# Edible Soft Matter 17th-19th April 2019 – Le Mans

**Soft Matter** and **Food Sciences** share many common features. Gels, emulsions, foams, suspensions, … are typical classes of soft materials investigated in Soft Matter. Foods are obvious examples of soft materials with everyday relevance, and it is well accepted that concepts and methods developed for research on soft condensed matter can serve to understand and study of their complex behavior. Numerical, theoretical and experimental investigations need cover a broad range of complementary space and time scales in order to achieve a complete description of the systems. Furthermore, a common goal of **Soft Matter** and **Food Sciences** is the rational design of functional advanced materials. To do so, **Soft Matter** and **Food Sciences** develop similar strategies based on the assembly of several building blocks (bio-sourced in food science and also synthetic for soft matter research in general) through either thermodynamic principles of self-assembly or out-of-equilibrium kinetically arrested organization.

Although differences in terms of language still exist, many soft matter physicists have started to work on food-related topics, highlighting the scientific interest of such multidisciplinary approach.

**The objectives of this SoftComp topical workshop is to highlight the connection between soft matter and food research through exchange, sharing and broadening of know-how between the two communities.**

## The organization committee


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SoftComp
SOFT MATTER COMPOSITES


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## Schedule :

### 17 april

| | | | |
|---|---|---|---|
| 13:30:00 | 13:45:00 | Introduction | |
| 13:45:00 | 14:45:00 | Microscopy techniques and structure dynamics in foods | Niklas Lorén |
| 15:00:00 | 16:00:00 | The use of light scattering in food-related soft matter | Johan Mattsson |
| 16:00:00 | 16:30:00 | Coffee break | |
| 16:30:00 | 17:30:00 | Rheology of gels: Manoeuvring in the low viscosity - high elasticity corner | Peter Fischer |
| 17:45:00 | 18:45:00 | Fluid interfaces in multiphase food systems: Structure, functionality and characterisation techniques | Claire Berton-Carabin |

### 18 april

| | | | |
|---|---|---|---|
| 09:00:00 | 09:30:00 | Recent developments in the field of edible double emulsions | Fernando Leal Calderon |
| 09:30:00 | 09:50:00 | Pickering emulsions stabilized by colloidal lipid particles: Potential for high chemical stability? | Anja Schröder |
| 09:50:00 | 10:10:00 | Synergistic stabilisation of emulsions by blends of dairy and plant proteins: Contribution of the interfacial composition | Emma B. A. Hinderink |
| 10:10:00 | 10:30:00 | Nonlinear surface rheology and interfacial microstructure imaging of WPI particles and their constituents | Jack Yang |
| 10:30:00 | 11:00:00 | Coffee break | |
| 11:00:00 | 11:30:00 | Features of water/water emulsions stabilized by particles | Lazhar Benyahia |
| 11:30:00 | 11:50:00 | Acid-induced gel properties of an alginate-in-whey protein emulsion | Ashkan Madadlou |
| 11:50:00 | 12:20:00 | Interfacial behaviour of plant proteins | Amélie Banc |
| 12:20:00 | 14:00:00 | Lunch | |
| 14:00:00 | 14:30:00 | Food oral processing: From structure to behaviour, perception and pleasure | Marcus Stieger |
| 14:30:00 | 14:50:00 | Viscosity of artificial chewed boluses of cereal foods | Florence Gibouin |
| 14:50:00 | 15:20:00 | Nanoscale Engineering of the Structure and Functionality of Fat and Oleogel Systems | Alejandro Marangoni |
| 15:20:00 | 15:40:00 | Microtechnology used as a tool in the development of novel food products | Karin Schroen |
| 15:40:00 | 16:10:00 | Coffee break | |
| 16:10:00 | 16:40:00 | Oleogels in complex composite samples | Paul Clegg |
| 16:40:00 | 17:00:00 | New approach for the characterisation of dairy protein foams stability | Valérie Lechevalier |
| 17:00:00 | 17:30:00 | Global Small-Angle X-ray Scattering Data Analysis of Triacylglycerols in the Molten State | Michael Rappolt |
| 17:30:00 | 18:00:00 | Functional protein-based colloids for controlling structure and stability of food | Christophe Schmitt |

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|---|---|---|---|
| 18:00:00 | 18:20:00 | Influence of kinetic and shear rate on whey protein aggregates structure: a small-angle x-ray scattering study | Alice Vilote |
| 18:20:00 | 18:50:00 | Understanding of structural heterogeneities in the starch hydrogels | Trey Koev |
| 19:30:00 | 23:00:00 | Gala Dinner | |

## 19 april

| | | | |
|---|---|---|---|
| 09:00:00 | 09:30:00 | Structure and Dynamics of Polymer Composites and Gels: A Simulation Perspective | Virginie Hugouvieux |
| 09:30:00 | 09:50:00 | Model of the swelling of protein gels in simulated gastric juice | Ruud van der Sman |
| 09:50:00 | 10:20:00 | Protein Gels and Glasses | Anna Stradner |
| 10:20:00 | 10:40:00 | Dry heating of beta lactoglobulin generates microparticles: role of pH and lactose | Marie Hélène Famelart |
| 10:40:00 | 11:10:00 | Coffee break | |
| 11:10:00 | 11:40:00 | Protein-fiber mixed systems to innovate in food and culinary applications | Sylvie Turgeon |
| 11:40:00 | 12:00:00 | Heat-induced gelation of mixtures of casein micelles with whey protein aggregates | Anna Kharlamova |
| 12:00:00 | 12:20:00 | Gelation kinetics of sodium caseinate induced by continuous acidification | Thomas Gibaud |
| 12:20:00 | 14:00:00 | Lunch | |
| 14:00:00 | 14:30:00 | Tackling the question of specific interactions in a complex blend of proteins | Marie Hélène Morel |
| 14:30:00 | 15:00:00 | Assembly of plant storage proteins: role of intrinsic disorder and charge anisotropy | Adeline Boire |
| 15:00:00 | 15:20:00 | Stable oil-in-water emulsions using an hydrophobically modified xanthan | Frederic Renou |
| 15:20:00 | 15:40:00 | Gellation of mixture of iota and kappa carrageenan | Viet TNT Bui |
| 15:40:00 | 15:50:00 | Closure speech | |

# Edible Soft Matter 17th-19th April 2019 – Le Mans

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# Edible Soft Matter 17th-19th April 2019 – Le Mans

## Invited lecturers:

Niklas Lorén (Chalmers University of Technology, Göteborg, Sweden) niklas.loren@ri.se
*Microscopy techniques and structure dynamics in foods*

Johan Mattsson (University of Leeds UK) k.j.l.mattsson@leeds.ac.uk
*The use of light scattering in food-related soft matter*

Peter Fischer (ETH Zurich Switzerland) peter.fischer@hest.ethz.ch
*Rheology of gels: Manoeuvring in the low viscosity - high elasticity corner*

Claire Berton Carabin (Wageningen University, Netherlands) claire.carabin-berton@wur.nl
*Fluid interfaces in multiphase food systems: Structure, functionality and characterisation techniques*

# Microscopy techniques and structure dynamics in foods

Niklas Lorén[1,2,3]

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[2] **Eva Olsson Group, Department of Physics, Chalmers University of Technology, Göteborg, Sweden**

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The microstructures at different length-scales are very important for the properties and functionality of foods. Several techniques are required to image the microstructure at different length-scales dependeing on the physical conditions of the food. In this talk, different examples on the coupling between microstructure and properties will be given. In addition, the principles, advantages and limitations of some powerful microscopy techniques useful for foods will be presented.

Two different aspects of structure dynamics will be discussed in this talk. They involve building up of structures as well as dynamics in terms of molecular diffusion. Diffusion is vital for many food properties such as water management in pasta and pastry products, oil migration induced fat bloom in chocolate and oral taste release. These examples show that it is important to have good control over the diffusion properties to obtain desired functionality. Therefore, thorough understanding of structure - mass transport relationships at different length scales in the structure and good measurement techniques for global and local for diffusion are essential. In this talk, the coupling between structure and diffusion[1] at different length scales in Foods and soft porous heterogeneous materials will be discussed.

Quantitative confocal microscopy allows for simultaneous determination of the detailed microstructure at micrometer level and local quantitative information regarding mass transport, electrostatic interactions, rheological properties etc. A brief overview of different microscopy-based techniques to characterize local diffusion will be given in this presentation. Confocal laser scanning microscopy (CLSM) in combination with Flourescence recovery after photobleaching (FRAP)[1] or raster image correlation spectroscopy (RICS) are versatile methods to determine quantitative diffusion properties locally directly in the microscope. They can be used in many types of soft porous homogeneous and heterogeneous foods and biomaterials. A new powerful FRAP technique that gives precise measurements on the local diffusion coefficient will be presented[2]. In addition, determination of the interplay between flow and diffusion using microscopy, FRAP and RICS[3] will be presented.

Food properties change as a function of time and surrounding conditions. CLSM-FRAP combined with different stages to control surrounding conditions is powerful to monitor kinetics. Here, results on microstructure and probe diffusion in phase separated biopolymer mixtures determined by FRAP and NMR diffusometry will be presented[4]. The effect of the characteristic wavelength and the equilibrium concentration on the diffusion in bicontinuous phase separated biopolymer mixtures will be demonstrated using quantitative microscopy and Lattice-Boltzmann simultations. In addition, the effect of confinement on the phase separation kinetics will be discussed[5]. Results that reveal the effects of charge density, size and concentration on diffusion of negative probes in positively charged β-lactoglobulin gels will be presented[6].

## References

1] Lorén et al. (2015) Quarterly Reviews of Biophysics 48, 3 (2015), pp. 323–387.
[2] Röding et al. (2018) Manuscript.
[3] Schuster et al. (2016) Soft Matter DOI: 10.1039/c6sm00294c
[4] Wassén et al. (2014) Soft Matter DOI: 10.1039/c4sm01513d
[5] Wassén et al. (2013) Soft Matter, 9, 2738
[6] Schuster et al. (2014) Biophysical J., 106, 253 – 262.

