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Protein Interactions / assemblies and subsequent properties

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Protein Interactions / assemblies and subsequent properties



STLOpen Days
19-21 March 2019



Marie-Hélène FAMELART / Thomas CROGUENNEC
Interactions - Structures - Functionalities



General introduction

- Additives are currently used to control dairy product quality (texture, heat stability, phase separation,...)
- New trends in Europe driven by consumer's expectations

- **More natural and healthier food products**
- **100% milk products**
(without non-dairy additives)
- **Innovative products**
(new uses and consumption habits)

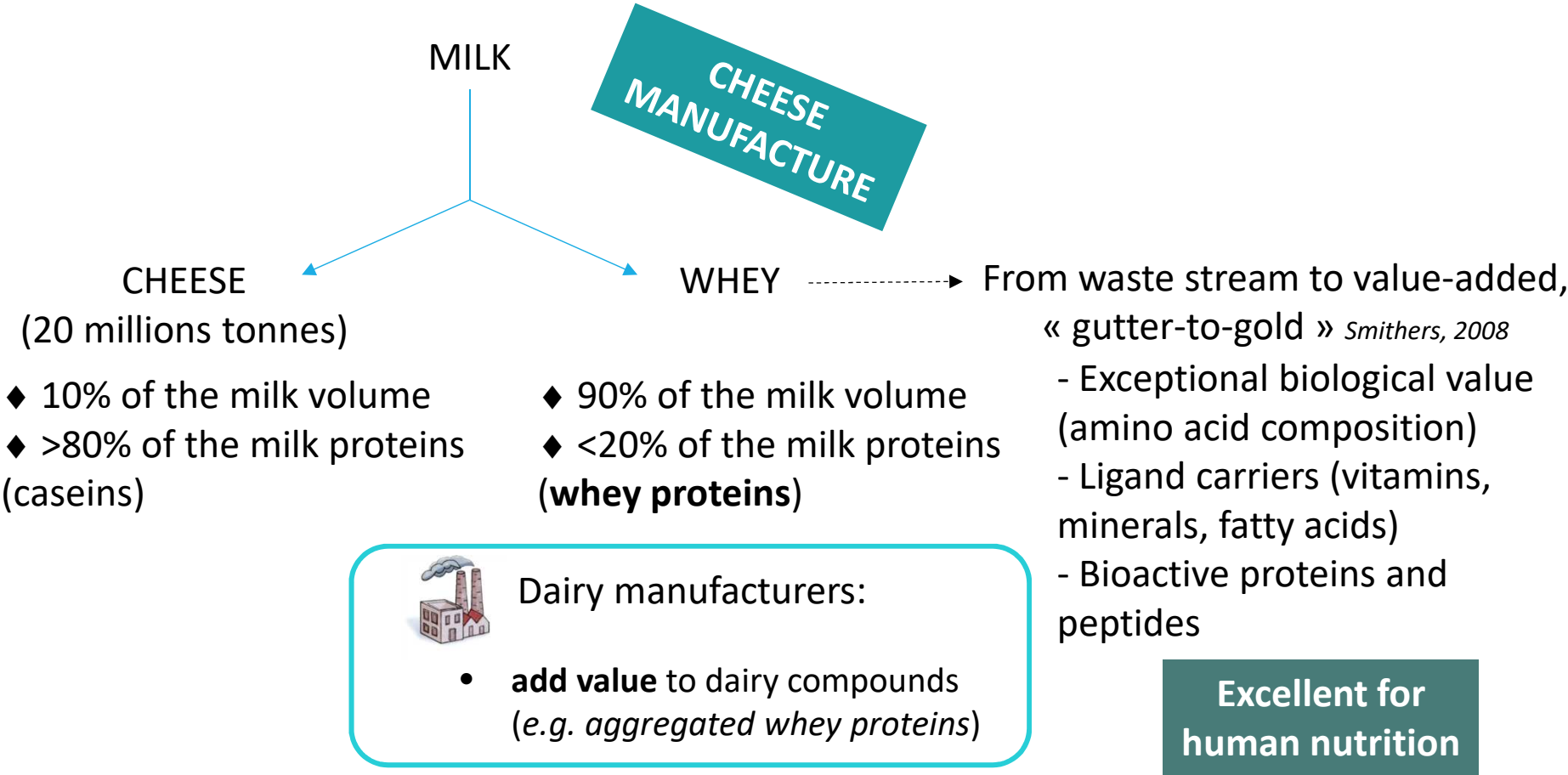


- Milk proteins are customizable into different assemblies that exhibit different properties (water holding capacity, heat stability,...) than native proteins → could be used to replace partly or totality food additives in dairy products



General Introduction

Whey proteins : Large amount available around the world



Topics of this presentation

1. Whey protein aggregates for controlling emulsion heat stability and texture
2. Whey protein aggregates as texturizing ingredients

Introduction: Why protein aggregates for controlling emulsion heat-stability and texture

- Whey proteins :

