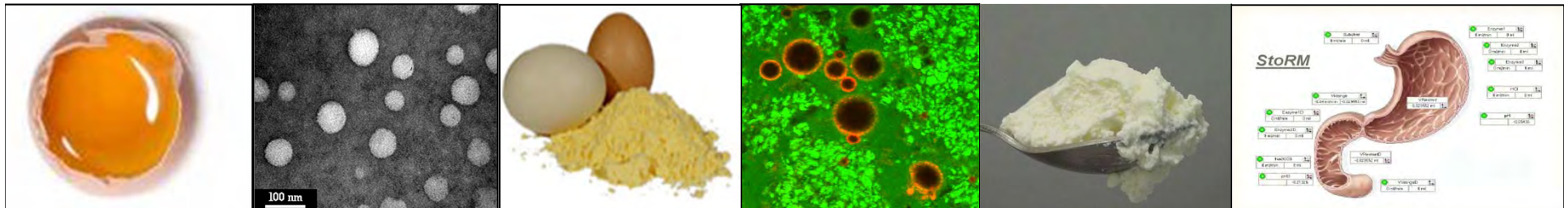




# Specificities of egg yolk in relation with applications and processes

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UR 1268, INRA Nantes, Biopolymers Interactions Assemblies Laboratory  
Interfaces and Dispersed Systems team  
BP 71627, 44316 Nantes, France



# Yolk specificities

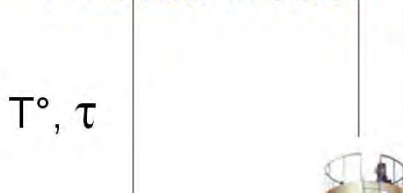
- ❑ source of nutrients and energy
  - vit., minerals, highly digestible lipids and proteins
- ❑ biological activities
- ❑ numerous functional properties
  - emulsifying, gelling, colouring, antioxidant ...
- ❑ natural **micro- and nano- structures**
  - impact on functional properties
- ❑ **role of processes on structures and properties ?**



Cooling



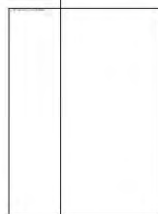
Pasteurisation



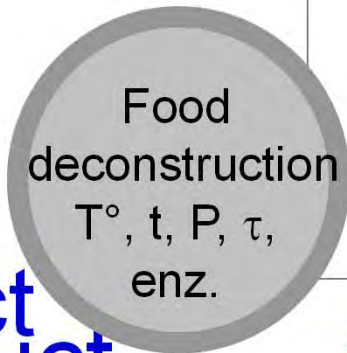
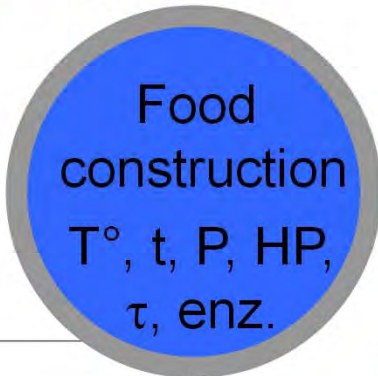
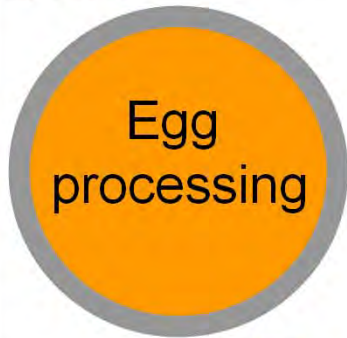
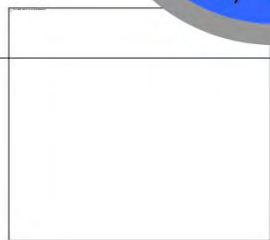
Spray-drying



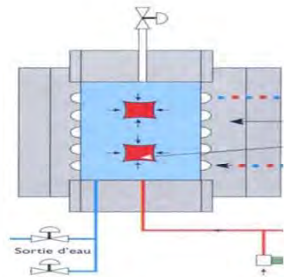
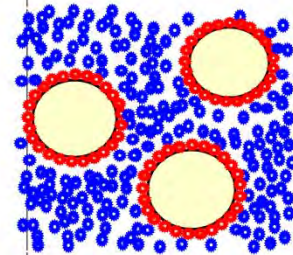
$T^\circ, P, \text{interface}, \text{dehydration}, \dots$