# Fluid interfaces in multiphase food systems: Structure, functionality and characterisation techniques

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Many food products contain two or more immiscible gas or liquid phases, with one or more phases dispersed in another as bubbles or droplets, forming foams (e.g., coffee foam), emulsions (e.g., mayonnaise, dressings, dairy drinks) or aerated emulsions (e.g., ice cream). An important feature of these systems is the large interfacial area that exists between the different phases, up to several $m^2$ per millilitre of dispersed phase. This fluid interface has to be physically stabilised with emulsifiers, which facilitate the break-up of droplets (or bubbles) during homogenisation, and contribute to the metastability of the systems post-homogenisation, by preventing coalescence. For food applications, two main categories of emulsifiers exist: Low molecular weight emulsifiers (LMWEs), and amphiphilic biopolymers, the latter category being mostly represented by proteins. Recently, interest has also been rising in using biobased particles with dual wettability instead of conventional emulsifiers, which can stabilise foams or emulsions through a Pickering mechanism [1].

A number of challenges may be encountered when attempting to design food dispersions with controlled properties. A first, obvious one, is to prevent the rapid physical destabilisation of the systems (e.g., flocculation, coalescence) which leads to unacceptable aspect and texture. A second one is to ensure the chemical stability of the systems; many food emulsions contain chemically labile molecules (e.g., polyunsaturated lipids, vitamins, phytochemicals), which can be damaged by oxidative reactions, leading to a deterioration of the sensory and nutritional quality. A third one is to control the digestive fate of emulsions, for example, to delay digestion such that satiety feelings are enhanced [2]. Interestingly, all of these challenges are related to the properties of the interfacial layer. It is thus of utmost importance to control the composition and structure of fluid interfaces in multiphase food systems.

Such a control is, however, intrinsically difficult. First, most food systems have a complex composition, including many surface-active molecules, that partition between the available phases and may compete for adsorption at the interface. Often, the amount of emulsifiers used is much higher compared to what is strictly needed for complete interface coverage, which implies that a large excess of non-adsorbed emulsifiers remains in the continuous phase; and that the overall composition of surface-active species does not necessarily reflect the composition of the interface. Second, the interfacial composition may evolve in time, with, e.g., interfacial protein polymerisation, or adsorption of chemical degradation products. And in addition, even when one is able to determine the composition of the interface, its structure still has to be unravelled, which may include lateral phase-separated domains, aggregates, multilayers, etc.

It is thus necessary to determine the composition and structure of fluid interfaces in multiphase food systems, which can be achieved through different approaches [3]: (i) in real systems (e.g., emulsions), with non-destructive methods; this refers mostly to a range of microscopy or spectroscopy techniques; (ii) in real systems, after phase separation (e.g., separation of the cream and aqueous phases of emulsions, followed by analysis of the separate phases); (iii) in model dispersions, e.g., foams or emulsions produced with microfluidics, which allows for high control of the production conditions, and investigation of interface stabilisation at short time scales; and (iv) on model, two-dimensional interfaces (air-water or oil-water), which allows for measurement of e.g., the rheology of the formed layers, their thickness, or their topography. Combining different approaches is needed to obtain a comprehensive description of such complex fluid interfaces, which can, in turn, help designing multiphase food systems with controlled properties.

## References

[1] Berton-Carabin & Schroën. Pickering emulsions for food applications: Background, trends, and challenges. *Annu. Rev. Food Sci. Technol.*, **2015**, 6, 263-97.

[2] Corstens et al. Food-grade micro-encapsulation systems that may induce satiety via delayed lipolysis: A review. *Crit. Rev. Food Sci. Nutr.*, **2017**, 57:10, 2218-44.

[3] Berton-Carabin et al. Formation, structure, and functionality of interfacial layers in food emulsions. *Annu. Rev. Food Sci. Technol.*, **2018**, 9, 551-87.

# The use of light scattering in food-related soft matter

Johan Mattsson

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Light scattering techniques are excellent tools to study both structure and dynamics in soft materials. For food systems, which are often characterised by complex structures and a broad range of motions both of molecular, supramolecular or colloidal structures, light scattering can be particularly useful for understanding the systems. Moreover, light scattering techniques can be used to characterise the rheological properties of soft matter and this can be particularly useful in systems that are sensitive to standard rheological testing.

In this presentation, I will provide an overview of how different light scattering techniques and approaches can be used to characterise the state of a particular soft material as well as the transition between different states. Important examples will include complex fluid mixtures, polymer solutions, polyelectrolytes, gels and glasses, both where the key building blocks are molecular, supramolecular or colloidal.

# Rheology of gels:
# Manoeuvring in the low viscosity - high elasticity corner

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Gelation, although commonly utilized in the design and production of food may issue several experimental challenges to the rheologist. The transformation from a liquid to a solid response asks for a wide sensitivity range of the rheometer, while slip due to syneresis compromise the data, shear deformation change the gel structure for good or bad, or gel fracture might terminate the rheological experiment instantaneously. But what, if the gel undoubtfully can be seen, touched, and deformed but the rheological data are not sophisticated at all? [1] Using two mucus-based systems, hagfish slime and sputum from cystic fibrosis patients, the rheology of low viscous but highly elastic materials will be discussed [2, 3]. The high water holding capacity of mucin generates a dilute viscous gel and simultaneously provides a widely spanning network structure introducing the elasticity to the sample. In Figure 1 the influence of sample, electrical, and inertia torque are discussed as one of the limiting factors in oscillatory measurements. Similar problems such as slip layer formation, rheometer sensitivity and inhomogeneous sample structure are discussed for hagfish slime, which is composed from mucus and long intermediate filaments. In a final step, the use of elongational measurements will be discussed as option for samples unsuitable for rotational or oscillatory experiments.

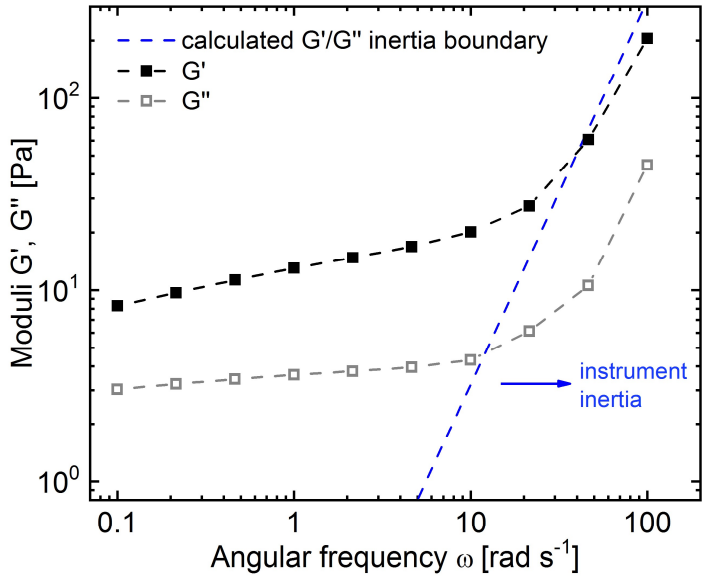


*Figure 1: Rheology of cystic fibrosis sputum. Frequency sweeps depicting G' (storage modulus and G" (loss modulus). The blue dashed line indicates the calculated instrument inertia limit (taken from [2]).*

**References**

[1] Ewold R et al.: Experimental Challenges of Shear Rheology: How to Avoid Bad Data, in Complex Fluids in Biological Systems Experiment, Theory, and Computation (Springer, 2015).

[2] Böni L, Fischer P, Böcker L, Kuster S, Rühs PA: Hagfish slime and mucin flow properties and their implications for defense, Scientific Reports 6 (2016) 30371.

[3] Radtke T, Böni L, Bohnacker P, Maggi-Beba M, Fischer P, Kriemler S, Benden C, Dressel H: Acute effects of combined exercise and oscillatory positive expiratory pressure therapy on sputum properties and lung diffusing capacity in cystic fibrosis: a randomized, controlled, crossover trial, BMC Pulmonary Medicine 18 (2018) 99.

# Edible Soft Matter 17th-19th April 2019 – Le Mans

## Key-note speakers:

Lazhar Benyahia (IMMM Le Mans, France) lazhar.benyahia@univ-lemans.fr
*Features of water/water emulsions stabilized by particles*

Adeline Boire (INRA BIA Nantes, France) adeline.boire@inra.fr
*Assembly of plant storage proteins: role of intrinsic disorder and charge anisotropy*

Paul Clegg (U. Edinburgh, UK) paul.clegg@ed.ac.uk
*Oleogels in complex composite samples*

Virginie Hugouvieux (INRA SPIRAL Montpellier, France) virginie.hugouvieux@inra.fr
*Structure and Dynamics of Polymer Composites and Gels: A Simulation Perspective*

Fernando Leal-Calderon (CBMN Bordeaux, France) fleal@enscbp.fr
*Recent developments in the field of edible double emulsions*

Alejandro G. Marangoni (U. Guelph, Canada) amarango@uoguelph.ca
*Nanoscale Engineering of the Structure and Functionality of Fat and Oleogel Systems*

Marie Hélène Morel (INRA IATE Montpellier, France) marie-helene.morel@inra.fr
*Tackling the question of specific interactions in a complex blend of proteins*

Michael Rappolt (U. Leeds, UK) m.rappolt@leeds.ac.uk
*Global Small-Angle X-ray Scattering Data Analysis of Triacylglycerols in the Molten State*

Christophe Schmitt (Nestlé Research Lausanne, Switzerland) christophe.schmitt@rdls.nestle.com
*Functional protein-based colloids for controlling structure and stability of food*

Marcus Stieger (Wageningen U., Netherlands) markus.stieger@wur.nl
*Food oral processing: From structure to behaviour, perception and pleasure*

Anna Stradner (U. Lund, Sweden) anna.stradner@fkem1.lu.se
*Protein Gels and Glasses*

Sylvie Turgeon (U. Laval, Canada) Sylvie.Turgeon@fsaa.ulaval.ca
*Protein-fiber mixed systems to innovate in food and culinary applications*

# Features of water/water emulsions stabilized by particles

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Emulsions are widely used in various applications like cosmetics, food... Indeed, mixing liquids or polymers is a well-known method to obtain new materials with combined and improved properties. The latter, are determined not only by those of the individual constituents, but also by the morphology that results from the combination of phase separation and interfacial properties especially when they are loaded with particles. Since the pioneering work of Pickering and Ramsden, it is well-known that particles can be very efficient stabilizers of emulsions, blends, and foams. Even centimetre size droplets can be stabilized by an adsorbed particle layer, which shows that the underlying stabilizing mechanism differs between systems stabilized with relatively large particles and with molecular surfactants. This talk will review interesting features of these particle-stabilized, so-called Pickering, emulsions by showing their structural and rheological properties. In particular water/water emulsions can be stabilized by particles and form a new class of stable emulsions making them potential candidates for food products.