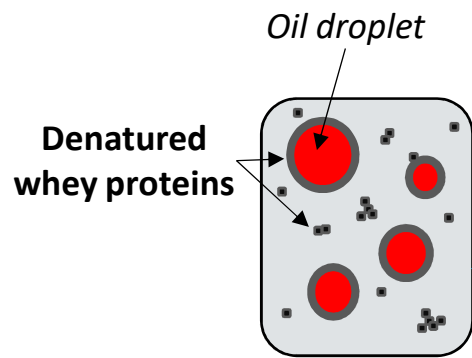


Fluid emulsions: Protein amount too low to build a continuous network

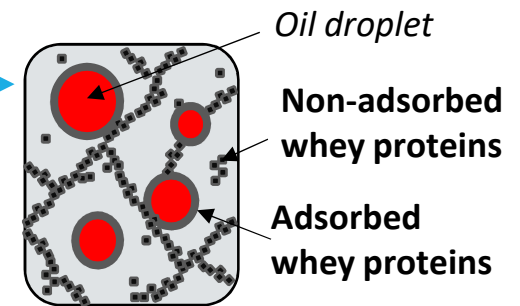
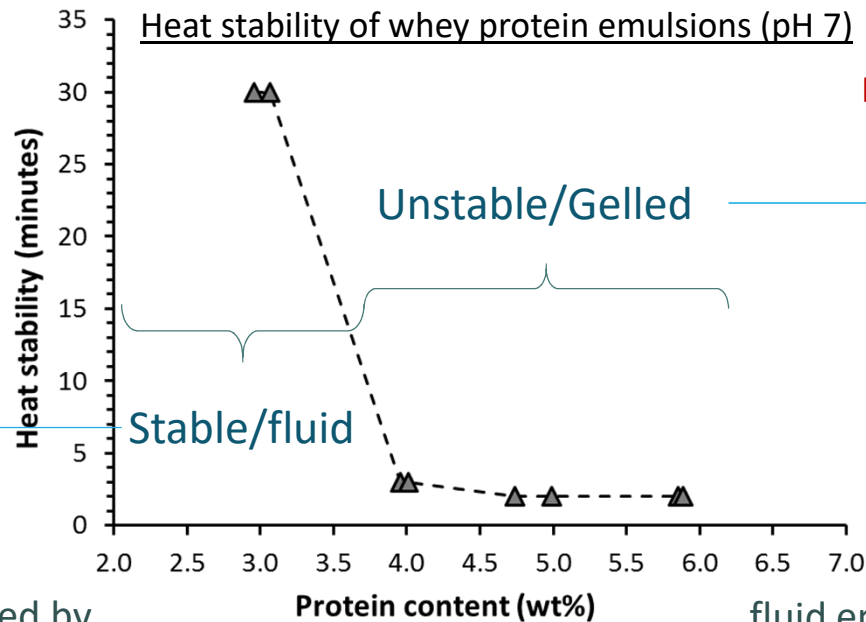
- natural emulsifiers (*adsorb to oil/water interface*)
- heat-sensitive proteins (*heat treatments are required to extent food product shelf life*)
 - heat sensitive emulsions
 - texturized (gelled) emulsions



Gelled emulsions : Network of proteins entrapping oil droplets



Gelled emulsions obtained by using non-dairy **gelling agents**



fluid emulsions obtained by using non-dairy **stabilizing agents**

Dairy industries

Research Questions



How to control the texture of whey protein emulsions in a large range of protein concentrations without non-dairy additives?

- To design whey protein emulsions at high protein concentration (>4%) that are fluid after heating?
- To design texturized (gelled) emulsions at low whey protein concentrations (<3%)?

How to design whey protein emulsions at high protein concentrations that are fluid after heating in the absence of non-dairy additives?

Strategy

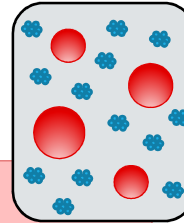


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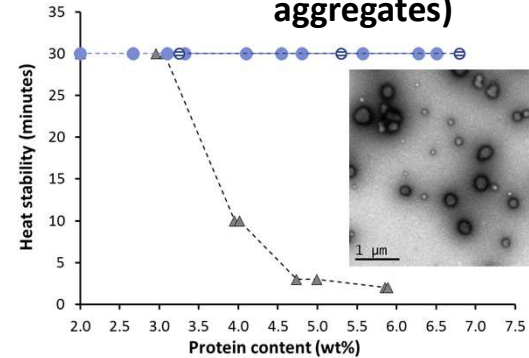
Competition for the oil droplet surface

1

Stability of the **continuous phase** (replace native whey proteins by aggregated whey proteins)

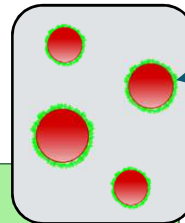


Protein in the continuous phase (dense and large whey protein aggregates)

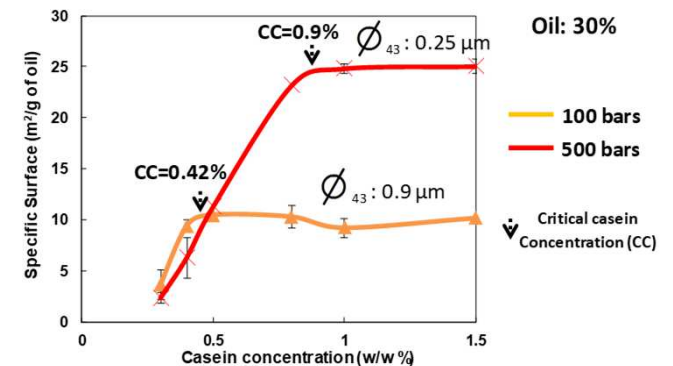


2

Stability of the **oil droplets** (replace native whey proteins by caseins)



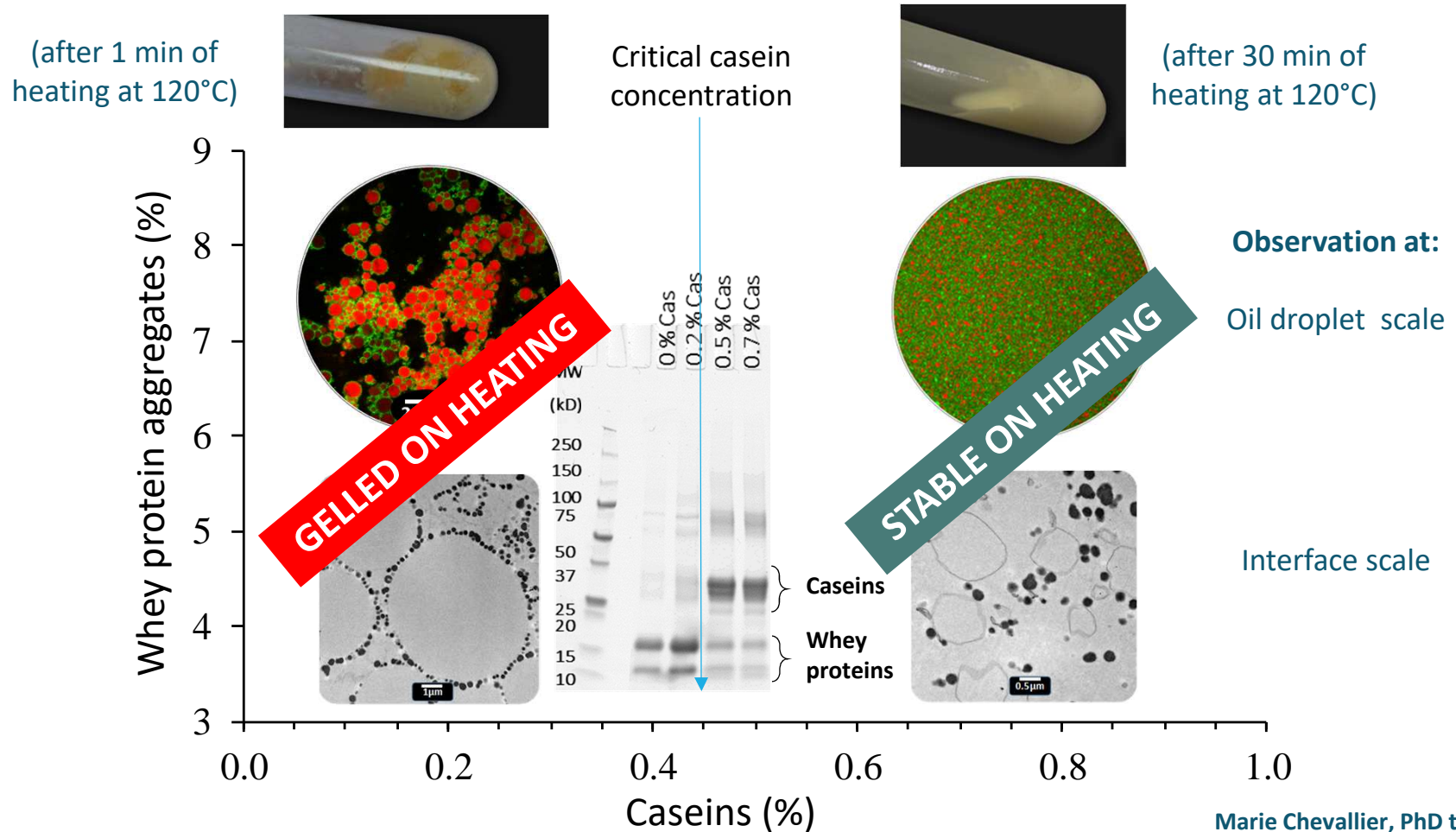
Adsorbed proteins (caseins)



