle systems, including microfluidics-based synthesis protocols. The proposed work is thus fully integrated in the current and future research lines of the group.

Work plan

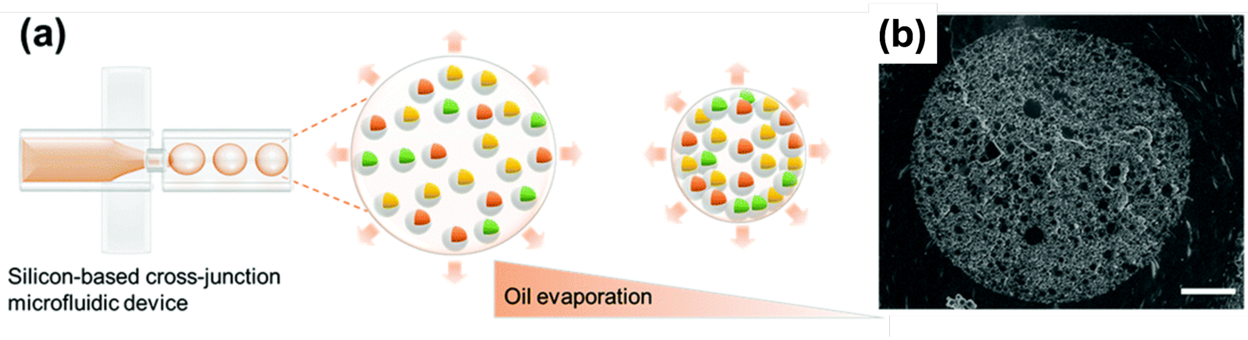
The work plan for the 3 years of the project will be organized according to the following work packages (WP), with the timeline described in the Gannt chart below (e.g. Q1.1 indicates the first quarter of the first year).

WP1: Supraparticle synthesis

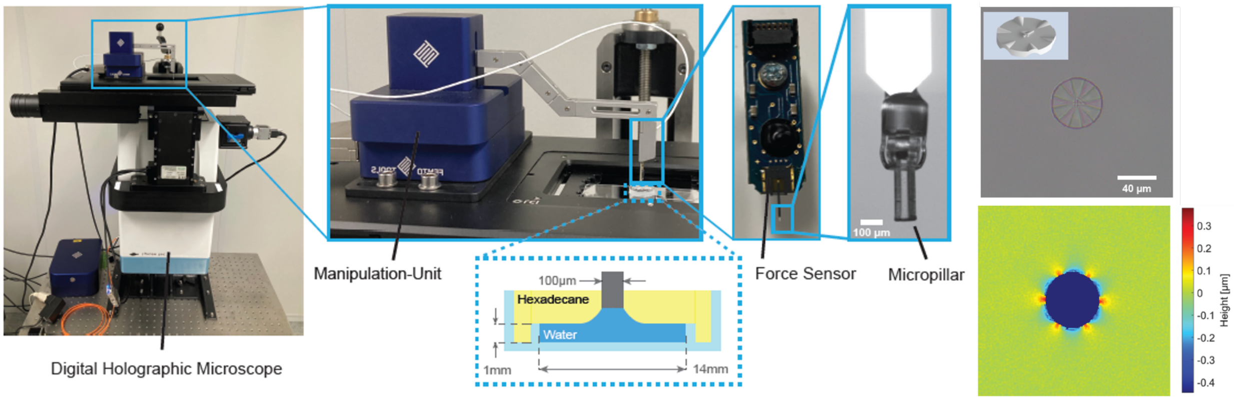
We will synthesize the following types of supraparticles/agglomerates in different length scales:

- Sub-100 micrometer: we will use a microfluidic emulsification method to encapsulate primary nanoparticles, e.g. ranging from 100 nm to 1 micron, inside droplets whose inner liquid phase will evaporate leaving porous supraparticles behind (see figure below). Both oil-in-water and water-in-oil emulsions can be produced, so that primary hydrophilic and hydrophobic particles can be used. In particular, we will use primary particles of silica (for which simple hydrophobization strategies exist) and polystyrene. In the synthesis we will change the supraparticle size (tuned by the initial droplet size before evaporation and the primary-particle solid loading), the supraparticle pore size (tuned by tuning the size of the primary particles) and chemical composition (tuned by tuning the ratio of hydrophilic/hydrophobic particles loaded in the droplets). Supraparticles produced in this way are only held together by van der Waals forces upon full solvent evaporation and can be disassembled during adsorption at the interface, if capillarity overcomes adhesion among the primary particles. We will furthermore produce permanently-linked supraparticles, e.g. by thermally sintering polystyrene particles[5] (few minutes at 80 °C) within homogeneous aggregates. Alternatively, polystyrene particles can be mixed together with silica particles and act as binders during sintering.
- Sub-millimeter/millimeter particles: we will use bulk emulsification processes or macroscopic droplets followed by the same evaporation protocols for supraparticle assembly, varying the same parameters mentioned above, in particular focusing on the scaling of the water imbibition process on the size of the supraparticles.

WP2: Kinetics of wetting of sintered particle aggregates



We will use a new experimental setup available in our group, which combines digital holographic microscopy (DHM) with direct force measurements at an air-water interface using a manipulation unit and a force sensor (see figure below). We will attach a micropillar to a force sensor that can rotate in a free joint and self-align with the interface. We will then glue a supraparticle to the micropillar and bring it into contact with the air-water interface. The force sensor allows monitoring the force during water imbibition and recording force-vs-distance curves when the supraparticles are pushed into/pulled away from the interface. Simultaneously, the DHM visualizes in real time the three-dimensional shape on the interface around the supraparticle, as shown by the images on the right for a microparticle with controlled morphology. We will screen the dispersion behavior of the supraparticles synthesized in WP1 by measuring the forces during interface adsorption/water imbibition and optically visualizing the process. This set of studies serves as the basis to verify and potentially extend existing models on the wetting of porous supraparticles. In particular, we will measure the equilibrium position of the supraparticle at the interface, i.e. their effective contact angle, and relate it to the supraparticle properties. We hypothesize that a fraction of hydrophilic primary particles is sufficient to drive full water imbibition into heterogeneous supraparticles. The hypothesis is that the hydrophilic particles can aid liquid penetration, and we will derive expressions for number and wettability ratios of primary particles to ensure full wetting.



WP3: Dissolution/erosion versus adsorption

We will repeat the experiments of WP3 with supraparticles that can disassemble at the interface and monitor the characteristic time scales for wetting/imbibition versus the ones for dissolution. We will test the conditions under which disassembly takes place, i.e. by tuning adhesion strength and sintering times during supraparticle synthesis. We will also quantify which fraction of the supraparticle disassembles and how many primary particles are transferred to the water phase as a function of the supraparticle parameters. These experiments will enable us to define compositional and structural parameters of particle aggregates that maximize dispersion.

	Q1.1	Q1.2	Q1.3	Q1.4	Q2.1	Q2.2	Q2.3	Q2.4	Q3.1	Q3.2	Q3.3	Q3.4
WP1	🟥	🟥	🟥	🟥	🟥							
WP2				🟩	🟩	🟩	🟩	🟩	🟩			
WP3										🟦	🟦	🟦

Industrial samples can be tested from the beginning of year 2.

Critical unknowns

The following elements can be considered in relation to feasibility and risk mitigation:

- Simple equilibrium modeling is not sufficient to understand the imbibition problem and more complex numerical approaches may be needed. The group has active collaborations with a theory group working on particles at interfaces (Dr. Martin Buzza, University of Hull, UK) who can be involved in the project if needed.
- Particle aggregates of industrial relevance may also release surfactants when brought in contact with the air-water interface. We can attempt to load our supraparticles with surfactants that stay trapped during evaporation and drying and will investigate their role.
- Humidity may play an important role in the imbibition/dispersion process. We will carry out the experiments under controlled humidity conditions.

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