# Assembly of plant storage proteins: role of intrinsic disorder and charge anisotropy.

Adeline Boire[1], Line Sahli[1], Chloé Amine[1], William Nicholas Ainis[2], Véronique Solé-Jamault[1] , Saïd Bouhallab[3] and Denis Renard[1]

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Increasing plant protein content in human diet constitutes a world challenge to meet protein needs of the growing world population. However, the assembly properties of such proteins are poorly understood as compared to their dietary animal counterparts. This limits their use as ingredients in food matrices. Most of plant proteins are storage proteins which are synthesized in seed and have to be efficiently stored and dehydrated during seed development. The overall objective of our research activities is to investigate the driving force of plant storage proteins assembly and the influence of their primary role of storage on their structure and functionality. Through this talk, we will first show using computational predictors that amino-acid sequences of plant proteins are predicted to be more disordered than globular animal proteins such as whey or egg proteins. Looking in more details in plant protein sequences reveals that most of them contain low complexity regions comprising polar and/or charged amino acids which are mostly predicted disordered. Then, we will discuss how protein flexibility as well as charge anisotropy can affect the assembly of protein-polysaccharide and protein-protein. We will compare two globular proteins: lysozyme, an egg-white protein, and napin, a rapeseed protein. Lysozyme and napin are very similar in terms of molecular weight and charge density but differ in their surface charge distribution as well as in their intrinsic flexibility. Finally, we will discuss how the use of model polypeptides can help to unravel the role of intrinsic disorder in plant protein self-assembly.

# Oleogels in complex composite samples

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Sitosterol and oryzanol self-assemble to form very firm gels in a range of organic solvents. [1] Unfortunately, due to the formation of sitosterol hydrate crystals, these gels are unstable in the presence of water, prohibiting the dispersal of water droplets throughout the gel matrix. We demonstrate that by using glycerol as the polar phase rather than water, droplets may be dispersed throughout the oil phase without disrupting the self-assembly of the gel.[2] As increasing volumes of water are added to the glycerol, the $G_0$ values decrease. This can be correlated to both a drop in water activity, and also the stability of the fibrils in the presence of glycerol compared to water, as elucidated by molecular dynamics simulations. At high glycerol loadings, multiple emulsions are observed to form.

We further demonstrate that by mixing the phytosterol-ester oryzanol with lecithin in an organic solvent, both components may be dispersed at much higher concentrations than they may be individually. [3] Dynamic light scattering and molecular dynamics simulations show that the mechanism for this is the formation of mixed micelles. Infrared spectroscopy and simulations suggest that these micelles are formed due in part to hydrogen bonding of the phosphate of the lecithin head-group, and the phenol group of the oryzanol. Rheology shows that by mixing these materials at an equimolar ratio, highly viscous suspensions are created. Furthermore, by adding water to these samples, a solid-like gel may be formed which offers mechanical properties close to those desired for a margarine type spread, whilst still solubilizing the oryzanol.

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# Structure and Dynamics of Polymer Composites and Gels: A Simulation Perspective

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Polymers or biopolymers are not only present in daily-life materials such as food, packaging or paints, but also in living organisms (plant cell wall, cytoplasm, extracellular matrix). The mechanical properties of these materials are strongly influenced by the structure and the dynamics of the polymers they are made of. In this context large-scale numerical simulations of the behaviour of the polymers can give insight into their collective properties at the nanoscopic scale and hence help to decipher the influence of the latter on the macroscopic properties of materials.

In this presentation we introduce the use of simulations of polymer systems at a coarse-grained level, and give an overview of the structural and dynamical properties which can be computed from this kind of approach, and discuss how they can be related to the macroscopic properties.

This is illustrated on two systems. The first one deals with nanoparticle-polymer composites: The simulations help to reveal the influence of nanoparticle size and volume fraction on the structure and dynamics of the polymers [1]. In the second example we consider a polymer solution which turns into a polymer gel due to the action of mobile catalysts and we show the implications of this process on the structuring of the resulting gel and on the time scales relevant to this sol-gel transition [2].

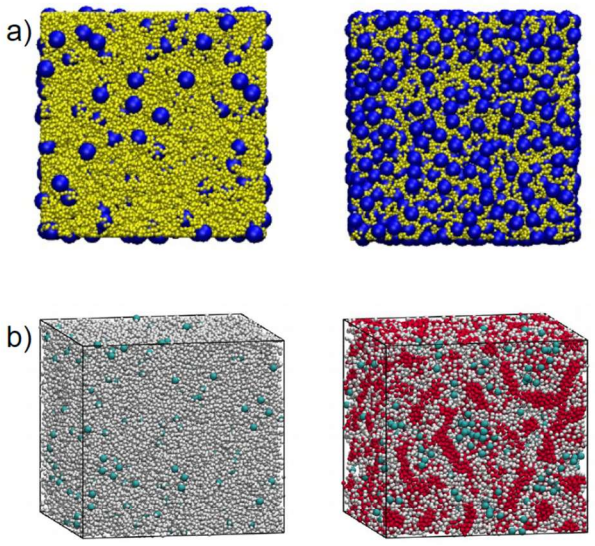


***Figure 1: a) Polymers (chains of yellow monomers) and nanoparticles (blue) at low (left) and high (right) nanoparticle volume fractions [1]; b) A solution of polymers (left) transforms into a polymer gel (right) due to the conversion by catalysts (blue) of repulsive monomers (white) into attractive monomers (red) [2].***

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# Recent developments in the field of edible double emulsions

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Water-in-Oil-in-Water ($W_1/O/W_2$) emulsions are made of oil globules (O) dispersed in an aqueous phase ($W_2$), with the globules themselves containing aqueous droplets ($W_1$). Generally, their stability is ensured by two surface-active species of opposite solubility (oil-soluble and water-soluble). As food products, these materials have many technological assets. Due to their compartmented structure, they can be used to encapsulate active species in the inner droplets and to control their delivery towards the external phase. They may also allow reducing the caloric intake without compromising taste. Fat in partially replaced by an aqueous phase, while tricking our tongue into thinking we are still eating a product with a full fat, creamy flavor. Despite these advantages, only a few commercial products based on double emulsions have been developed so far. The main difficulty with double emulsions is the mastering of their complex kinetic evolution. This complexity is naturally arising from their internal dynamics which are due to the liquid state of the components. However, their behavior is now quite well understood and significant advances has been made to improve their formulation and functional properties. Once fabricated they can become trapped in deep metastable states, allowing storage for several months with minimal leakage of the encapsulated species. Because they are made of soft matter, essentially liquids, there are many possible strategies to disassemble the comparted structure and to trigger delivery on demand.

The purpose of this lecture is to emphasize recent developments. This will be illustrated by two examples:

- A gelation process based on the osmotically driven water flux between the two aqueous compartments of double emulsions [1]. We first prepare fluid water-in-oil-in-water ($W_1/O/W_2$) double emulsions whose external aqueous phase contains hydrocolloids and/or proteins at moderate concentration. The initial osmotic pressure in the innermost droplets is considerably larger than that in the external phase. An inward water transfer thus occurs in order to restore osmotic equilibrium. In the initial state, the globules are large and so the transfer is slow because of the limited exchange surface area. The emulsions are then submitted to a short and intense shear that provokes globule breakup, in order to increase the rate of water diffusion. As a consequence, the initially fluid materials undergo a sudden rheological transition. During that process, the hydrocolloids and/or proteins are concentrated in the continuous phase until a point that a gel is formed. The proposed approach demonstrates a simple, yet versatile and adaptable solution for making texturized emulsions with reduced fat content and limited amount of hydrocolloids/proteins.
- The design double emulsions devoid of lipophilic surfactant, based on the use of a crystallizable oil and proteins. Simple $W_1/O$ emulsions stabilized solely by fat crystals are first prepared by dispersing the $W_1$ aqueous phase in a surfactant-less fat phase at a temperature above its melting range, followed by cooling down to trigger bulk fat crystallization. The resulting $W_1/O$ emulsions are arrested systems that are stable against gravitational and colloidal instabilities upon storage. The primary emulsions are in turn dispersed in a highly viscous external aqueous phase containing proteins to obtain $W_1/O/W_2$ emulsions. The resulting materials have enhanced properties compared to conventional double emulsions including i) very slow passive delivery of the encapsulated species, ii) resistance to osmotic stress, iii) resistance to coalescence, and iv) thermo-responsiveness as the double globules could release the inner droplets' content upon warming. We generalize the concept to the preparation of air-in-oil-in-water multiple emulsions.

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# Nanoscale Engineering of the Structure and Functionality of Fat and Oleogel Systems

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Fats and oils are extremely useful natural products which are widely used in foods, cosmetics and industrial applications. As the concern for the environment and health grows, consumers are demanding more natural, green and sustainable materials in everyday consumer products. Fats and oils are complex multicomponent mixtures of triacylglycerol molecular species. The nature of these molecular species are a function of both fatty acid composition and distribution within the TAG molecule. The purpose of this talk is to discuss the structure of fats and oils, from constituent TAG molecules to the crystals they form. Upon crystallization, TAG molecules form lamellae (shown in blue), which stack to form a highly asymmetric nanoplatelet with about ~8 TAG lamella (Figure 1)[1]. We have been able to engineer the thickness of these nanoplatelets by using specific surfactants and affecting the surface energy and surface nucleation behavior of TAGs on these crystalline nanoplatelets[2]. These nanoplatelets rapidly aggregate into colloidal structures of differing morphologies and size depending on external fields and concentration, forming networks which are responsible for the binding of oil, water vapour barrier properties, and mechanical properties of the fat. Our work has focused on developing and understanding of the functionality of fats from a structural perspective. Early work focused on the quantification of structure using small deformation rheological techniques. More recent work has focused on the use of scattering methods, in particular Ultra-Small Angle X-ray Scattering at synchrotron facilities to quantify atomic scale structure to mesoscale structure simulataneously, in a non-destructive fashion[3]. Increasing public concerns over excessive saturated and *trans* fat intake from manufactured food products has lead to the search for alternative strategies to structure liquid oils into semisolid fats without addition of large amounts of unhealthy trans and saturated fats. Surfactant-like small molecules have been shown to self-assemble into long fibrils, effectively causing oil gelation at concentrations as low as 0.5%. Phytosterols, ceramides, waxes and 12-hydroxystearic acid have been shown to be effective organogelators. Liquid oils can also be structured by microencapsulation within multilamellar vesicles, with walls composed of monoglyceride hydrates in the alpha-gel state. The surface potential of these monoglyceride vesicles is then adjusted so as to maximize inter-vesicle interactions and the formation of a cellular solid with oil-filled cells. These monoglyceride gels have recently been proven to have excellent functional characteristics in baking applications as well as for omega-3 oil stabilization. High-molecular weight polymers such as ethylcellulose have also been successfully used by our group to gel oil in the absence of water. This development of a polymer-stabilized organogel is very promising since these polymers are widely available and are food-grade. The development of a new way to make fat exploiting the self-assembly properties of food-grade molecules is at hand. A final perspective of future challenges will be offered.