How to design whey protein emulsions at high protein concentrations that are fluid after heating in the absence of non-dairy additives?

Results

Thermal Stability of the emulsions

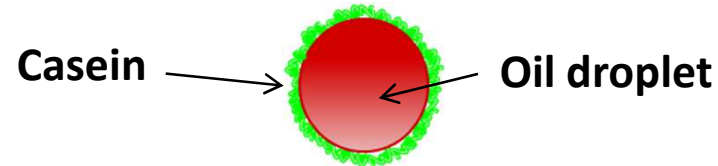


How to design whey protein emulsions at high protein concentrations that are fluid after heating in the absence of non-dairy additives?

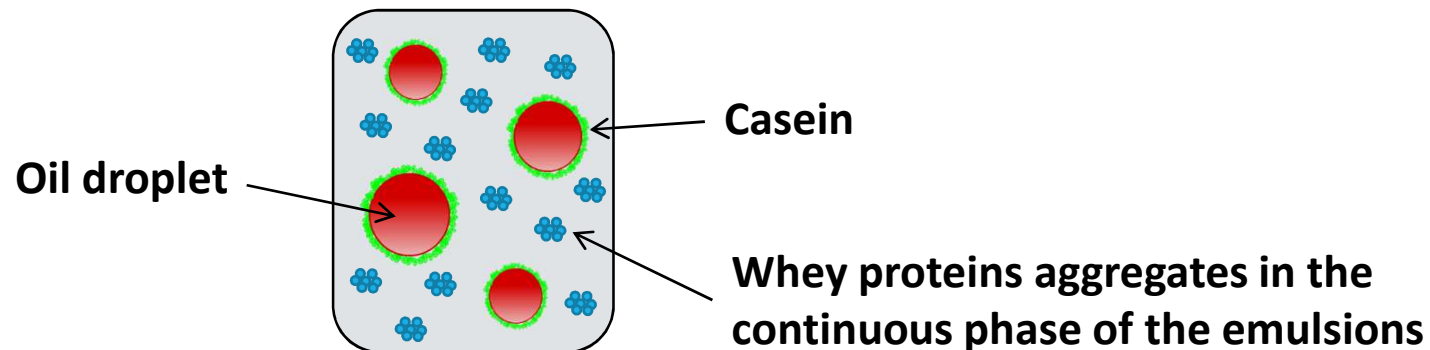
Main findings

- by adding sufficient amount of caseins to cover oil droplet surface (control of the size and stability of the oil droplets)

→ estimated value: mass of oil (g) × specific surface (m^2/g of oil) × protein interfacial load (g/m^2)
(protein interfacial load $\sim 2\text{mg}/\text{m}^2$ for caseins)



- By selecting large and dense whey protein aggregates (*small number, low interfacial adsorption rate and low reactivity on heating*)

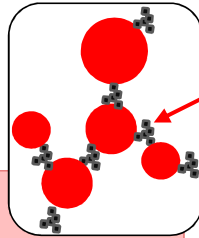


How to obtain texturized (gelled) emulsions at low whey protein concentrations without non-dairy additives ?

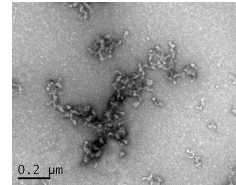
Strategy

1

Connect oil droplets with whey proteins aggregates (low density)



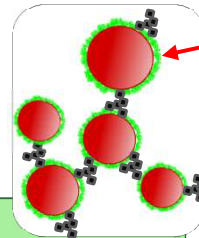
Whey protein aggregates used as connectors
(low density/elongated aggregates → factual aggregates)



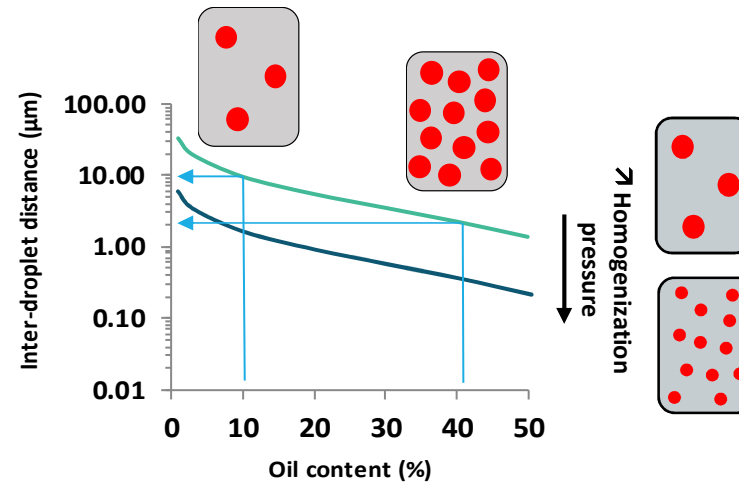
Size of the whey protein aggregates
≈
inter-droplet distance

2

Control inter-droplet distance (oil content/homogenization pressure)

