Research Proposal
Syneresis of Colloidal Dispersions
Investigator: Professor Emanuela **Del Gado**, Georgetown University, Washington DC

Answers to questions from IFPRI members.

Question 1 - Experiments: We are unclear whether you are proposing to do some experiments yourself, or you will rely on experimental work done by Jan Vermant and/or Lilian Hsiao for developing and validating your models. Do you have specific plans in mind, or do you hope to develop them "osmotically" through your IFPRI interactions? Are Jan and Lilian already doing relevant research, or do you need them to initiate new work in support of your project? It would be helpful to know that Jan and Lilian have "bought in" to a collaboration, if this is necessary for your project to succeed.

<u>Answer</u>: I do not plan to perform experiments myself, as my expertise is in theory and computational investigations. Lilian Hsiao and Jan Vermant are already doing relevant experimental research and I have specifically discussed my research proposal with them. Within the context of Lilian Hsiao's IFPRI project, her accelerated aging approach based on high frequency ultrasound perturbations of colloidal gels will provide novel microstructural information about how local changes can trigger large scale catastrophic events and failure, including syneresis. This information is ideally suited to complement the modeling and simulation work I have planned in this proposal. Specifically, Lilian and I have agreed that it is possible to build a feedback between the rheological and imaging analysis that she is developing, with and without acoustic stimulation, and the numerical simulation studies planned for this proposal, during year 1 and especially year 2.
Jan Vermant has been developing extensive capacities to measure non-affine microscopic rearrangements underpinning the rheology of colloidal gels with smooth and rough particles, and to gain access to local stresses. In the discussions with Jan, it has become clear that the data they have been producing, within their IFPRI project but not only, can provide novel insight into microstructural changes and elastoplastic processes during yielding which can be also relevant to gel syneresis. In particular, the data being generated in Jan's group would be ideal candidates to support and validate the studies and analysis proposed here especially in year 1 and 3. We have therefore agreed to exchange information and develop collaborations as our work progresses.

Question 2 - Theory: Wilson commented that you need to amplify on how you plan to model boundary interactions, since syneresis requires retraction of the gel from a vessel boundary. In his words: To simulate that requires non-periodic boundary conditions in at least one, and preferably two spatial dimensions. I don't think anyone has ever actually done a simulation of such 'syneresis proper' before. To set up a simulation model that does this convincingly would open the way to significant advances downstream.

<u>Answer</u>: This is indeed an excellent point. I agree that modeling boundary interactions and using non periodic boundary conditions is central to the question of syneresis. Performing such study would be a major progress and it is in my plans. I have therefore included relevant more explicit plans for this point in the revised proposal.

Question 3 - Simulations: You plan to change particle softness in your simulations, but in practice this is likely to be impractical. Use of fillers or modifiers in your simulation may be a more pragmatic focus. (We may have misunderstood your intent for varying softness, in which case you may want to clarify the reasons for studying this parameter).

<u>Answer</u>: The idea of varying the particles softness came from a recent study of syneresis in colloidal gels (Wu et al. PRL 2020, ref. [9] in the proposal) which suggested that gels made of liquid droplets or soft elastic particles (e.g. rubber) may have stronger syneretic behavior compared to gels made of stiffer (e.g. polystyrene) particles. In the past, conversations with an industrial collaborator had suggested that varying particle stiffness or softness could be practically relevant to specific types of personal care products or food. These two circumstances motivated my interest in this direction. Nevertheless, I agree that changing the particle softness may be impractical in most cases and that investigating the role of fillers and modifiers is far more interesting and generally relevant. I have revised the proposal to reflect these considerations.

In the proposal, I have highlighted the revised text in blue.

Research Proposal - revised
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Objectives:

[1] Develop a numerical simulations approach to complement and inform experimental studies of syneresis in colloidal gels.

[2] Use the numerical approach, in concert with experiments, to identify the variables controlling extent and rate of gel shrinkage.

[3] Investigate how the control variables can be used to manipulate the gel evolution, and devise strategies, in feedback with experimental and industrial partners, to reduce, eliminate, or enhance syneresis.