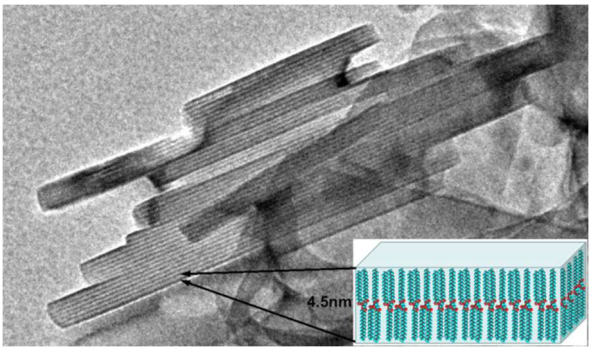


Figure: Cross-sectional view of a TAG nanoplatelet showing epitaxial molecular packing in the [001] direction

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# Tackling the question of specific interactions in a complex blend of proteins

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Natural protein sources often display a huge complexity, being composed of a blend of polypeptides of various molecular weight, pHi and charge density. Gluten, the proteins extracted from wheat flour is one of such. Gluten is widely used for its viscoelastic properties as an improver of cereal products (bread, pastry, etc.). It is composed of two classes of proteins, named gliadin and glutenin, similar in their amounts in glutamine (30%) and proline (10%). The more than 25 different polypeptides belonging to the gliadin class are hard to fractionate into individual components because of high redundancy in the primary sequences. Glutenin are in the form of polymers made from several distinct polypeptides concatenated through inter-chain disulfide bonds. Their molecular weights are evenly distributed from 100 kg/mol to 7,000 kg/mol.

While it is well established that gliadin confers viscosity to gluten whereas glutenin polymers are at the origin of its elastic resistance, the interactions existing between both classes of gluten protein remain unknown. We previously showed by SLS and multi-angle DLS that gluten proteins suspended in ethanol/water (50/50, v/v), a theta solvent, includes large proteins assemblies (26,000 kg/mol, Rh 100-128 nm) displaying an internal dynamic. To get a better insight of the composition of those assemblies, we combined biochemical and physicochemical approaches. On the one hand, gluten proteins suspended in ethanol/water were fractionated by Asymmetrical- Flow-Field-Flow Fractionation (A4F) coupled to UV, SLS and QELS detectors. On the other hand, gluten proteins were partitioned by liquid-phase decomposition in respect with temperature. Protein composition of partitioned phases and eluting fractions recovered from A4F were characterized by size-exclusion chromatography. Consistent results were obtained demonstrating a specific interaction between omega-gliadin and glutenin polymers. The work illustrates how a detailed analysis of the phase behavior of a complex blend of proteins may reveal their supramolecular assembly states.

# Global Small-Angle X-ray Scattering Data Analysis of Triacylglycerols in the Molten State

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The study of triacylglycerols (TAGs) in their molten state is of fundamental importance for a deeper understanding of TAG-crystallization processes, being highly relevant for both, manufacturing and medical applications. Whilst different models have been proposed to explain the nanostructured nature of the fluid state of TAGs, none of them are fully satisfactory. In this paper, we propose a new model consisting of positionally uncorrelated lamellar TAG-assemblies embedded in an isotropic medium, that assist as pre-nucleating structures. This model was validated by applying a novel global fitting method, resulting in excellent agreement with the small angle X-ray scattering data. Deeper analysis of the scattering patterns at different temperatures, both in cooling and heating direction, allowed us further to detect crystalline traces of TAGs even after heating to 40 °C, and record on cooling the onset of crystallization at 30-25 °C. The application of the presented novel model not only explains the outstandingly structured fluid of molten TAGs, but also lays the basis for analysing first crystallization steps in greater detail, which is outlined in our follow-up study 'Global Small-Angle X-ray Scattering Data Analysis of Triacylglycerols in the α-Phase (Part II)' [1].

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# Functional protein-based colloids for controlling structure and stability of food

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Native globular whey proteins are sensitive to heat treatment above their denaturation temperature. Heating induces molecular changes, leading to an activated non-native protein form that is able to self-aggregate. Depending on the processing conditions (pH, ionic strength, protein concentration, heating temperature and heating time), various types of protein aggregates are obtained.[1]

In this talk, we will describe whey protein microgels (WPM), a peculiar type of aggregate obtained upon heat treatment slightly above the IEP of whey proteins.[2] The WPM are characterized by fairly spherical shape, narrow polydispersity, high surface charge density and particle size ranging from 200 to 400 nm. These features confer milky appearance and colloidal stability upon storage to WPM dispersions. The internal structure of WPM is maintained by hydrophobic/hydrogen bonds and disulfide bridges. This allows high physical and chemical stability of these new ingredients in various subsequent food processes.[3]

We will show how WPM can be concentrated using microfiltration in order to reach high protein contents while keeping the system liquid. The thermal stability of WPM in presence of salts as well as their use as whitening agent in low fat coffee creamers will be presented.[4] Whey protein microgels can also be used to stabilized Pickering-type of emulsions close to their IEP.[5] Finally, we will discuss the use of these colloids as texture modulators in whey protein acid gels.[6]

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# Food oral processing: From structure to behaviour, perception and pleasure

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Food oral processing as the bridge between transformation of food structure during consumption, eating behaviour, sensory perception and food acceptability has gained enormous interest in the last decades. An overview of the interplay between food structure, oral processing and eating behaviour, sensory perception and hedonic evaluation of foods is provided comparing different consumer groups. To design foods which are targeted to different consumer groups, food structures and its oral breakdown properties should be matched with preferred behaviour to optimize pleasure upon consumption.

It is demonstrated that food oral processing depends on both food properties and consumer characteristics. Consumers strongly adapt oral processing behaviour with respect to bite size, consumption time, and eating rate to rheological and mechanical properties of liquid, semi-solid and solid foods. Liking and familiarity influence oral processing behaviour, but by a considerable lower degree than rheological and mechanical properties. Correlations between instrumental texture properties of solid foods and oral processing behaviour provide guidance on parameters that are likely to produce ‘faster’ and ‘slower’ versions of foods. This demonstrates how food texture modifications can be applied to moderate eating rate and energy intake.

It is shown how age, gender, and ethnicity affect oral processing behaviour of liquid, semi-solid and solid foods differently. Consumer groups adapt eating rate in different ways by modifying bite size, consumption time or both. Parameters describing oral physiology explain differences in oral processing behaviour between groups only to a limited extend. Other oral physiological and cultural factors might contribute more to differences in oral processing behaviour between groups. While age, gender and ethnicity can influence oral behaviour, bolus properties do not necessarily differ between groups suggesting that although oral behaviour may vary somewhat between groups, similar bolus properties can be reached. However, large differences in oral behaviour between groups (fast and slow eaters) lead to considerable differences in bolus properties leading to differences in sensory perception and food intake.

Many foods are composed of multiple components with considerably different mechanical properties on micro- or macroscopic length scales, for example breads with toppings or soups with vegetable pieces. Mechanical contrast between food components can lead to contrasting texture sensations, which can enhance palatability and reduce energy intake. The influence of mechanical contrast caused by inhomogeneity in food structure at different length scales on oral processing behaviour, sensory perception and palatability is discussed. Combining food components with contrasting mechanical properties at different length scales allows to control oral processing behaviour, bolus properties and determines texture perception and palatability.

# Protein Gels and Glasses

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Gels and glasses represent important soft matter classes in today's food science and technology. Currently the vast majority of food gels is based on energy-intensive processes using heat and pressure treatments. On the other hand, colloid scientists have studied various liquid-solid transitions such as dynamical arrest, jamming and gelation intensively during the last decade, and the thus gained insight could potentially have a considerable importance for food science and the possibility to create food gels through different novel routes [1]. Here we will present first a short summary of our current understanding of colloidal gels and glasses, and introduce key concepts such as arrested spinodal decomposition or cluster formation and arrest in colloids with competing attractive and repulsive interactions. We will then demonstrate that such arrest scenarios can also be found for proteins and food colloids, and show how we can use a combination of scattering methods [1-6] (small-angle neutron and x-ray scattering, diffusing wave spectroscopy), confocal microscopy [1,5,6] and micro- [7] and macrorheology [1,5,6] to characterize the structural and dynamic properties of these complex liquids and solids at all relevant length and time scales.

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# Protein-fiber mixed systems to innovate in food and culinary applications

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Protein and fiber are two food constituents of growing interest to health-conscious consumers. In recent years, the molecular interactions between these two macromolecules and the behavior of mixed systems have received increasing research attention in order to design food product with extended applications. Indeed, protein and some constituents of fiber, especially pectin, can form complexes at acidic pH, mostly through electrostatic interactions between these two oppositely charged macromolecules. These complexes could improve the functionality of foods. However, studies on these complexes in real food conditions are missing and their utilization in culinary applications is inexistent. Approaches allowing complex formation using purified and crude fiber sources to develop functional ingredients will be presented. First, water (WAC) and oil (OAC) absorption capacity of plant proteins (soy, pea) and sugar beet pectin complexes were evaluated. The effect on WAC is source dependent as complexes produced with one soy protein source showed a 24% increase (ratio 1:1) in comparison to individual biopolymers while the pea protein showed a reduction (25%). OAC of individual ingredients is increased (from 36-60%) after complex formation. Secondly, complex formation between proteins and blueberry puree was studied. After the addition of a whey protein isolate (WPI) into purees, the soluble pectin and protein contents and the viscosity of the resulting mixtures were determined. The decrease in the solubility of pectin and proteins showed the formation of protein-pectin complexes by electrostatic interactions at pH 3.5, contributing to increase the mixture viscosity. This mixture was also incorporated in a smoothie. The interactions between blueberry pectin of a puree and whey proteins allowed to design a novel functional ingredient that may be used to formulate high-fiber and high-protein beverages. Finally, the potential of using vegetable puree and some fractions for culinary innovations will be presented using parsnip as a model. The intelligent association between protein and fiber offer many new opportunities to add functional and nutritional values into processed foods and culinary applications.