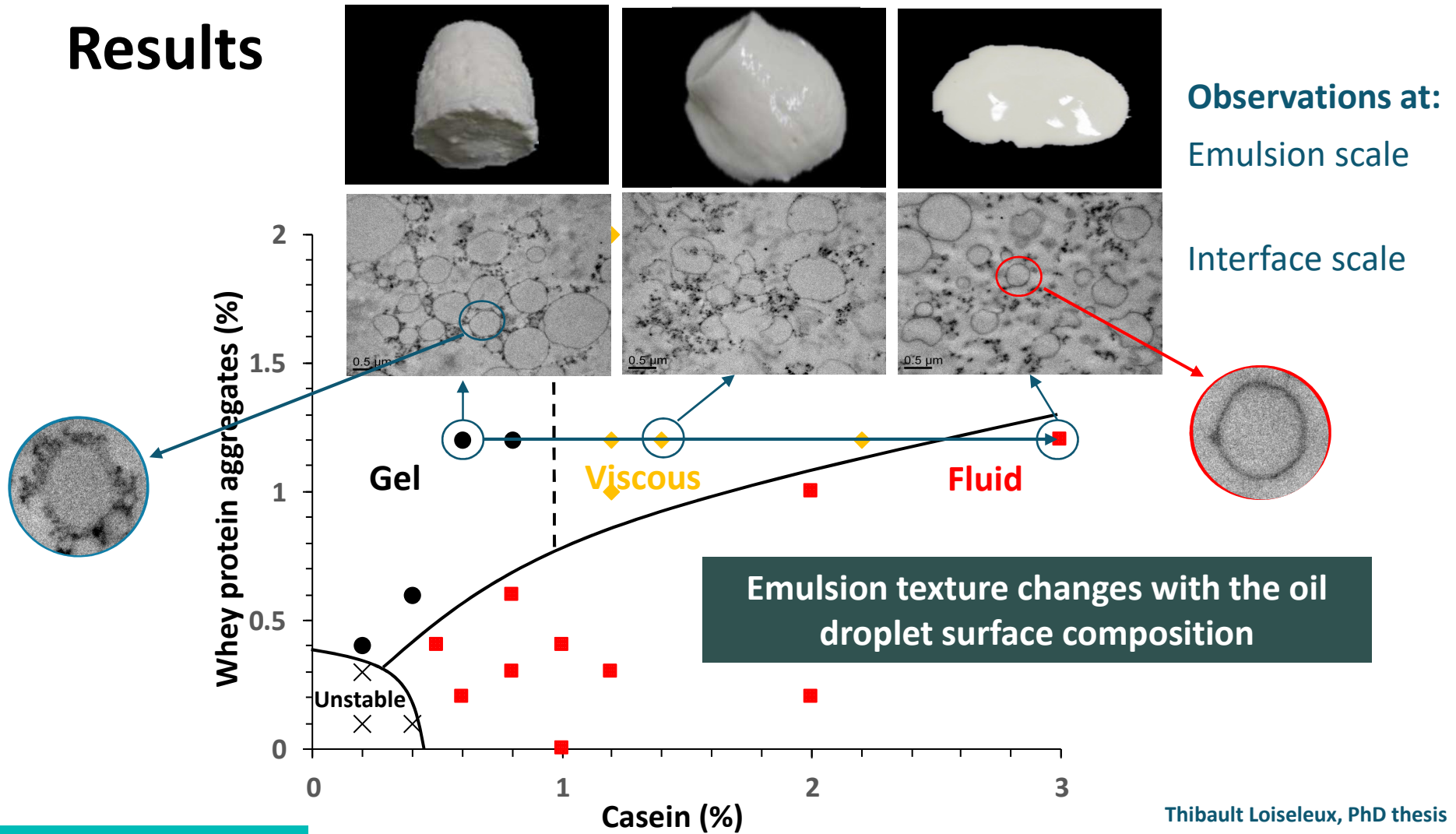


Caseins for stabilizing oil droplets interface



How to obtain texturized (gelled) emulsions at low whey protein concentrations without non-dairy additives ?

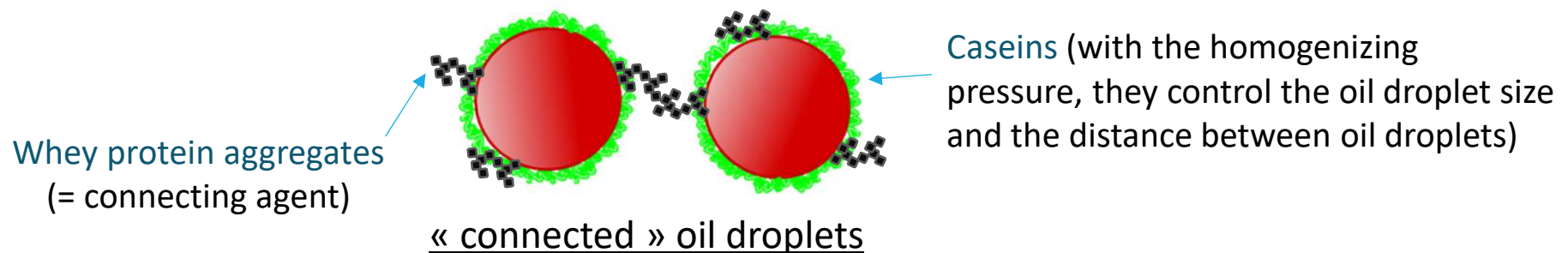
Results



How to obtain texturized (gelled) emulsions at low whey protein concentrations without non-dairy additives ?

Main findings

- Select aggregates of low density (fractal aggregates of whey proteins)
- Use whey protein aggregates as « connector » at the surface of the oil droplets (size of the aggregates ~ distance between oil droplets)
- In combination with the homogenization pressure, use caseins as emulsifiers to control the size of the oil droplets (distance between oil droplets)

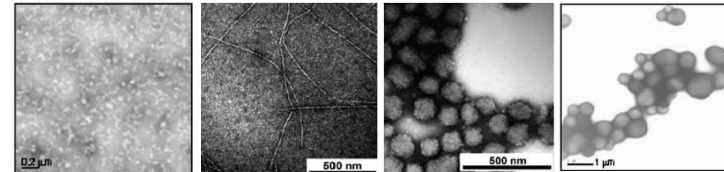


The number of « connectors » defines the texture of the emulsions (gel, viscous, fluid)

Introduction: whey proteins as texturizing ingredients

Whey proteins:

- Heat-induced aggregates produced by heating treatments in solution for increased functional properties



