

**Tuning Complex Colloidal Systems to meet Industrial challenges:**

**Exploiting thixotropy and handling ageing**

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**Host Organization: IESL-FORTH, Crete**

**Duration of proposed research work: 36 months**

**Outline:**

We propose to develop and characterize model colloidal systems, with varying tunable interactions that can mimic the basic ingredients of complex industrial colloidal formulations. The latter have complex compositions, with interparticle interactions and surface effects often not well understood as well as significant shape and/or size polydispersity. Such effects render a detailed mechanistic analysis and prediction of their rheological response difficult. Therefore tailored design of new materials and formulations with improved properties is not possible since as in-depth understanding of the underlying science is not available. On the other hand colloidal particles used as model systems in academic research are well characterized, but their simplicity hides the rheological behavior exhibited by their industrial counterparts.

An example is systems that exhibit *“thixotropy”*, a rheological response detected in many complex industrial formulations where rheological properties are affected by the mechanical history [1]. Such response has been studied in model colloidal gels where external fields (such as steady or oscillatory pre-shear shear) were demonstrated to affect or even tune their mechanical properties. Another related phenomenon is *“ageing”*, i.e. the time evolution of the underlying structure and/or particle interactions affecting the mechanical properties of a system. Understanding the origins of such time evolution at rest and under external stimuli (shear/flow/shaking etc.) requires probing them structure and dynamics at microscopic or even single particle level.

The knowledge of the underlying mechanisms responsible for thixotropy and ageing may be applied to a variety of similar industrial formulations (such as paints, slurries, foodstuff, cosmetics, agrochemicals etc.) enabling design of improved products, and fine tuning of industrial processes (for example in oil recovery, pipe flows, concrete setting etc.).

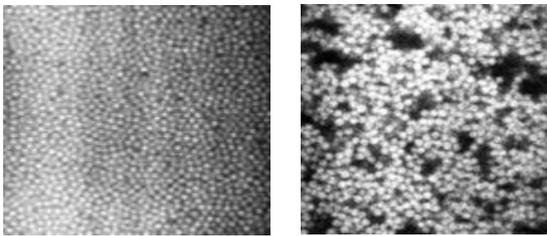
Towards this aim the first goal of this project is to ascertain what properties need to be included in model formulations (e.g. particle shape, roughness, porosity, surface chemistry) to reproduce behavior of real formulations. These systems will then allow efficient and detailed experimental studies providing answers to important problems of industrial systems. To this end **our specific aim is to develop structure-property relationships as a basis for designing materials with tunable mechanical properties via the application of external shear/flow and to be able to predict and alter ageing effects.**

To achieve these goals **we plan to work in close collaboration with IFPRI industrial partners** in order to i) determine open problems to be targeted and ii) develop model Simplified Industrial Formulations (SIFs). These will be real industrial formulations properly modified synthetically to strip down their complexity but keep their basic rheological response. As an example two systems that may be studied are simplified agrochemical formulations (in collaboration with Syngenta) and simplified paints (in collaboration with Chemours). In parallel a series of model systems commonly used in academia (where FORTH has large experience) will be tuned and incrementally evolve to reproduce the response of SIFs. Such Complex Academic Formulations (CAFs) together with the SIFs will allow bridging the two worlds (applied industrial with fundamental academic research)

Using SIFs we will perform state-of-the-art experiments to investigate their mechanical properties and link to underlying structure and dynamics at different length scales. Similar measurements in CAFs in addition to prior knowledge on model systems will allow further tuning of SIFs to attack the specific industrial problems under consideration.

### **State of the art**

Understanding the **flow and microscopic dynamics** of complex colloidal systems is of profound scientific and technological importance since these systems cover a broad range of applications such as traditional consumer products (foodstuff, paints, agrochemicals etc.), cutting-edge emerging technologies (photonics, phononics, optoelectronics, 3D printing), oil recovery, mining flows, biological applications and complex intracellular functions [1, 2]. When mesoscopic units (typically 10 nm to 10  $\mu\text{m}$ ), such as colloidal particles or polymer chains are dispersed in a medium (usually liquid solvent) Brownian motion is of central importance and the interplay between equilibrium thermodynamic phases (fluids and crystals) and metastable states (glasses and gels) is dictated by the volume fraction and details of interparticle interactions (e.g. strength and range of attractions)[3, 4]. Tuning of the final macroscopic material properties (mechanical, thermal, electrical) may be achieved by either changing constituents and interactions or imposing external fields. The latter can lead to temporary structural (and mechanical) changes (e.g. equilibrium phases in electric/magnetic fields) or even permanent effects in the case of metastable frustrated states [1, 5].