[4] Investigate the relationship between syneresis and phenomena such as delayed collapse and consolidation to achieve a comprehensive understanding of particle gels instabilities.

Motivation

Gelation of colloidal dispersions is an important strategy to design and extend the shelf-life of colloidal materials, relevant to a broad range of industries and technologies. Aggregation processes driven by surface forces or depletant agents, and mediated by the solvent, turn the particulate component into a gelled structure, whose mechanical strength can delay or hinder particle flocculation, sedimentation, or separation, therefore promoting a mid- or long-term stability of products [1, 2].

However, the stability and the mechanics of these gels is determined by a complex interplay between the surface interactions or even molecular cohesion developed at the colloidal particle contacts that are formed during gelation, the aggregation kinetics that drive formation of various types of structures, and the effect of external forces, or evolving environmental conditions, that can promote breaking or reforming of the gel structure [3, 4]. The solidification, or quasi-solidification, processes corresponding to gel formation are typically sources of frozen-in stresses in the load bearing part of the gel and build a memory of the processing history. Moreover, the disorder in the gel structure, and in its stress-bearing backbone, promotes and enhances stress localization under load [5]. The feedback between stress heterogeneities, structural disorder, and nonequilibrium conditions, is therefore likely a key ingredient in the long-term mechanical stability of gelled colloidal dispersions.

Colloidal gel products have in fact a finite shelf-life, and syneresis, where the gel structure remains largely intact but shrinks and contracts expelling a small volume fraction of a dilute particle phase, is broadly observed [6–10]. While it is clear that the nature of the interparticle contacts and their evolution, or aging, under different environmental conditions, plays a central role in this phenomenon, there is still limited understanding of the variables controlling the extent and the rate of the gel shrinkage. Moreover, it has become increasingly clear that only elucidating the physical-chemistry of the particle contacts, of the solvent and possible additives, is not sufficient to completely understand syneresis, since a key unknown is how changes in the particle contacts,

and in the forces acting on them, translate into stress redistribution triggering changes in the gel structures at larger scales.

To address these outstanding questions, computational methods offer now unique opportunities to integrate different levels of complexity in a controlled manner, complement experimental studies, and help develop a more comprehensive theoretical framework. Particle based numerical models especially have proven effective to unravel the space- and time-resolved microscopic dynamics in colloidal gels at rest or under deformation [11–17], thanks to large scale simulations that can help disentangle the dynamical processes at the particle-level (single bond-breaking or forming) and the large scale reorganization at level of the network structure (gel shrinkage).

With the goal to develop new fundamental knowledge and understanding of the syneresis phenomenon, I propose to build on my group's expertise to design a numerical simulation approach that can complement new experimental studies, promote insightful interactions and feedback with IFPRI industrial and academic members, and create novel synergies between academic and industrial research.

Relevant contributions

The focus of the research in my group is in unraveling the microstructural underpinnings and the spatio-temporal microscopic dynamical processes in the rheology of soft materials. For colloidal gels, this means being able to extract the backbone that carries stresses (Figure 1) and analyze how it evolves with time and under deformation. Building on this concept, a few of my group's contributions are specifically relevant to the research on syneresis proposed here, and I briefly highlight them here.

In addition to developing a suite of computational tools for modeling colloidal gels with varying capacity to restructure under deformation, we have pioneered the use of microscopic models that include more complex interactions (three-body), to better describe the nature of the surface contacts between particles [11, 14, 18–20]. Adhesion or surface roughness, in fact, can limit particle relative rotations and introduce bending stiffness to the particle bonds, with potential implications, still poorly understood, for the gel syneresis.
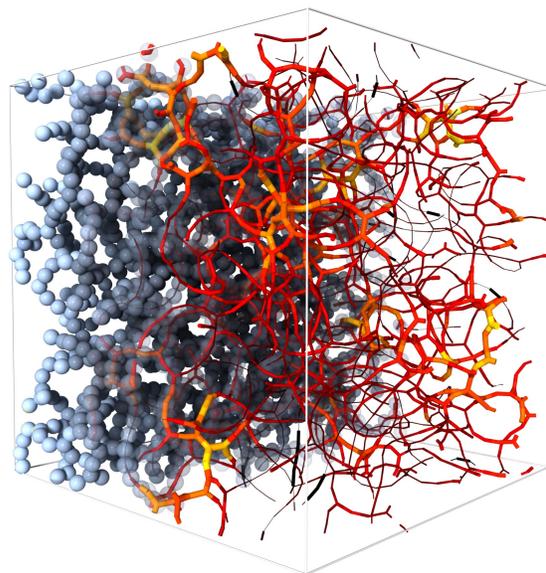

Figure 1: Snapshot from simulations of a model colloidal gel showing the gel structure and load-bearing backbone which controls elasticity as in [17].