- Dry heating or heating a protein powder: process used for white egg powders for increasing foaming, emulsifying and gelling properties (Kato et al. 1989),
- Dry heating of dairy powders: less studied and not used
- Dry heating: a way to produce other changes of whey proteins
 - ✓ Limited diffusion of solutes = less aggregation
 - ✓ Traces or addition of lactose, degradation products of Maillard intermediates such as dicarbonyl
⇒ crosslinks

Research Questions

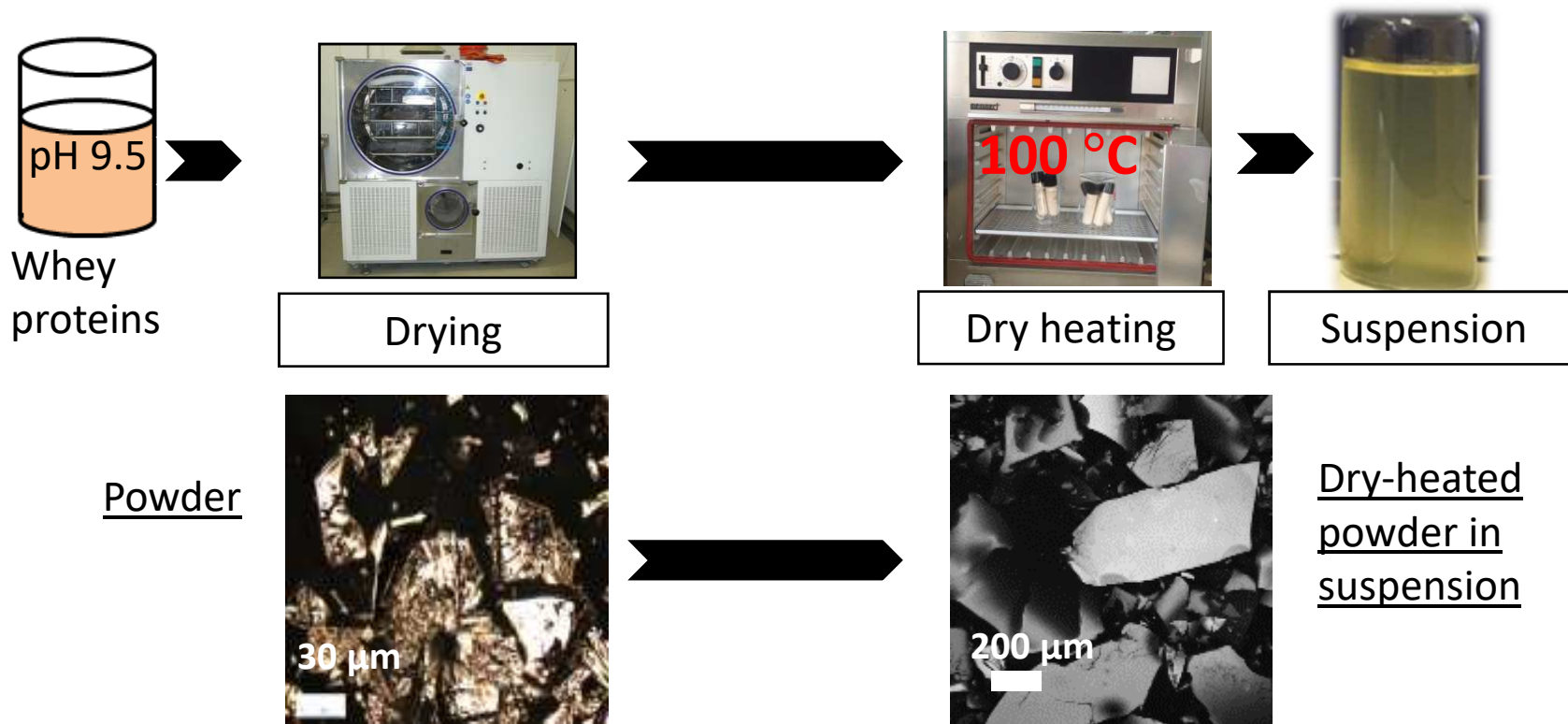


How to custom protein assemblies with targeted sizes?

How to custom their functional properties such as their ability to entrap large amounts of water and deliver high viscosities?

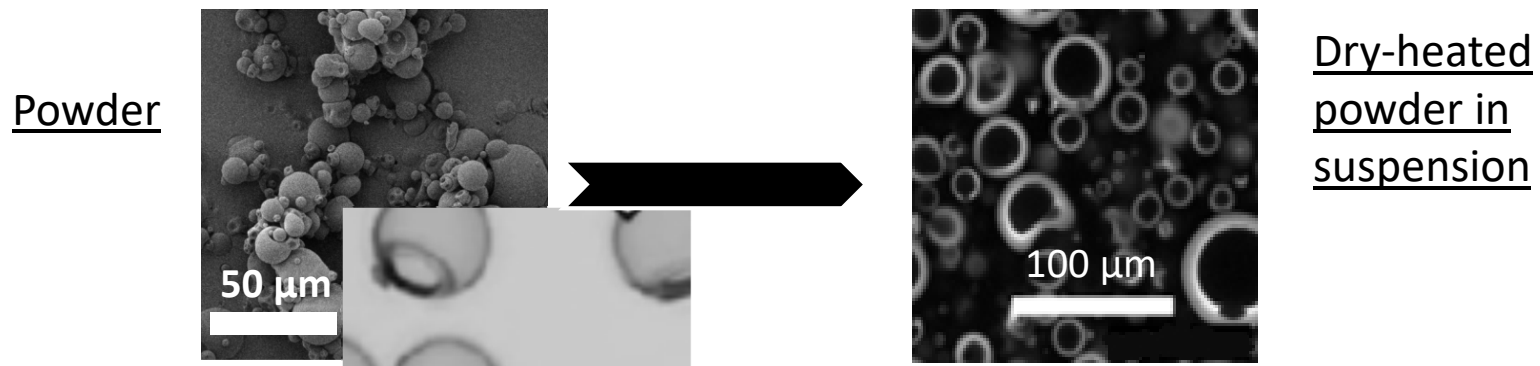
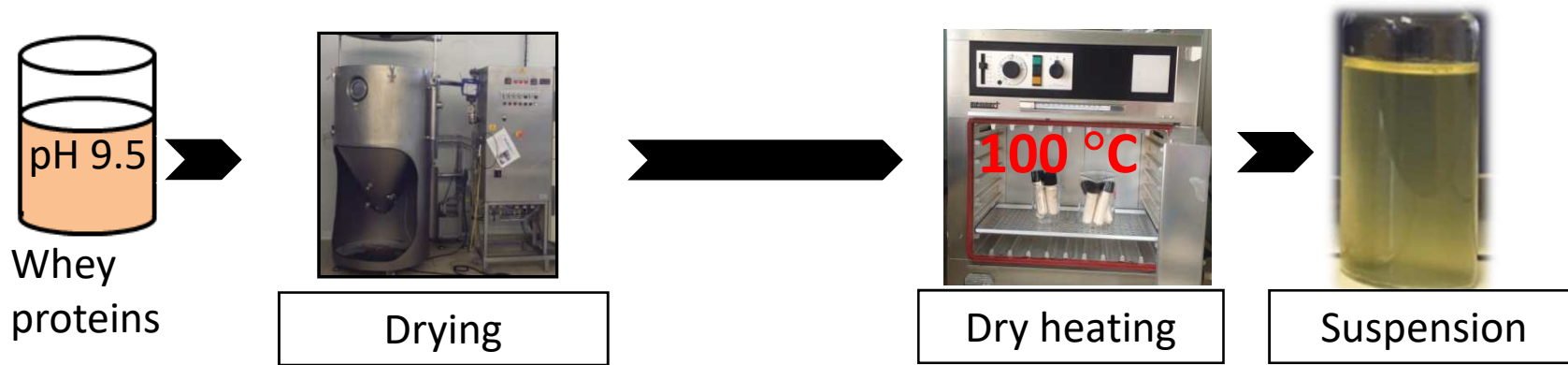
- to replace food texturizing additives