**Figure 1:** Confocal Microscopy Images from (left) a sterically stabilized PMMA particles in a glass state ( $\phi=0.6$ ) and (right) a depletion gel at intermediate volume fraction ( $\phi=0.44$ , interaction energy,  $U=-16kT$ , and attraction range  $\xi=0.05$ ). From Koumakis et al. Soft Matter, 2015 [6]

### *Out-of-equilibrium, metastable states: Colloidal glasses and gels as model systems for industrial products and processes*

Concentrated colloidal suspensions, emulsions and polymers undergo a transition from a fluid phase to disordered, **out-of-equilibrium solid states such as glasses or gels** which exhibit **complex internal dynamics, viscoelastic properties, yield stress and ageing** [1]. This often involves strong thixotropic response, i.e., time-evolving properties that depend on the preparation history [1, 7].

The glass transition arises when many constituents interact cooperatively and prevent the system from reaching equilibrium, with a classic colloidal paradigm the one of hard spheres that are trapped in the glass state at volume fractions  $\phi \geq 0.58$  (figure 1, left), whereas the thermodynamic equilibrium state would be that of an FCC crystal [4]. Moreover when attractive interactions are present, colloidal systems (similarly to polymers) also form gels (figure 1, right) where particles agglomerate in clusters and form a space spanning network with a solid like response. In general, kinetic arrest describes the different ways (density, temperature, flow) by which the ability of a system to flow is lost [1, 8].

The interplay between thermodynamic equilibrium and metastable (out-of-equilibrium) states is also affected from (or other times leads into) ageing, i.e. a time evolution of macroscopic (and microscopic) properties with waiting time. In colloidal gels for example microstructure coarsening through bond reorganisation usually leads to an increase of the gel strength and an evolution of its rheological properties [9, 10], while often times gravitational effects intervene causing a delayed gel collapse [11, 12], a phenomenon that originates from an interplay of structural coarsening of the gel (more pronounced at low and intermediate volume fractions gels with weak attractions), and gravity induced stresses on the gel network.

### *Tunability of material's properties by shear and flow*

While thixotropy is a common phenomenon in industrial colloidal systems such as carbon black or clay suspensions, bentonite slurries etc., several investigations in model systems such as colloid-polymer depletion gels have showed how external fields can be used to tailor colloidal gel structure formation, mechanical and flow properties [1].

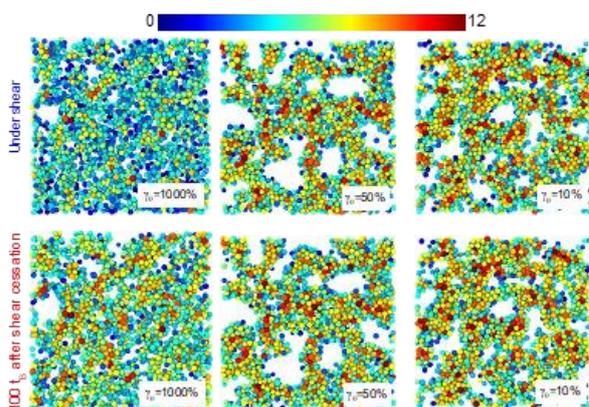


Figure 2: Shear-induced tuning of colloidal gels: Varying strain amplitude under oscillatory shear or shear rate under steady shear leads to metastable gel states with different structural heterogeneities and tunable linear and nonlinear mechanical properties. From Moghimi et al. *Soft Matter*, 2016 [5].

One way to tune metastable states is by external fields such as steady or oscillatory preshear which allows the system to access microstructures (figure 2) that cannot be easily reached by changing thermodynamic variables [5, 6]. Shearing these systems produces a wide

variety of structures with different mechanical properties [5, 6, 13]. Depending on the shear rate, enhanced cluster formation or strong bond breaking may take place. Eventually shearing at high rates (or strain amplitude) leads to stronger and more homogeneous gels, as opposed to lower shear rates which create inhomogeneities and weaker gels. Such effects have strong impact also on the yield stress, delayed yielding and collapse of a gel network [5, 6] and are important in various technological applications. Examples include processing conditions that affect structure and mechanical properties, vitrification during solvent evaporation and film formation that may localize internal stresses and create inhomogeneities, ageing and sedimentation of attractive colloidal formulations that alters their mechanical and flow properties or re-dispersion effects during mixing.