We have shown that in colloidal gels even reconfiguration simply triggered by thermal fluctuations at rest, continuously breaking and reforming particle connections, takes place through extensively cooperative modes, so that breakage/reformation of particle contacts have consequences further away [18]. With a time- and space-resolved analysis obtained through a combination of Molecular Dynamics and Monte Carlo techniques [14], we have provided new fundamental understanding of aging processes central to gel syneresis: the intermit-

tent and strongly correlated relaxation dynamics detected in experiments [21, 22] is due to frozen-in stress heterogeneities triggering microscopic rearrangements dominated by the elasticity stored in the gel structure.

The way stresses are transmitted in colloidal gels structures is one of the most important unknowns in the syneresis problem. We have developed the concept of correlated rigidity percolation to understand the emergence of rigidity in colloidal gels and revealed how during gelation, spatio-temporal correlations in the particle aggregation kinetics can shift the onset of rigidity to lower volume fractions by promoting the growth of "smart" rigid lean structures optimized to carry stress, akin to Warren trusses or other lean, load bearing structures in structural engineering [23]. We have provided the first quantitative evidence of the presence of force chains in colloidal gels, demonstrating that a subset of the microstructure, not obviously recognizable through microscopy, carries stresses and is responsible for rigidity [24]. Recently, we have finally identified the microstructural origin of the power-law viscoelastic spectra of colloidal gels in the hierarchical build-up of a load-bearing backbone during gelation, which naturally introduces a memory of the gelation process [20]. The interplay between external load, and evolving local forces and structures, is another crucial point to elucidate in gel syneresis, and, under shear, we were able to establish a direct connection between the spatial redistribution of local stresses during shear star-up, the mechanical response, and flow localization phenomena [11], an insight that was recognized by the 2016 Journal of Rheology Publication Award. We also introduced the idea that the network topology itself can qualitatively change the material beyond the properties of the single components (fiber, particles or agglomerates), and could be used to design softening or stiffening materials [25]. Our capacity to address these questions and the experience gained in these investigations ideally place us to tackle syneresis.

Project description for the first 3 years.

The first step will be building colloidal gel structures representative of model experimental systems, and considering also boundary interactions, i.e., with non-periodic boundary conditions in at least one or two of the three spatial dimensions. We will then trigger local structural changes by: 1) preparing gel structures with specific stress states and stress heterogeneities, representing frozen-in stresses developed during gelation and stresses induced by, or against, the boundaries; 2) have the contact forces evolve over time, mimicking the aging of the mechanical contacts between particles or with the walls, due to adhesion, hardening or detachment; 3) modify the boundary conditions under which the gel was initially formed (for example introducing tension or compression) to mimic changes in the external environment and in the boundary stresses. We will then analyze the changes in local stresses, the dynamical processes, and the structural evolution over time, and identify in which cases they are associated to shrinkage and contraction.

The concept for the simulations is that self-assembly of coarse grained elementary units (particles or small aggregates typical of colloidal materials) through effective interactions that contain minimal, but crucial, information about the physical-chemistry of interest, leads to gel formation. The time evolution is obtained by integrating the many-body equations of motion for the whole set of microscopic degrees of freedom and with a set of boundary conditions that corresponds to the specific problem of interest [11, 19]. Microscopic collective dynamics will be investigated with large samples ($\sim 10^6$ units), needed to identify the appropriate level of coarse-graining, build connections across lengthscales and perform the required disorder-averages, fully resolving mesoscale

structure and accurately capturing macroscopic rheology. To guarantee high computational efficiency and portability, most of these simulations will be built using the publicly available LAMMPS software [26].