How to custom protein assemblies with targeted sizes?



Elise Schong, PhD thesis

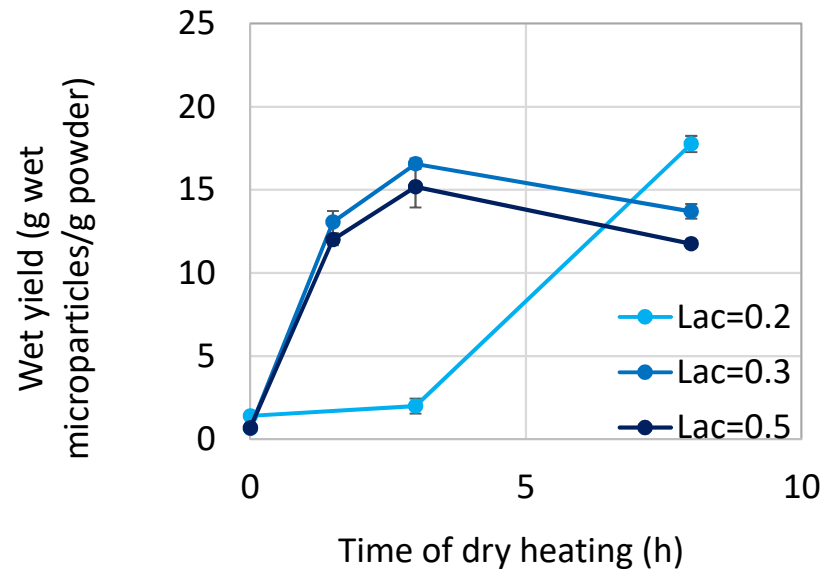
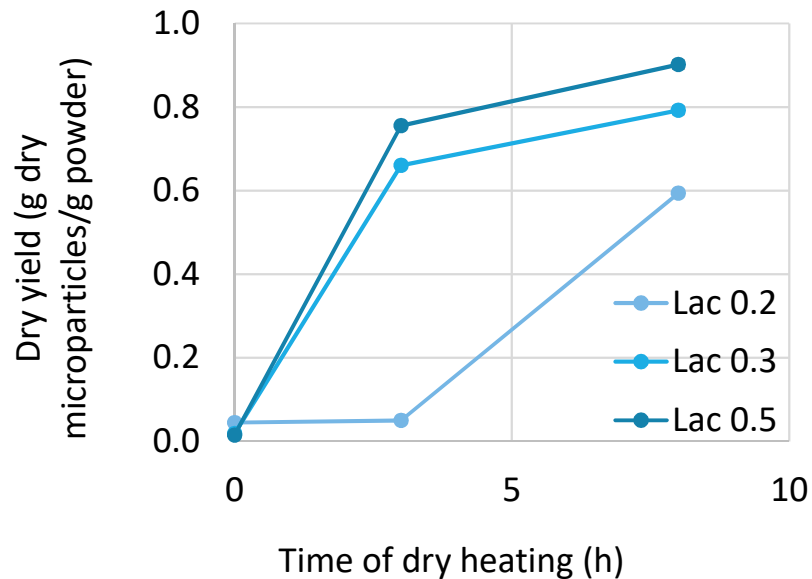
How to custom protein assemblies with targeted sizes?



- Dry heating ⇒ powder no longer soluble
- Crosslinks between proteins
- Microparticles have a size and shape related to the size of the powder before dry heating

How to custom their functional properties such as their ability to entrap large amounts of water and deliver high viscosities?

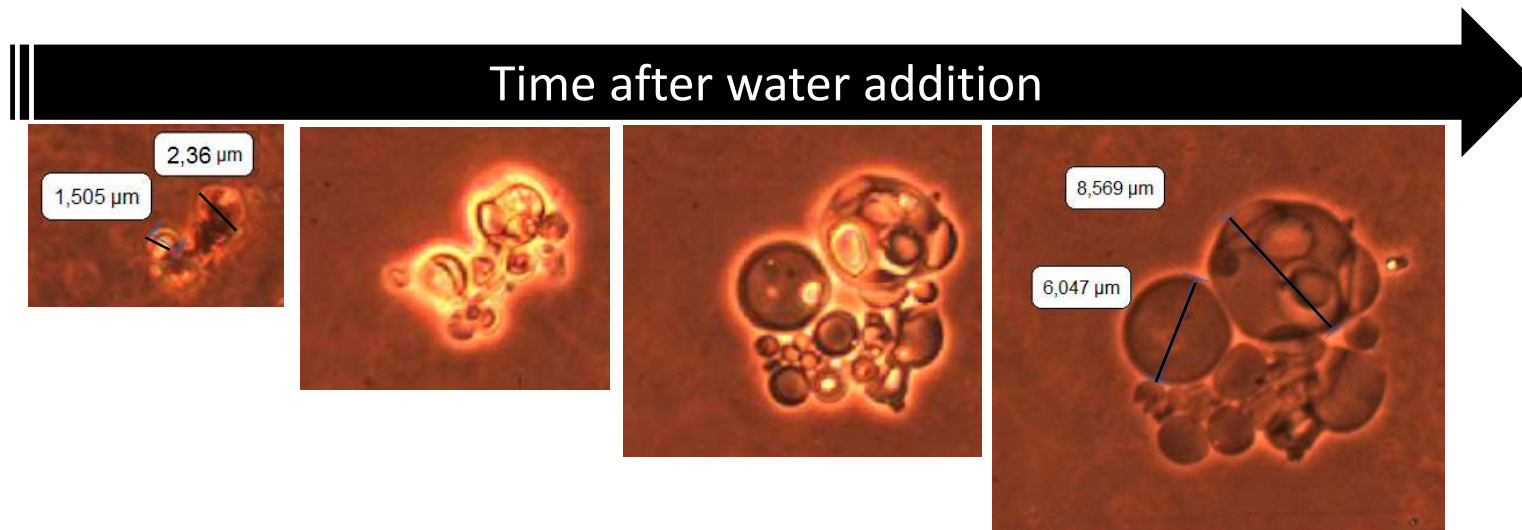
- Yield of transfer of whey proteins in microparticles with:
 - ✓ time of dry heating
 - ✓ addition of lactose (0.2, 0.3 and 0.5 g/10 g protein)