# Edible Soft Matter 17th-19th April 2019 – Le Mans

## Oral Contributions :

| | |
|---|---|
| Pickering emulsions stabilized by colloidal lipid particles: Potential for high chemical stability? | **Anja Schröder** |
| Synergistic stabilisation of emulsions by blends of dairy and plant proteins: Contribution of the interfacial composition | **Emma B. A. Hinderink** |
| Nonlinear surface rheology and interfacial microstructure imaging of WPI particles and their constituents | **Jack Yang** |
| Acid-induced gel properties of an alginate-in-whey protein emulsion | **Ashkan Madadlou** |
| Interfacial behaviour of plant proteins | **Amélie Banc** |
| Viscosity of artificial chewed boluses of cereal foods | **Florence Gibouin** |
| Microtechnology used as a tool in the development of novel food products | **Karin Schroen** |
| New approach for the characterisation of dairy protein foams stability | **Valérie Lechevalier** |
| Influence of kinetic and shear rate on whey protein aggregates structure: a small-angle x-ray scattering study | **Alice Vilote** |
| Understanding of structural heterogeneities in the starch hydrogels | **Trey Koev** |
| Model of the swelling of protein gels in simulated gastric juice | **Ruud van der Sman** |
| Dry heating of beta lactoglobulin generates microparticles: role of pH and lactose | **Marie Hélène Famelart** |
| Heat-induced gelation of mixtures of casein micelles with whey protein aggregates | **Anna Kharlamova** |
| Gelation kinetics of sodium caseinate induced by continuous acidification | **Thomas Gibaud** |
| Stable oil-in-water emulsions using an hydrophobically modified xanthan | **Frédéric Renou** |
| Gelation of mixture of iota and kappa carrageenan | **Viet TNT Bui** |

# Pickering emulsions stabilized by colloidal lipid particles: Potential for high chemical stability?

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Many food, pharmaceutical, cosmetic, and agrochemical products exist as dispersions of immiscible liquids (typically, oil and water), i.e., are emulsions. These emulsion products may undergo a range of physical and chemical destabilization events over their production, storage and end-use. Pickering emulsions have shown to provide definite advantages with respect to physical stability of emulsions compared to conventional emulsifiers, and are emerging in the food area. In addition to controlling the physical stability of food emulsions, preventing adverse chemical degradation is also a challenge, and in particular, oxidation of the unsaturated lipids. Often, lipid oxidation in emulsions is tentatively prevented by using oil-soluble antioxidants (e.g., tocopherols). These components are highly hydrophobic and therefore located inside the oil droplets. However, lipid oxidation is initiated at the oil-water interface, so the efficiency of these antioxidants is far from optimal and could be enhanced when present at the interface [1]. A way to achieve this could be to entrap antioxidants within Pickering particles, thus locating them at the droplet surface. In the present work, we study lipid oxidation in two Pickering emulsions stabilized by colloidal lipid particles (CLPs) [2], with the exact same composition, but with a different physical location of the antioxidant α-tocopherol: either within the CLPs (Figure 1, left), or in the core of the oil droplets (Figure 1, right). Pickering emulsions containing the antioxidant in the CLPs oxidize slower and to a lesser extent compared to Pickering emulsions containing the antioxidant in the core of the droplet [3]. Although, according to our initial hypothesis, the interfacial localization of CLP-entrapped antioxidant may explain these results, other possible mechanisms are currently under consideration, such as the possibility that antioxidant-loaded CLPs would behave as an antioxidant reservoir with progressive release in time. This work opens up new perspectives to develop physically and chemically stable food emulsions with high levels of unsaturated lipids, and optimized levels of antioxidants.

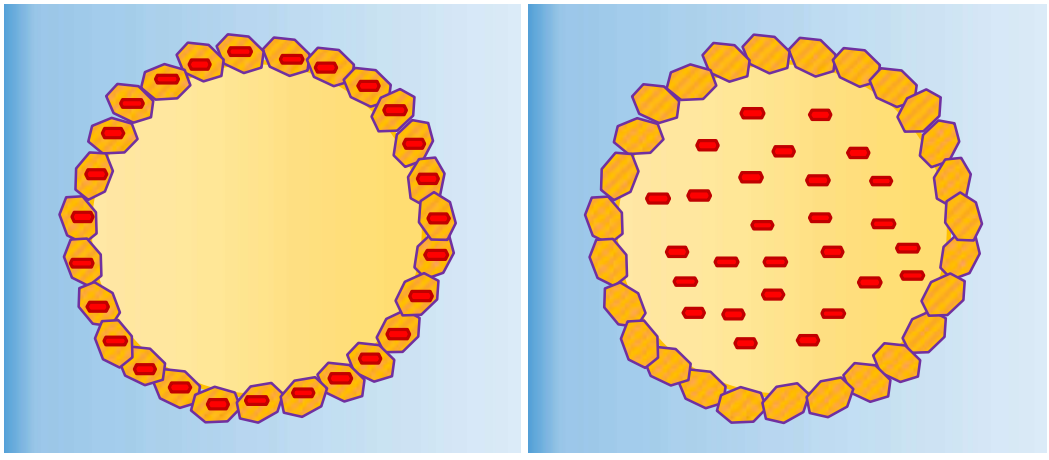

***Figure 1: Schematic representation of CLP-stabilized Pickering oil-in-water emulsions: (left) with α-tocopherol incorporated in the particles and (right) with α-tocopherol in the liquid oil droplets.***

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# Synergistic stabilisation of emulsions by blends of dairy and plant proteins: Contribution of the interfacial composition

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In the food industry, dairy proteins are often used to formulate emulsions. These animal-derived proteins have a high environmental impact and therefore there is a drive to replace them by plant proteins. It is challenging to fully replace dairy proteins by plant proteins in food emulsions, as this will affect the physicochemical stability of the emulsions and the final product quality (e.g., nutritional value and taste). Alternatively, a blend of dairy and plant proteins can be used to improve sustainability, while not compromising on functionality and product quality.

In the present project, the use of blends of pea protein isolate (PPI) with whey protein isolate (WPI) or sodium caseinate (SC) to physically stabilise emulsions has been investigated. Emulsion stability, surface load and interfacial compositions were determined and compared to those of individual protein-stabilised emulsions. The $d_{3,2}$ and surface load measured over a concentration range (0.2-1.6 wt.% protein) were the lowest for SC- and WPI-stabilised emulsions, and the highest for PPI-stabilised emulsions, whereas emulsions stabilised by the blends (1:1 ratio) had intermediate $d_{3,2}$ values and surface loads. Although individual PPI and SC-stabilised emulsions showed some physical destabilisation over 14 days of storage, the WPI-PPI or SC-PPI blends formed stable emulsion systems, suggesting synergistic effects. In the case of the blends, both dairy proteins and plant protein adsorbed at the oil-water interface, but compositional rearrangements at the interface were noticed over three days. More specifically, whey proteins were able to displace pea proteins from the interface, which were themselves able to displace SC. However, such a displacement was possible only when the displacing protein was present in sufficient amount in the system. These effects are important to understand the stabilisation mechanisms of protein blend-stabilised emulsions, and to propose design rules for related applications.

Keywords: Interfacial displacement, protein mixtures, dairy protein, plant protein, emulsion stability, SDS-PAGE

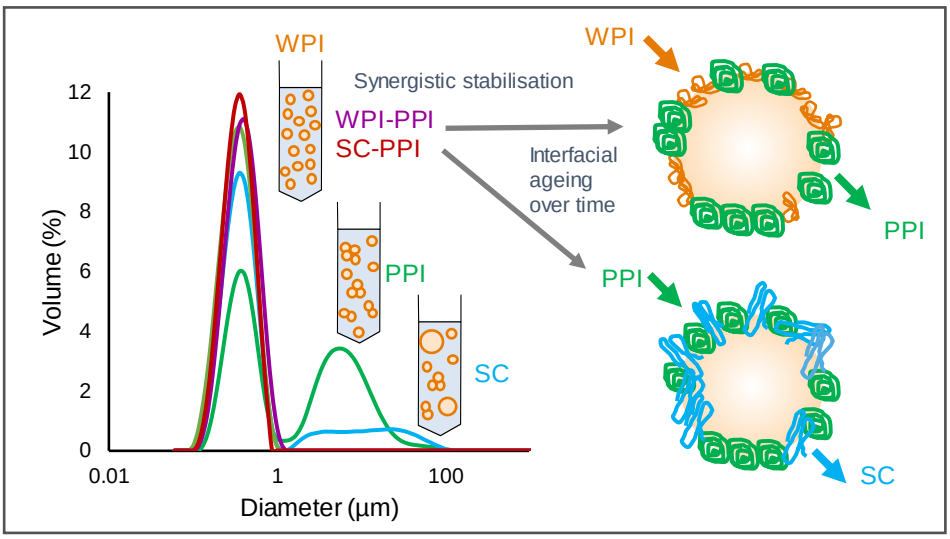


***Figure X: Graphical abstract***

# Nonlinear surface rheology and interfacial microstructure imaging of WPI particles and their constituents

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KEYWORDS: Protein Pickering stabilizer, air/water interface, microstructure, surface rheology, Lissajous plots, atomic force microscopy

In recent years, food-grade Pickering stabilizers have gained great interest, because of their ability to form very stable emulsions and foams. Food-grade Pickering stabilizers are often produced by cross-linking proteins, which typically results in a mixture of cross-linked particles and non-cross-linked proteins. This smaller material could potentially contribute to the interfacial behaviour of the total mixture. The aim of this work was to understand the interfacial properties of air/water interfaces stabilized by whey protein isolate (WPI) particle suspensions. The particles were produced by cold-induced gelation of WPI aggregates, using calcium nanocrystals. To understand the interfacial properties of the total mixture, we have studied the whole hierarchy of structures, including native WPI, WPI aggregates, and WPI particles by combining surface dilatational and shear rheology, and microstructure imaging using atomic force microscopy (AFM).