We will identify parameter choices that allow us to be as close as possible to model experimental systems. Particularly relevant is experimental research by Jan Vermant (ETHZ) and Lilian Hsiao (NC State University) within their on-going IFPRI projects and I have have planned collaborations with them throughout this project.

Establishing a direct connection between simulations on model colloidal gels and experiments is often quite challenging: particles size and shape, interactions, solvent properties can be accurately matched, but the conditions in which the gel self-assembly occurs remain very far between simulations experiments, so that even apparently similar structures end up having quite different rheology. To overcome these difficulties, we will characterize the rheological responses of the gels through a broad range of rheological tests in the linear and nonlinear regime. The goal is to build digital twins, as close as possible to model materials that are being tested in experiments.

The plan for the first three years of the project is as follows.

Year 1: We will build on existing computational tools in my group, on the existing literature, and on the interactions with the IFPRI community, to devise suitable colloidal gel structures in the simulations. To start with, we will consider spherical particles and include the solvent simply through the drag that it exerts on the particles. The simulations we plan allow for large flexibility in the choice of particle interactions, contact forces, and aggregation kinetics. We will initially consider two distinct cases: 1) smooth particles that form gels with thick, dense, strands and 2) rough particles that tend instead to form gels with thinner strands and more open structures [27–29]. We will explicitly consider the presence of boundaries (walls) with which the gel particles are in mechanical contact, in one or two of the three spatial dimensions. The interactions and contacts with the boundaries will be varied to study the effect of smooth/rough boundaries, and short/longer range interactions that can induce concentration gradients and restructuring close to the walls. We are specifically interested in the interplay between frozen-in stresses in the bulk and at the boundaries. Throughout these simulations we will quantify rearrangements, changes in local density, and changes in the network topology, and identify those that are indeed relevant to syneresis. A spatio-temporal analysis of the microscopic dynamics will allow us to identify the locally floppy regions where typically non-affine rearrangements (NAR) will tend to accumulate. The spatial maps of NAR will provide insight into timescales associated with various structural changes and help us build the connection between the changes in the local structures and those in the macroscopic response [11, 30]. We will then compare the results obtained and the dynamical regimes associated to syneresis with experimental observations in the literature and in the new IFPRI funded projects by Vermant and Hsiao, to draw conclusions about the variables controlling the extent and the rate of shrinkage, which will include not only the particle volume fraction and the rate governing the gelation kinetics, but also interaction strengths, particle contacts, network topology and overall stress states.

Year 2: During the second year, we will use the knowledge developed so far to devise strategies that can control or soppress syneresis. Lubrication forces could also be included, as well as non

spherical particles. One idea is that it may be possible to reduce syneresis by subjecting the gels to cyclic deformations, ultrasound or other mechanical treatment that can help relax some of the stress heterogeneities at its origin, creating gel configurations that are more mechanical stable locally and therefore specifically more resistent to syneresis [31,32]. Another interesting strategy to be tested involves introducing fillers and additional interpenetrated gel networks, to see how (and if) the filler-reinforcement or the coupling across multiple networks can be used to enhance or reduce syneresis. If possible, we will also use a combination of classical density functional theory (DFT) and coarse-grained simulations developed in [33] (that we have already tested in other contexts) to compute adsorption/desorption of water and test imbibition of the various porous structures, to determine their durability in different environmental conditions.

Year 3: We will investigate the connections between syneresis and other mechanical instabilities, in particular the delayed collapse, in which the structure of the gel is entirely destroyed, and the consolidation, in which the bottom of the gel consolidates under the weight of the gel above it [34,35]. At this stage we could also consider more sophisticated, and computationally costly, description of the solvent with long-range hydrodynamics. The scope of the research in this third year will be to identify possible common gel features that play a role across the different instabilities and understand deeper the connection between the gel topology, the stress state created during gelation (in the bulk and at the boundaries), and the development of the instabilities. In particular, it may be possible to identify microscopic precursors of the different instabilities, and we will investigate how they could be soppressed or enhanced through the different strategies to reduce syneresis analyzed in the previous year.