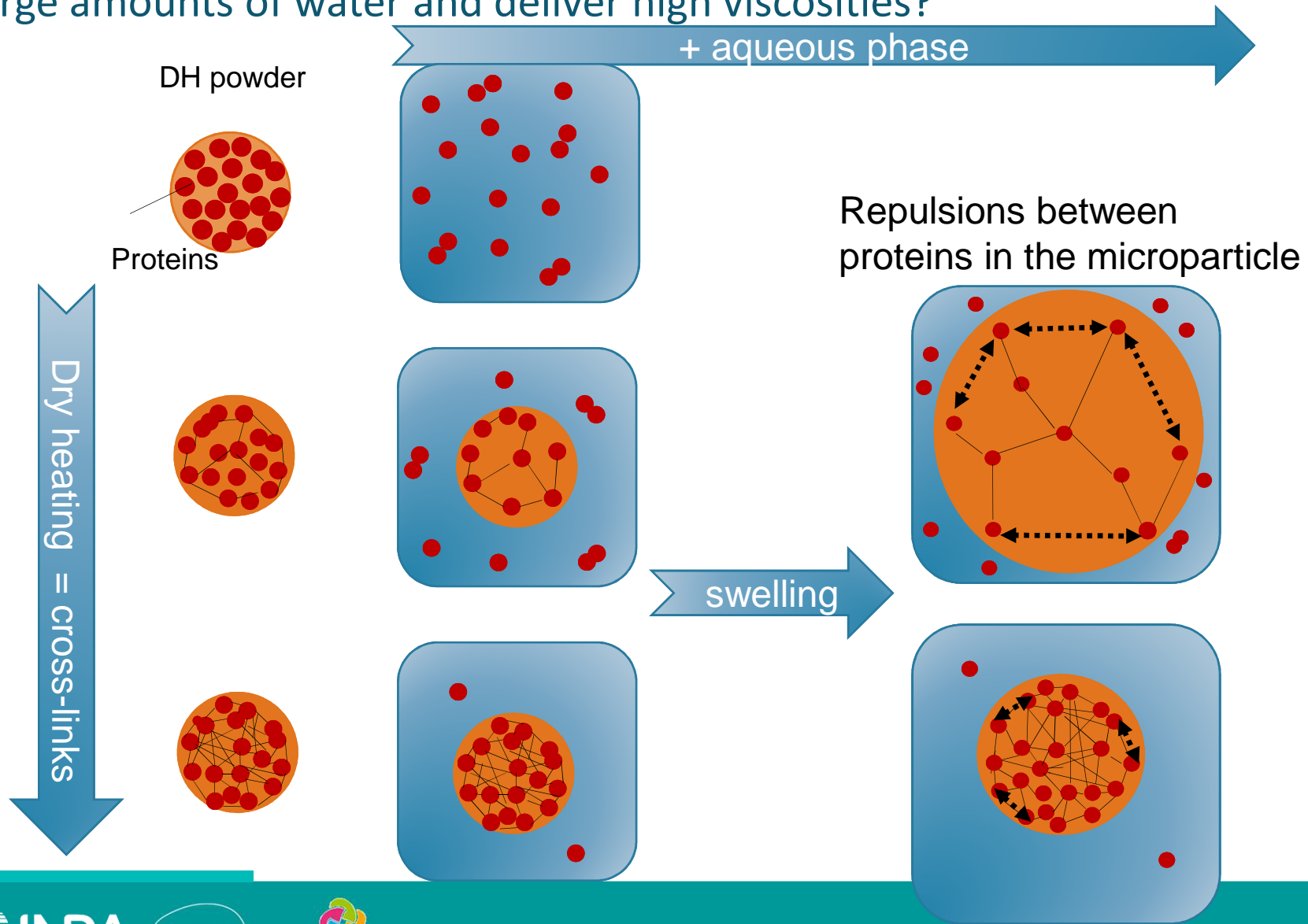
- 1 g of powder can lead to 0.9 g of microparticles
- 1 g of powder leads to around 15 g of wet particles
- The water content is around 95% of the wet weigh of microparticles
- Due to the porous structure of powders

How to custom their functional properties such as their ability to entrap large amounts of water and deliver high viscosities?

- Porous structure of powders \Rightarrow Microparticles entrap a large amount of water
- Ability of microparticles to swell in the water phase: by a factor around 4