Air-water interfaces were subjected to large amplitude oscillatory dilatation (LAOD) and shear (LAOS) using a drop tensiometer and a double wall ring (DWR) geometry coupled to a stress-controlled rheometer. The non-linear responses of the LAOD and LAOS experiments were analysed using Lissajous plots of stress versus deformation. Lissajous plots of native WPI- and aggregates-stabilized interfaces in LAOD and LAOS showed a rheological behaviour of a viscoelastic solid, while interfaces stabilized by the particles tended to have a weaker and more fluid-like behaviour.

The microstructure of the interface was analysed by imaging Langmuir-Blodgett films of the three protein systems using AFM. For the WPI interface, we found a highly heterogeneous structure in which the proteins form a dense clustered network. For the WPI particles we observed that they are present in the interfacial film, but are scattered throughout the film, separated by large areas, where smaller material is present. This suggests the presence of smaller material between the particles and also explains the weak layer found in the surface rheology experiments. The smaller material present in this WPI particle suspensions is surface active and plays an important role in interface stabilization, and could also influence the macroscopic properties of foams and emulsions. Based on these observations the WPI particle system does not behave as a classical Pickering system, but instead forms mixed interfaces consisting of particles and non-cross linked proteins.

# Acid-induced gel properties of an alginate-in-whey protein emulsion

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Water-in-water (W/W) or aqueous two-phase system (ATPS) emulsions are finding increasing applications in diverse fields of technology, for instance as protocells [1], and reactors for the synthesis of hydrogel particles [2], and enzyme-laden microgels [3]. Successful ATPS emulsification depends on thermodynamic incompatibility between two (bio)polymers, causing segregative phase separation [4]. Herein, we demonstrate that hydrophobization of whey proteins, by grafting acetyl moieties and heat denaturation, makes the proteins immiscible with a co-charged polysaccharide solution (alginate). Addition of erythritol, which is a low-calorie and zero-glycemic sugar alcohol, to the hydrophobized protein solution, enhanced emulsification and increased the stability of the resulting emulsion. Subsequently, the acid-induced gel properties of the emulsion was studied by dynamic rheometry and confocal microscopy.
Erythritol addition reduced the surface tension (at the air-water interface) of the hydrophobized protein solution, enhancing the incompatibility between protein and alginate. It also postponed the gelation time of the hydrophobized protein solution and resulted in formation of a softer gel. Confocal imaging of the emulsion gel confirmed micro-phase separation of alginate and the droplets aggregation in the protein-rich matrix.

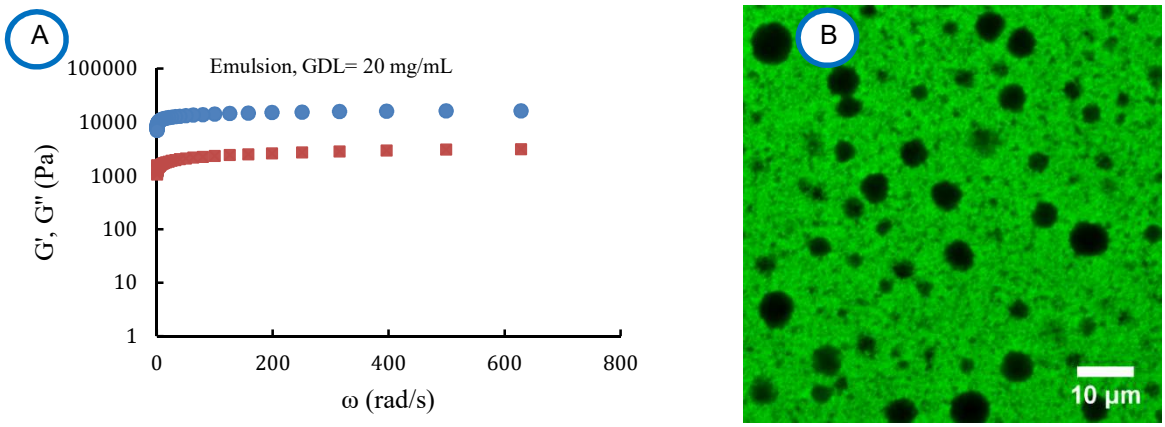


Fig. 1. A: G', storage (circles) and G'', loss (cubes) moduli of the alginate-in-whey protein emulsion gel measured by a frequency sweep test; and B: a typical CLSM image of the emulsion gel.

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# Interfacial behaviour of plant proteins

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Challenges of public health and sustainable development require replacing in food products animal proteins by plant proteins. In this optics, it is crucial to understand the structure and kinetic of formation of a film of plant proteins in order to improve the control of emulsions and foams stabilized by these proteins.
In this talk we will present experimental results on the behaviour interfacial properties of wheat gluten, sunflower and rapeseed proteins at liquid interfaces. Thanks to a combination of tensiometry, dilatational rheology and ellipsometry, rational physical pictures of the dynamics of the interfacial properties are achieved, for the various proteins and at both air/water and oil/water interfaces.
For gluten proteins, a time-concentration superposition of the data is evidenced whatever the subphase concentration, which reveals that the kinetics of protein adsorption at the interface is dominated by bulk diffusion. We propose a consistent physical picture of the multistep diffusion-controlled irreversible adsorption of the gliadin proteins at an air/water interface, and evidence surface-induced conformational changes of the proteins followed by film gelation [1].
Sunflower and rapeseed proteins by contrast do not reorganize once adsorbed at an interface and display a simpler dynamics of film formation. In addition the failure at high concentration of the time-concentration superposition of the tensiometry and viscoelastic data strongly suggest a surface-induced aggregation process, which we confirm with turbidity measurements.
By quantitatively comparing the surface pressure dependence viscoelasticity of the various interfaces, we hightlight the crucial role on the behavior of plant proteins at liquid interfaces of the solvent quality and of the protein softness, that is discussed in regard to the protein structure.

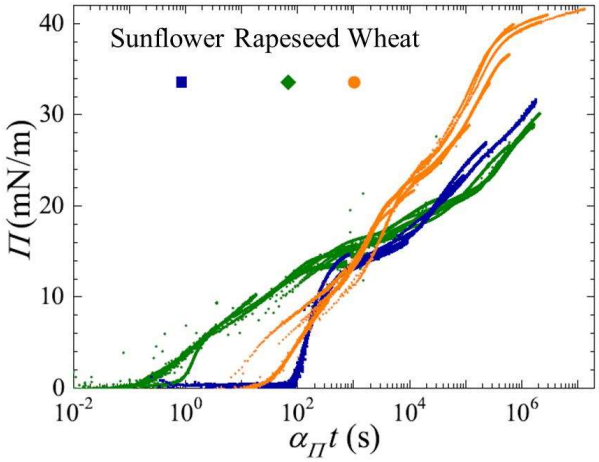


Figure 1: Air-water interface surface pressure master curves obtained for solutions of sunflower, rapeseed and wheat proteins comprised between $10^{-2}$ and 10g/L.

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# Viscosity of artificial chewed boluses of cereal foods

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Food Oral Processing (FOP) is a key step for foods assimilation and the benefit of their nutrient properties, especially for elderly whom oral physiology is altered. The main objective of this process is to form a food bolus that can be swallowed safely. Nevertheless, most of the studies about relationships between FOP, oral physiology and food bolus properties focus on particle size and dental status, saliva is only partly considered. However, for cereal products, food bolus viscosity is a function of the added saliva [1], which evidences the interaction between food and saliva. Our aim is to establish a model to determine a coefficient that characterizes this interaction.

To do so, we first study sponge cakes, one sample is standard and the other one is enriched with pea isolates. Artificial boluses composed of crushed sponge cake and a surrounding fluid, representative of saliva, are prepared. Four fluids are used: three of them are Newtonian, water and two Dextran solutions of viscosities 3mPa.s and 10mPa.s. The fourth fluid is shear thinning, composed of different salts and mucin distilled in water, as already used in different studies [2-4]. Viscosity measurements (shear and elongational) are realized using capillary rheometry, including Bagley's corrections. The shear viscosity of boluses follows a power law model from which the consistency K can be derived. A phenomenological model of the consistency is obtained (Figure 1): $K = K_0\, e^{-\alpha\, \Delta WC}$, where $\alpha$ is the interaction coefficient and $\Delta WC$ is the difference of water content between the food bolus and the sponge cake. Results also show that the viscosity plays a minor role, compared with its concentration. By varying properties of the surrounding fluid, the interaction between food and saliva can be assessed.

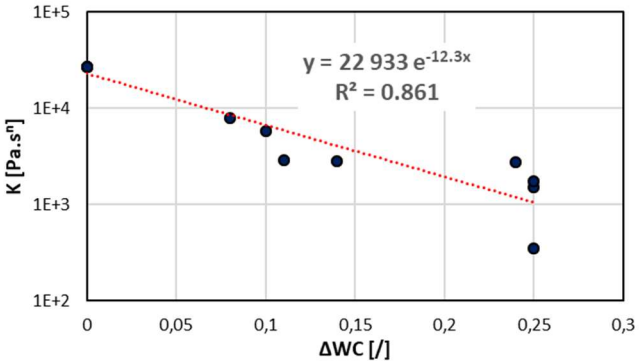


***Figure 1: Phenomenological model of the consistency for a standard sponge cake. Red line is a fit by an exponential function that gives the interaction coefficient: α = 12.3.***

This study is part of the project "**Mo**delling interactions of **Foo**ds with **SA**liva during oral processing and application to the design of cereal foods enriched with plant proteins (MoFooSA)" that has been supported by the Region Pays de Loire, via the RFI project "Food for tomorrow".

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# Microtechnology used as a tool in the development of novel food products

**Karin SCHROËN**

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In this presentation, I will take examples from the work done at the food micro-technology group of Wageningen University, and use them to illustrate how the insights can be used in mild separation technology, and in the production of novel foods.

Ingredients used in food production revolve around a limited amount of crops, and mostly only the fruits of these crops, whereas for example the leaves and stems etc. could also be used. In order to be flexible, separation technology is needed to fractionate the starting materials. Membrane separation will be highlighted using results obtained with miniaturised membranes that help us uncover underlying mechanisms at colloidal scale, which has led to various discoveries for efficient fractionation.