### **Main Goal & Objectives**

Our goal is to **unravel the main mechanisms related with thixotropy and ageing in specific industrial formulations and exploit them in order to tune and control their microstructure and mechanical properties**. Emphasis will be given on effects of shear and ageing on the mechanical properties of industrial formulations in simplified forms that consist of colloidal gels, concentrated colloidal suspensions and mixtures.

We propose to study simplified systems (SIFs) of two main system categories: a) based on colloids stabilized by steric or electrostatic repulsions and b) colloidal systems with dominant and/or time evolving attractive interactions. Along these lines SIFs' properties and their evolution with time will be studied under different conditions, i.e. both at rest (as during storage) as well as under shear and flow (such as in processing, spreading, mixing, spraying, printing, etc.). Our research program will cover an extensive range of the parameter space relevant to industrial applications, by carefully varying single particle properties (size, shape, polydispersity), changing interparticle and surface interactions (range and strength of attractions or repulsions, surface roughness), particle concentrations, composition and mixing ratios, as well as environment (temperature, pH, pressure) and external fields (shear and flow rates, confinement in constricted flows at and near surface etc).

**Research Methodology/Implementation plan:** Below we present a detailed research plan of the proposed program (for the initial 3 year period) and the experimental resources that will be used:

### **Model industrial prototypes (SIFs)**

The characterisation of interactions, aggregation phenomena and rheological properties as a function of ageing time after slow sedimentation (mimicking long time storage), and subsequent re-dispersion via shear/shaking/mixing under different conditions (shear rate/time etc) will be explored within **three main case studies**. The effect of ageing and shear induced redispersion (or rejuvenation) or shear/shaking induced agglomeration will be studied via linear and nonlinear rheometry. More specifically the shear thinning response (with limiting zero and high shear viscosities as well as intermediate rate behavior) and the existence and variation of the yield stress and thixotropic

response will be examined under various conditions (over time, after and under shear, with changing temperature, pressure and/or pH).

*We expect to work mainly on the following three case studies:*

**1) Simplified paint formulations:**

Extensive rheological testing in a variety of conditions and ageing times will be performed in SIFs prepared by IFPRI partner industries (for example Chemours) based on real industrial products such as PVC latex paints. These may contain water based mixtures of polymer particles with calcium carbonate particles ( $\text{CaCO}_3$ ) or silica particles and or  $\text{TiO}_2$  particles. Typical volume fractions will range from 30 to 50%, similarly to what is used in commercial paints. Within this framework different SIFs with varying composition of  $\text{TiO}_2$  or  $\text{CaCO}_3$  and resin will be used to investigate ageing and shear induced effects on the rheology. The latter will be linked with the microscopic structure and interparticle and surface interactions via combined experimental techniques including scattering, microscopy and rheometry. Note that the lab has extensive experience on rheological studies of similar type model systems as well as with their industrial counterparts.

**2) Simplified colloidal agrochemical formulations:**

These systems typically comprise of polydisperse micron size particles (of organic crystals) dispersed in water with suitable dispersants, initially at volume fractions of 30-40%, while they may be further diluted with the addition of components, including high molecular surfactants. Different SIFs will be designed together with IFPRI partners (such as Syngenta) incorporating particles (possible prepared with a variety of procedures), ionic dispersants, macromolecular anti-settling agents (such as xanthan gum and/or bentonite clay particles), and salts. The effort here will be to understand the key mechanisms affecting colloidal stability, aggregation and sediment formation over time, as well as possible procedures (shaking/shearing etc) that may allow full and efficient re-dispersion of the system under different conditions (temperature for example). The target is the design of systems with minimal ageing (evolution of interactions and size) and sediment formation that are also fully rejuvenatable via shearing/shaking etc. Different competing mechanisms will be probed and will be contrasted with current knowledge in model colloidal and polymeric systems. For example introduction of depletion attractions by the addition of polymeric species versus stabilization and increase of medium viscosity against sedimentation of dispersed particles.