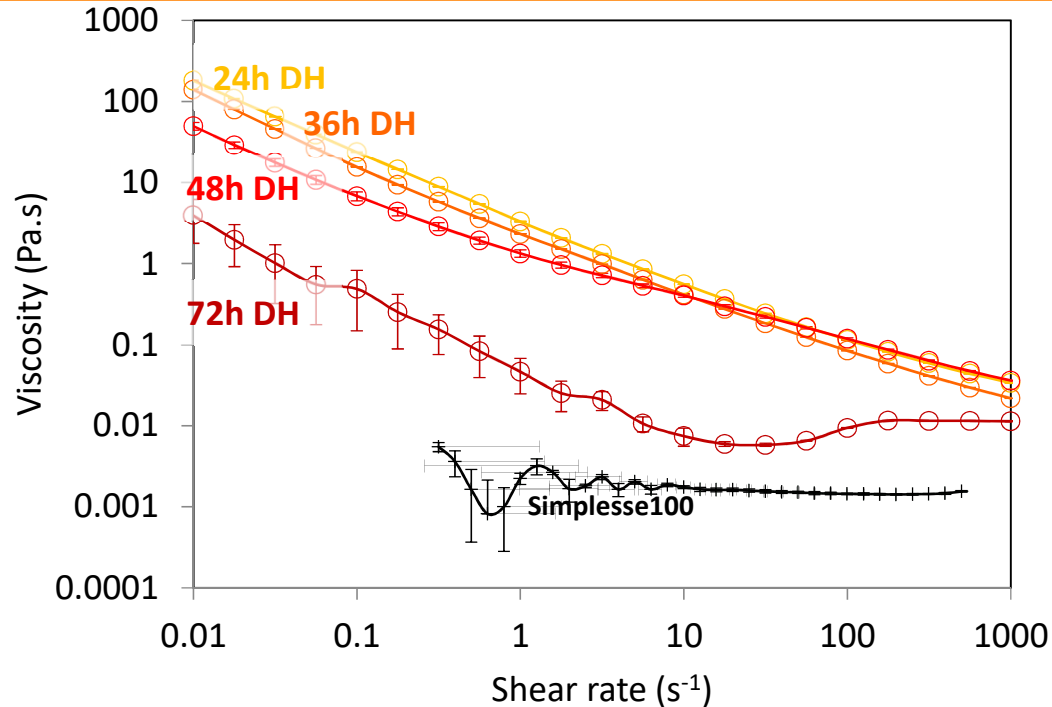


How to custom their functional properties such as their ability to entrap large amounts of water and deliver high viscosities?



How to custom their functional properties such as their ability to entrap large amounts of water and deliver high viscosities?

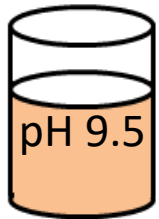
Spray dried powder: 23 g macroparticles/kg suspension



- Very high viscosity as compared to micro-particulated whey proteins ($d[4,3] \sim 10 \mu\text{m}$)
- Viscosity decreases with increased dry heating duration
 - ✓ reduced $d[4,3]$
 - ✓ reduced water content

Conclusions

- Mechanism of formation and nature of the protein crosslinks is still speculative



Whey proteins

- We can form microparticles only at $\text{pH} > 8.0$
- The longer the whey protein solution is stored at $\text{pH} 9.5$, the higher the amount of microparticles

- Role of:
 - ✓ alkaline $\text{pH} \Rightarrow$ protein denaturation? Increased exposure of lysine residues?
 - ✓ lactose \Rightarrow Degradation via Maillard reactions? or degradation products of lactose at high temperature?

Is still under study.

General conclusions

- Whey protein aggregates: high diversity of structures \Rightarrow High diversity of functionalities
 - ✓ Large and dense aggregates (microgels) \rightarrow heat-stability (solutions/emulsions)
 - ✓ Low density aggregates (fractal) \rightarrow functionality dependent on the size
 - Small fractal aggregates : cold-gelation (CaCl_2 or acidic pH), limited syneresis
 - Medium fractal aggregates : connectivity between droplets, texture
 - Large fractal aggregates : increase viscosity
 - ✓ Very large porous aggregates (microparticles) \rightarrow water entrapment, texture
- Whey protein aggregates can be produced at the industrial scale (poster N°4 - Domitille de Guibert: “***Designing innovative technological routes for the production and stabilization by drying of protein fractal assemblies***”).

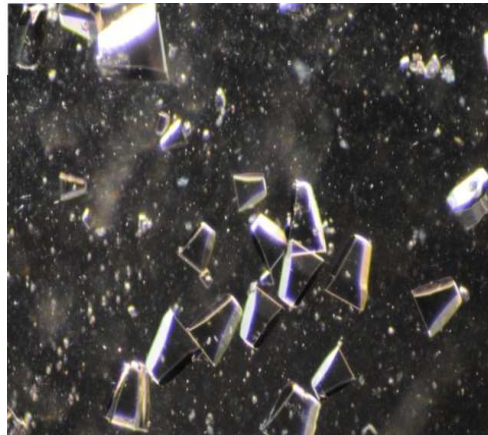
Publications in relation to the study

- Chevallier, M., Riaublanc, A., Cauty, C., Hamon, F., Rousseau, F., Thevenot, J., Lopez, C., Croguennec, T., **2019**, The repartition of whey protein microgels and caseins between fat droplet surface and the continuous phase governs the heat stability of emulsions. *Colloids and surface A*, 563, 217-225.
- Schong, E., Famelart M.H., **2019**, Influence of lactose on the formation of whey protein microparticles obtained by dry heating at alkaline pH. *Food Hydrocolloids*, 87, 477-486.
- Chevallier, M., Riaublanc, A., Lopez, C., Hamon, P., Rousseau, F., Thevenot, J., Croguennec, T., **2018**, Increasing the heat-stability of whey protein-rich emulsions by combining the functional role of WPM and caseins. *Food hydrocolloids*, 76, 164-172.
- Kharlamova, A., 2017, texture des matrices laitières avec des agrégats de protéines laitières. PhD thesis, Université du Maine, France.
- Loiseleux, T., Rolland-Sabate, A., Garnier, C., Guilois, S., Croguennec, T., Anton, M., Riaublanc, A., **2018**, Determination of hydro-colloidal characteristics of milk protein aggregates using Asymmetrical Flow Field-Flow Fractionation coupled with Multiangle Laser Light Scattering and Differential Refractometer (AF4-MALLS-DRi). *Food hydrocolloids*, 74, 197-206
- Schong, E., Famelart M.H., **2018**, Dry heating of whey proteins leads to formation of microspheres with useful functional properties. *Food Research International*, 113, 210-220.
- Schong, E., Famelart, M.H., **2017**, Dry heating of whey proteins. *Food Research International*, 100, 31-44.
- Famelart, M.H., Schong, E., Croguennec T., **2018**, Dry heating a freeze-dried whey protein powder: Formation of microparticles at pH 9.5. *J. Food Eng.*, 224, 112-120.
- Chevallier, M., Riaublanc, A., Lopez, C., Hamon, P., Rousseau, F., Croguennec, T., **2016**, Aggregated whey proteins and trace of caseins synergistically improve the heat stability of whey protein-rich emulsions. *Food hydrocolloids*, 61, 487-495.
- Patent WO2018185192 (A1) - **2018-10-11** - « Stabilized protein aggregate particules and process for the preparation of said particles », M. H. Famelart, T. Croguennec, P. Schuck, E. Schong, T. Sevrin.



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