Goals and expected accomplishments in each year

Year 1: Establishment of the model and of the simulations, together with the analysis tools, and in feedback with experiments. Identification of the variables that control extent and rate of shrinkage.

Year 2: Exploration of strategies to reduce or suppress syneresis. Use of cyclic shear and ultrasound vibrations in feedback with experiments. Use of filler reinforcement and network interpenetration.

Year 3: Comparison of control variables, microscopic changes, precursors, and dynamics across syneresis, delayed collapse, and consolidation. Implications of the microscopic insight gained for the macroscopic rheological behavior.

Leveraging into the group's existing programs.

My group has developed unique capacities to analyze microscopic stresses and perform computational linear and non-linear rheological tests, which allow for direct comparison with experiments and constitute a powerful tool to unravel the connection between microscopic structures and macroscopic mechanical responses [11,19,25,36,37]. In close collaborations with experimentalists, we have implemented a computational version of time-resolved rheology based on Optimally Windowed CHirps [36], which allows to obtain the whole viscoelastic response in one simulation with high

computational efficiency and accuracy. We have also implemented a computational version of the Sequence of Physical Processes approach originally developed for experiments [38] to investigate the nonlinear rheological response through Large Amplitude Oscillatory Shear tests [37]. Within a theoretical collaboration, instead, we are developing new computational and analytical tools to characterize spatial correlations of microscopic stresses, rigidity, and prestress dependence of elastic moduli in colloidal gels [24, 39]. Finally we are building new capacity to characterize the complex topology of colloidal gels through topological characteristics whose evolution closely follows the rheological behavior [40].

Current activities in the group include modelling of nanocomposite gels and of jammed emulsions and microgels. The goal is to understand reinforcement, toughening and failure of hydrogels with varying nanofiller concentrations and nanofiller-gels interactions [41], of demixed multicomponent colloidal gels [42], and of interpenetrated self-assembled gel networks that are designed as synthetic alternatives of the extracellular matrix [43, 44]. In these different contexts we are developing new understanding into how the interactions between the various components modify the stress transmission and the mechanics of the initial hydrogel, changing their capacity to stiffen or increasing their deformability and toughness. The program on jammed emulsions and microgel suspensions is focused instead on yielding and resolidification after flow cessation. Recently, we have developed new simulations and analytical tools to investigate the microstructural underpinnings of the shear thinning and thickening in dense suspensions [45].

Finally we have a long-standing program on reactive colloidal gels in the context of cement hydration [46–48], where my group has pioneered a statistical mechanics description and computational approach to quantitatively investigate nanoscale gelation and densification of cement hydrates. We have now expanded this activity to clay based reactive gels, of interest for low carbon cement mixtures, for their geophysical and geotechnical implications, and in the context of construction in space . The syneresis related to curing of cement hydrates and to humidity changes or freeze-thaw cycles that hydrated clay gels undergo in soil is clearly relevant to our work. We are specifically interested in how nanoscale forces and their evolution during cement hydration controls the morphology of these gels and steer compressive or tensile stresses as the material progressively densifies and solidifies. These investigations led us to develop a semi-atomistic approach to compute the ion-specific nanoscale forces due to the confinement of ion and water in cement and clays [49,50].

Plans for interactions with IFPRI members

I expect plenty of interactions and feedback with IFPRI members, along all the different parts of the project. The feedback from industrial researchers will be particularly interesting to identify the ingredients that will allow us to translate the outcomes of this study into practically relevant insight. I can anticipate extensive interactions with the IFPRI members mentioned in the Project Brief, that have long standing interests and experience in colloidal gels, such as Wilson Poon (University of Edinburgh), Mike Solomon (University of Michigan), Eric Furst (University of Delaware) and others. These interactions will constitute an incredibly important resource. Finally, we will directly connect the numerical models and the gel structures obtained in the simulations to the current projects by Jan Vermant (ETHZ) and Lilian Hsiao (NC State University), having already planned interactions and joint work. Plans of regular meetings, student exchanges, and also exchanges of analytical tools across simulations and experiments, will be integrated in this research

proposal. The integration of computational and experimental work built throughout this project will set the basis for new synergies and productive interactions among IFPRI members.

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