**3) Other applications potentially relevant to industrially systems**

In addition we wish to explore the use of existing state-of-the-art experimental infrastructure and our know-how in colloid and polymer rheology and dynamics for other potential industrial problems related with the **effects of high pressure** (as an alternative thermodynamic) on bulk systems, and thixotropic/ageing phenomena in **surfaces and interfaces**. Related with the former we can monitor the stability and aggregation process in certain formulations under high pressure (up to 1000 bar) via dedicated high pressure scattering and microscopy set-ups. Regarding the latter, near wall DLS and interfacial rheometry provide powerful tools to study such effects in 2D. During the first 6 months we will explore any relevant interest among IFPRI partners for such studies that are relevant to applications such as flow of drilling muds and oil products underground and/or in confined environments and in surface/interfaces.

**Synergies with ongoing studies and expertise:** Ongoing studies in our lab on colloidal glasses and gels of spherical and rod-like particles, as well as in soft polymer grafted colloids, ultrasoft polymer microgels and multiarm stars demonstrate our strong know-how and foster extensive collaborations with several world-class experts in synthetic chemistry, computer simulations and theory. The large in-house expertise in powerful combinations of experimental techniques (in-situ rheometry /scattering /microscopy) will provide additional warranty for a smooth progress of the project.

**Local research team - Expertise and state-of-the-art infrastructure:** The work will be performed at the **Polymer & Colloid Lab (Univ. Crete, Dept. Materials Science & Technology and IESL/FORTH)**.

The lab consists has a longstanding experience in the fundamental study of structure, dynamics and rheology of polymer and colloid-based materials. Its strength is the combination of a broad range of dynamic techniques in order to address the molecular origin of the materials response. The group collaborates closely with leading groups around the globe, including world class chemists. The group currently includes 2 post-doctoral fellows, 7 graduate students and 2 technicians and is part of large European Soft Matter Infrastructure (EUSMI, Horizon-2020, 2017-2021). External collaborations are foreseen with existing collaborators such as Univ. Edinburgh (W.C.K. Poon), Caltech (J. F. Brady), ETH/Zurich (J. Vermant), Univ. Dusseldorf (S.U. Egelhaaf) and others.

**The local team members** (with expertise and allocated time) that involved in the project are:

**Prof. George Petekidis (PI)** (Light scattering, rheology colloidal glasses and gels, 15% of his time),

**Prof. Dimitris Vlassopoulos (co-PI)**. (Rheology of soft matter systems, 10% of his time),

**Dr Benoit Loppinet** (Light, X-ray and neutron scattering, interfacial phenomena, 5% of his time),

**Mr. Antonis Mavromanolakis** (technician, Polymer and Colloid lab, 10% of his time).

Within the project we plan to additionally hire **1 new PhD student (36 months)** and **1 new Post-doc researcher (24 months)** with background in soft matter physics (experiments and/or simulations).

They will work full time on the project.

**Experimental Techniques** (Provide broad spatio-temporal range via a combination of techniques):

a) Light Scattering (Static/Dynamic) for particle characterization (size, polydispersity, interactions), study of aggregation and particle dynamics in concentrated suspensions, 3D-DLS for studies of turbid media and multispeckle DLS for slow dynamics and ageing in non-ergodic systems,

b) Shear rheometry with several strain and stress controlled rheometers (9 in total) covering applications on solutions, melts, low and high temperatures, as well as interfacial rheometry (via a Langmuir-Blodgett trough and bicone geometry) are available,

c) Light Scattering (SALS or LS-echo) under shear (with rheometer and shear cells) allowing structural probe under shear and detection of particle dynamics and irreversible rearranges under LAOS,

d) Fluorescent rheo-confocal, rheo-imaging and Rheo-DDM (Dynamic Differential Microscopy) for monitoring particle structure and dynamics at different length scales,

e) Static and dynamic light scattering (DLS, SALS, DWS), enabling also microrheology, under high pressure (up to 1000 bar). Complementary, real space imaging with a confocal microscope under high pressure is also available.