Besides, the functionality of the fractions is key for application. For example, whether animal based proteins can be replaced by their plant based counterparts is highly dependent on their surface activity. We have developed various microfluidic devices with which this can be monitored for small droplets and at short time scales. This allows screening, comparison of ingredients, and even establishing a link with more classic process technology, and also digestive functionality. Also here we started at the colloidal scale and used these insights to design products starting from nano- and micrometer scale.

# New approach for the characterisation of dairy protein foams stability

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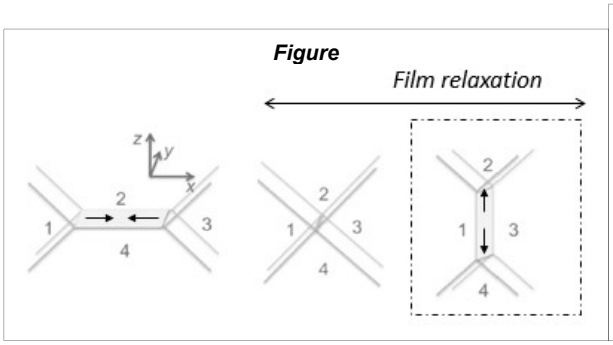
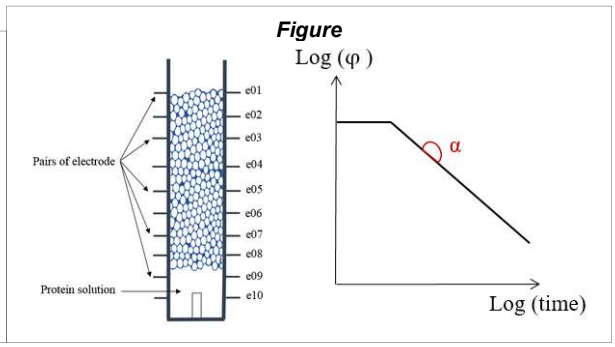
The main destabilisation processes in aqueous foams are liquid drainage, coalescence and disproportionation. In food sciences, the measurement of protein foam stability generally integrates all of them in a "global stability", and a challenge is to correlate the stability and rheology of foams to the properties of interfaces.

We adopted a multi-scale approach by combining the interfacial rheology of proteins adsorbed at the air–water interface, the dynamics of protein films after T1 topological rearrangements (Fig. 1), and macroscopic foam characterisations: the foam stability against drainage was evaluated by following the evolution of the liquid fraction as a function of time and height (Fig. 2) [1], and the foam complex modulus and yield stress were measured under oscillatory shear. We investigated the behaviour of dairy proteins (whey protein isolate and purified β-lactoglobulin), either in the native state or after modification by dry-heating and/or pH adjustment prior to dehydration.

Our results show that small-extent structural modifications of proteins have a dramatic impact on interfacial rheology, liquid film dynamics, foam stability and foam rheology.

This approach, correlating multiple investigation scales, sheds light on the contribution of the interfacial rheology to protein foam properties, in particular through the involvement of film relaxation dynamics.

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# Influence of kinetic and shear rate on whey protein aggregates structure: a small-angle x-ray scattering study

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Whey proteins are of interest because of their nutritional and functional properties in food application. Heat-induced aggregation coupled with process conditions of whey proteins gives them new functional properties that can be used to impart specific structural and physical properties of food products. Then, aggregation process needs to be well understood and controlled to design specific functional whey protein aggregates.

Most of previous studies has focused on the role of the physicochemical conditions on the structure and size of protein aggregates [1], whereas process parameters have not been clearly investigated. In this study we will study the role of process parameters, i.e. shear rate, heat treatment and time on the size and structure of protein aggregates to control the aggregation process.

However, the main difficulty to understand the respective role of each parameter is to separate the kinetics of denaturation and aggregation and the flow from the thermal history. In this study, we have developed a continuous process of aggregation at small-scale (<1 mm) to have laminar flow conditions for various shear rates and a fine control of the thermal history. Thermal and flow conditions can thus be controlled independently. This feature is clearly a novelty compared to previous studies [2] in which aggregation was limited by heat transfers. This small-scale continuous process allows us to vary, in one hand, the residence time and thus to establish the kinetics of aggregation, and in the other hand, the shear rate up to 500s-1.
This set-up has been used to test the role of several process parameters on the kinetics and structure of whey protein aggregates by small angle X-ray scattering (SAXS) techniques for given physicochemical conditions (pH and ionic strength) leading to sub-micrometric aggregates. We follow the kinetics of aggregation from the protein scale (few nanometres) to the aggregate scales (< 1 µm). Structure of whey protein aggregates larger than few micrometres are also investigated by quantitative fluorescent microscopy and image analysis methodology developed for this purpose.

We show that the kinetics leads to the formation of new aggregates and not to their enlargement. Secondly, we show that the flow process has a large impact on the size and structure of the aggregates: the size of the aggregates is increased by a factor 3 when comparing the ones obtained under static conditions and the ones obtained under flow, whereas their internal structure remains unchanged. The shear rate, on the other hand, leads to an increase of the size of the aggregates without increasing their density.

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# Understanding of structural heterogeneities in the starch hydrogels

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**Abstract**

As an easily accessible, renewable and environmentally friendly material, and a pivotal part of the human diet, starch holds great promise for a wide variety of structural, pharmaceutical and biomedical applications. Starch hydrogels are unique three-dimensional, semi-solid structures able to hold a large amount of water and other solvents with unique rheological, physicochemical and biochemical properties. As representatives of molecular gels, starch hydrogels simultaneously feature domains with highly distinct manner of organisation, packing and molecular mobility, which introduces considerable difficulties to their full experimental characterisation.

In this project, we have applied NMR methods specifically tailored to the identification of rigid and mobile components, such as $^{1}H$-$^{13}C$ CP and CPSP-MAS NMR[1–6], which are novel to the field of starch hydrogels. Hydrogel materials were produced by different hydrothermal treatment methods using five separate maize cultivars, featuring different levels of composite glucans, degree of modification and resistant starch character.

Our initial investigations resulted in the identification of previously unpublished distinct carbon sites exhibiting increased mobility in low amylose starch hydrogels, when compared to their high amylose counterparts. Data obtained from these investigations were cross-referenced with rheological and thermal analyses of the maize hydrogels. These findings were hypothesised to be a consequence of the predominantly linear structure of amylose, compared to its highly branched glucan analogue, facilitating inter-chain association during the period of gelatinisation.

We aim to use our findings for the development of previously unexplored starch hydrogel-based materials for applications in the pharmaceutical and biomedical sphere, as novel biocompatible prosthetic implants and “smart” drug delivery methods as targeted, stimuli-responsive and controlled drug release loading materials.

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# Model of the swelling of protein gels in simulated gastric juice

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Soy gels at different crosslink densities has been subjected to immersion in a simulated gastric juice. Via titration the pH of the juice is kept at pH=2 level. Due to strong buffering effect of the soy protein the pH inside the gel is only slowly changing. Soy protein is a polyelectrolyte gel, whose charge depends on pH due to dissociation of acidic and basic groups.

We have modelled the experiments via extending Flory-Rehner theory with Donnan-equilibrium, to account for the ionic contribution to the swelling pressure, cf.[1]. The swelling pressure is plugged into Darcy's law to describe swelling kinetics. Furthermore, the kinetics in the total of bound and free protons inside the gel has been modelled, taking into account diffusion of free protons, convection of protons due to swelling, and the buffering capacity of the soy gel.

The experiment and model show a rich dynamics of the gel, which shows shrinkage after an initial swelling stage. This indicate also a rich dynamics inside in-vivo gastric environment, where also the action of pepsin enzyme has to be added to the system. Its activity is strongly dependent on pH, and its diffusion is modulated by the mesh width of the shrinking/swelling gel.

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# Dry heating of β-lactoglobulin generates microparticles: role of pH and lactose

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Heat treatment of whey proteins is known to increase the functionality of these high nutritional proteins such as their viscosity or gelling properties [1]. While heating a whey protein solution is a widespread practice, heating them as a powder, or dry heating, is a less known process. We have experimented the dry heating at 100°C of whey proteins with traces of lactose. Dry heating of a whey protein powder at pH 9.5 has been shown to generate microparticles [2,3]. Is has been demonstrated that crosslinks of whey proteins in the powder during its dry heating make the powder partially insoluble, leading to microparticles having a shape close to that of the powder. Due to the porous structure of the powder, the microparticles formed by dry heating are able to entrap a huge amount of water (20-40 g water/g microparticle), with a yield of formation > 0.5 g microparticle/g of powder. They could be used as a 100% dairy ingredient in food products to increase their viscosity

With the aim to understand the process of formation of these microparticles, experiments were performed with pure β-lactoglobulin (β-Lg) in solution stored at 4°C with or without lactose, at pH 9.5 or 6.5, then freeze-dried and finally dry heated.

Analyses were performed at 3 steps, during storage of the β-Lg solution before its drying, after its drying and after dry heating of the β-Lg powder. Residual native proteins and secondary structures of proteins, the browning of powders, the yield of conversion of β-Lg into microparticles and their ability to entrap water were measured along the process.

In conclusion, the alkaline pH and the presence of lactose are crucial for the production of microparticles, but these two factors act at different steps of the process. The alkaline pH is only required during the storage of the β-Lg solution before drying and hardly plays a role during dry heating, while the presence of lactose is only crucial during the dry heating and is useless during the storage of β-Lg solution.

These results help understanding the formation of microparticles by dry heating.