**Outline of Work Plan:** Our work plan will be organized in work-packages (WPs) as follows:

**WP1: Identify relevant industrial systems and problems (duration: month 1-4)**

Collaborate with IFPRI member companies to define the open problems and the composition of the relevant industrial formulations and the function of their ingredients,

**WP2: Preparation of Systems (month 2-12; Fine tuning throughout the project)**

*Task 1:* Prepare a detailed plan to produce SIFs from industrial formulation by removing ingredients believed to have minimal impact on rheological behavior. Synthesis will be provided by IFPRI member companies,

*Task 2:* Utilize model colloidal systems, appropriately modified (CAFs) to resemble industrial formulations. Example are sterically or charged stabilized particles (polymeric or silica), soft colloids (polymer-grafted or microgel particles, rubbery and rough particles) and attractive colloids (thermosensitive sticky particles or depletion systems).

**WP3: Characterization of SIFs (month 3-18; Fine tuning throughout the project)**

*Task 1:* Perform a comprehensive characterization of chosen SIFs: a) single particle characterization (sizes, shapes, interactions etc.) and b) concentrated phase behavior and structure

*Task 2:* Map to model system response of the basic rheological behavior of SIFs and CAFs

**WP4: Understand simplified paints (month 12-36)**

Explore via combination of experimental techniques the identified problems discussed above.

**WP5: Understand simplified agrochemical formulations (month 12-36)**

Explore via combination of experimental techniques the identified problems discussed above.

**WP6: Exploration of other relevant industrial problems (month 18 -36)**

Identify additional industrial problems and explored related with applications under high pressure, in confinement and near surfaces/interfaces.

**Contingency planning:**

Regular assessment of the specific project tasks and consulting with IFPRI partner (every 3months) will reveal unforeseen problems and critical unknowns. We will then proceed with the appropriate redesign of systems and experiments to ensure successful completion of the project.

**Deliverables:** A yearly report and presentation of results in meetings planned with IFPRI partners

**Indicative proposal budget: (36000 \$ or ~32000 euro per year)**

**The total budget for 3 years (about 96000 euro) will cover the following:**

- **Personnel cost (80000 euro):** We foresee the following personnel costs throughout the project:  
a) 36 PhD months (27000 euro), b) 24 post-doc months (38000 euro) and c) other (15000 euro).
- **Travel (10000 euro):** Will cover 4-5 trips of FORTH members to IFPRI partners and 3-4 visits of members of IFPRI partners in FORTH/Crete.
- **Consumables (10000 euro):** Will cover various running lab costs

**References**

1. Mewis, J. and N.J. Wagner, *Colloidal Suspension Rheology*. 2012, Cambridge: Cambridge University Press.
2. Larson, R.G., *The Structure and Rheology of Complex Fluids*. 1999, Oxford: Clarendon Press.
3. Poon, W.C.K., *The physics of a model colloid-polymer mixture*. *Journal of Physics Condensed Matter*, 2002. **14**(33): p. R859-R880.
4. Pusey, P.N., *Liquids, Freezing and the Glass Transition*, in *Les Houches Session 51*, D. Lesvesque, J.P. Hansen, and J. Zinn-Justin, Editors. 1991: North-Holland, Amsterdam.
5. Moghimi, E., et al., *Colloidal gels tuned by oscillatory shear*. *Soft Matter*, 2017. **13**(12): p. 2371-2383.
6. Koumakis, N., et al., *Tuning colloidal gels by shear*. *Soft Matter*, 2015. **11**(23): p. 4640-4648.
7. Mewis, J. and N.J. Wagner, *Thixotropy*. *Advances in Colloid and Interface Science*, 2009. **147-148**(0): p. 214-227.
8. Trappe, V., et al., *Jamming phase diagram for attractive particles*. *Nature*, 2001. **411**(6839): p. 772-775.
9. Joshi, Y.M., *Dynamics of Colloidal Glasses and Gels*. *Annual Review of Chemical and Biomolecular Engineering*, 2014. **5**(1): p. 181-202.
10. Zia, R.N., 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*, 2014. **58**(5): p. 1121-1157.
11. Harich, R., et al., *Gravitational collapse of depletion-induced colloidal gels*. *Soft Matter*, 2016. **12**(19): p. 4300-4308.
12. Poon, W.C.K., et al., *Delayed sedimentation of transient gels in colloid-polymer mixtures: dark-field observation, rheology and dynamic light scattering studies*. *Faraday Discussions*, 1999. **112**: p. 143-154.
13. Koumakis, N., A.B. Schofield, and G. Petekidis, *Effects of shear induced crystallization on the rheology and ageing of hard sphere glasses*. *Soft Matter*, 2008. **4**(10): p. 2008-2018.