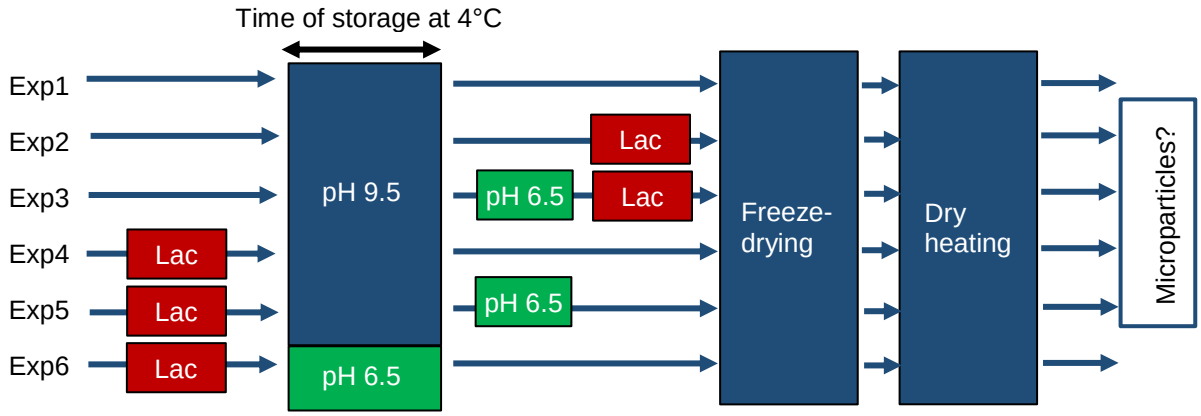


***Figure 1: experiment plan***

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# Heat-induced gelation of mixtures of casein micelles with whey protein aggregates

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In this study we explore the functional properties of whey proteins found in the milk serum. Whey proteins are well known for their texturizing properties such as gelation, stabilization of foams and emulsions, film formation (Nicolai, Britten, and Schmitt, 2011). Current consumer demand for heathier, simpler ingredients in foods produced the terms such as “clean label” and “clean eating”. Whey proteins can be considered as an excellent “clean label” alternative to traditional E-number texturizing ingredients used in products, such as gelatine or modified starches, because they are percieved as healthy by most consumers and do not require approval by the European Food Safety Authority.

It was previously established that during heating at certain conditions whey proteins form suspensions of stable aggregates. Three types of aggregates with different functionality have been discribed in the literature – fractal aggregates, microgels and fibrils, with fractal aggregates having the most interesting functional properties for applications in food products. In particular, stable suspensions of fractal aggregates can form gels at ambient temperatures upon acidification or addition of salt – a process known as “cold gelation”. Cold gelation of whey protein fractal aggregates was previously studied in detail in our resarch group. It was found that cold gelation is a thermally activated process with an activation energy of 210 kJ/mol for gelation induced by addition of calcium chloride and 155 kJ/mol for acid-induced gelation (Kharlamova, Nicolai, and Chassenieux, 2018 a&b).

On the other hand, gelation of complex association colloids called casein micelles, that represent the major protein fraction in milk, was found to be characterized by a critical gelation temperature $t_c$. Gelation of micelles in water suspensions does not occur even after prolonged heating at tempratures below $t_c$, while happens almost immediately at and above $t_c$ (Thomar & Nicolai, 2016).

In presented talk we discuss gelation of mixtures of casein micelles with whey protein fractal aggregates (Fig. 1). We show that addition of fractal aggregates to micelles results in formation of a hybrid protein network at a lower temperature. The mechanism of gelation of such systems is suggested. The results of the study can be used as a benchmark for application of whey protein aggregates as a gelling agent in more complex dairy systems.

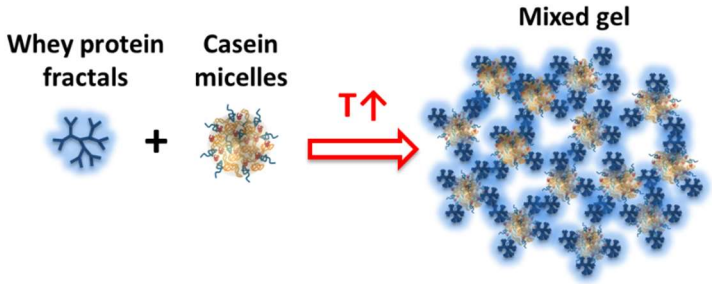


***Figure 1: Schematic representation of gelation in mixtures of micelles with fractal whey protein aggregates.***

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# Gelation kinetics of sodium caseinate induced by continuous acidification

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Sodium caseinate is a milk protein which is used in pharmaceutical products and food. This protein is stable in water at pH=7 due to surface charges that induce an electrostatic repulsion. However, as the pH decreases and reaches this isoelectric point, pI=4.6, electrostatic repulsions vanish and the Van der Waals forces induces the flocculation of the caseinates. Here, we add GDL to the caseinate dispersion, a molecule that slowly and homogeneously reduces the pH from 7 to 3 and therefore leads to gelation [1]. Using a combination of rheology, X-ray scattering and confocal microscopy we study the gelation process.

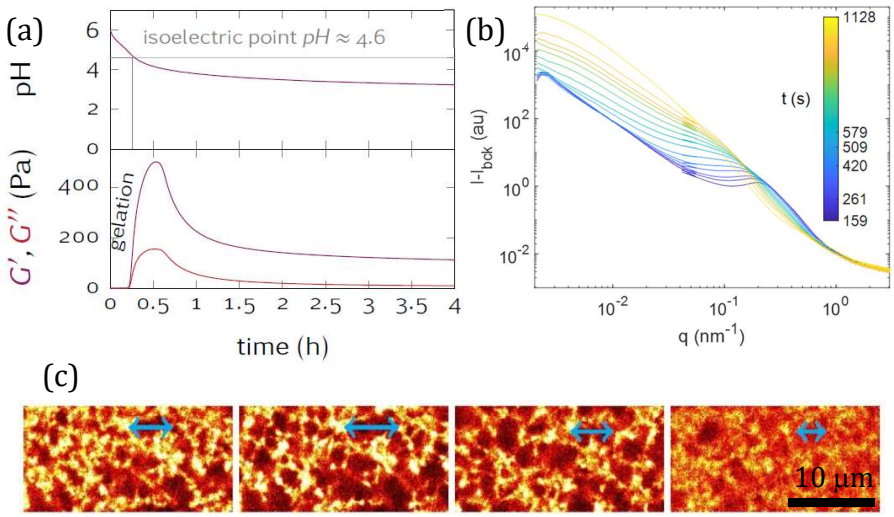


***Figure 1: (a) rheology: evolution of the elastic G' and loss G'' modulus as a function of time and pH. (b) Saxs: evolution of the scattering intensity as function of the wave number q and time. (c) Confocal microscopy: snapshot of the gel at different times.***

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# Stable oil-in-water emulsions using an hydrophobically modified xanthan

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Polysaccharides are widely employed in many industries such as food or cosmetic mainly to stabilize oil-in-water emulsions and to control their rheological properties. Among the others, xanthan gum is the most used due to its outstanding thickening properties of aqueous solutions. However, because of its poor interfacial properties, it requires the addition of an emulsifier to disperse and stabilize the oil droplets. Unfortunately, the use of low molecular weight surfactants has many disadvantages related to toxicological and environmental considerations. On this basis, macromolecular surfactants have been developed during the last decades, most being synthetics while the nowadays demand of natural ones is considerably growing. To overcome this problem, octyl residues were grafted onto the backbone of xanthan to confer new amphiphilic properties[1]. Moreover, xanthan can adopt two different conformations[2], with distinct rheological properties[3] depending on the experimental conditions: an ordered semi-rigid helical structure or a disordered flexible coil.

The objective of the present work is to study and understand the phenomenon involved in the stability of oil-in-water emulsions containing amphiphilic xanthan.

Oil-in-water emulsions using no surfactant but containing pristine or modified xanthan have been studied and compared. As expected in emulsion, unmodified xanthan is not able to stabilize the emulsions as phase separation occurred within only few hours. Oppositely, emulsions obtained with modified xanthan are stable over months (see fig. 1).
These results clearly demonstrate the high potential for hydrophobically modified xanthan as emulsion's stabilizer which has been studied as a function concentration and grafting density.


***Figure 1**. Oil in water emulsions containing 1g/L of pristine xanthan one day after preparation (left) and modified xanthan 2 months after preparation(right)*

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# Gelation of mixture of iota and kappa carrageenan

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We will discuss the rheological properties and microstructure of mixture of native kappa carrageenan (κ-car) and iota carrageenan (ι-car) in the presence of salts ($CaCl_2$ and/ or KCl). For κ-car solution, increasing the $CaCl_2$ between 5 and 40 mM increased the elastic modulus ($G_{el}$) and the gelling temperature ($T_g$). However, further increase of the $CaCl_2$ concentration did not lead to a further increase of the elasticity. Adding $CaCl_2$ between 5 and 20 mM to ι-car also enhanced $T_g$ and $G_{el}$, but in this case $G_{el}$ remained constantly above 20 mM $CaCl_2$. Mixtures of κ-car and ι-car showed a two-step gelation process at temperatures that coincided with the one of pure κ-car and ι-car solutions, respectively. However, the elastic modulus of the mixtures at low temperatures was much higher than the sum of those of the pure systems within the same conditions.

For the gelation of mixed gel in presence of both KCl or $CaCl_2$, $G_{el}$ was higher than samples with just one type of salt at the same concentration. $G_{el}$ increased when increasing the fraction of $CaCl_2$ in mixed salt up to 50%, further adding $CaCl_2$ led to a decrease of the storage modulus. However, $T_g$ increased gradually with increasing fraction $CaCl_2$. At a fixed ratio of KCl and $CaCl_2$ of 50:50, $G_{el}$ of mixed carrageenan increased with increasing total salts up to 40 mM and remained the same at higher concentrations (Fig.1).

In parallel, the influence of these salts on the structure of mixed gels was studied by confocal laser scanning microscopy (CLSM). In the mixtures, κ-car and ι-car could be distinguished because they were covalently labelled with different fluorescent dyes. CLSM images show that ι-car in pure or mixed gel is distributed more homogeneously than κ-car both in presence of KCl and/or $CaCl_2$. However, κ-car appears more homogeneously distributed in the mixed gel than in the individual gels. In addtion, κ-car in the mixed gels with mixed salts appear more homogeneous than that in presence of $CaCl_2$. Furthermore, the tubidity of mixed systems was evaluated as a function of temperature and time. The results showed that there are synergistic effects between κ-car and ι-car in mixed gels and between KCl and $CaCl_2$ in gels with mixed salts.

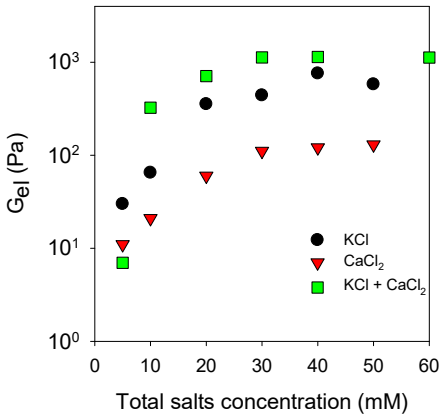


**Fig 1**. Elastic modulus of mixed carrageenan at 5-5 g/L after one hour at 5 °C as a function of total $CaCl_2$ and/ or KCl concentration.