$T^\circ / \text{time}$

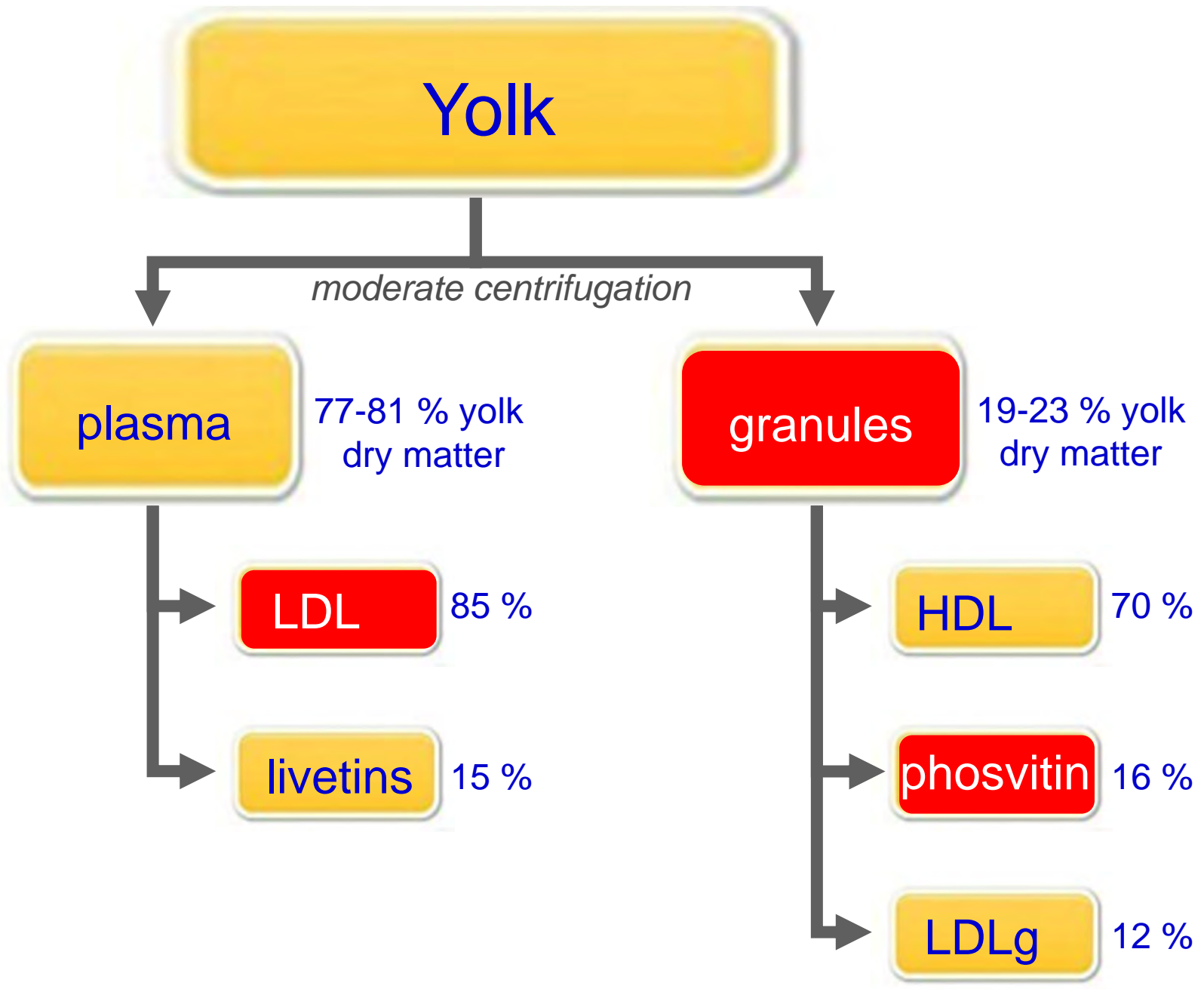


Yolk product processes

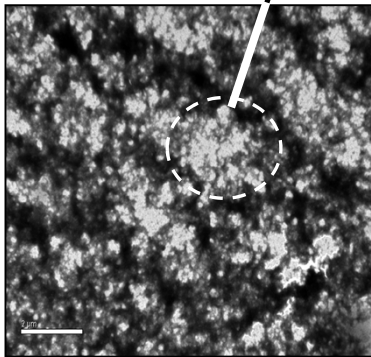
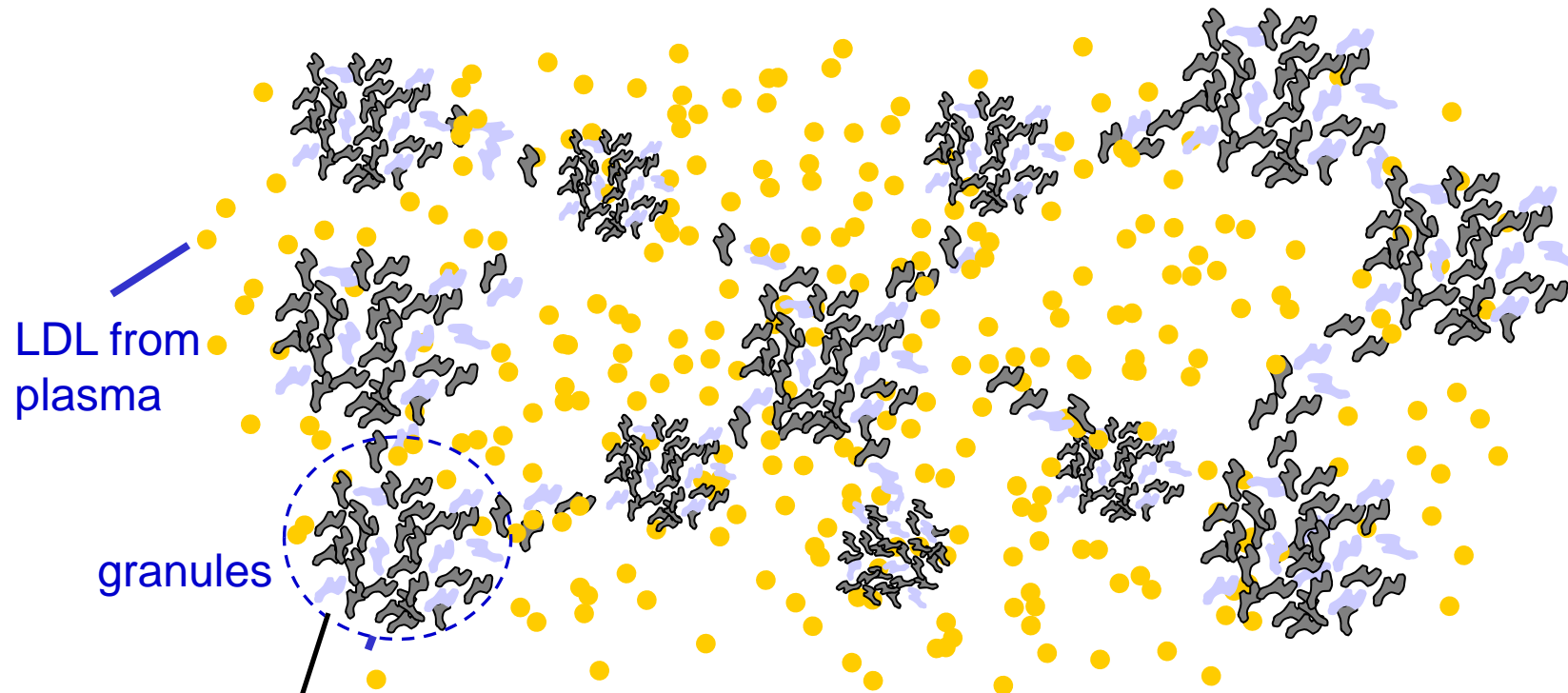


- ❑ Yolk constituents and structures
- ❑ Yolk constituent adsorption at interfaces
- ❑ Impact of various processes on structures and functionalities

# Yolk constituents and structures

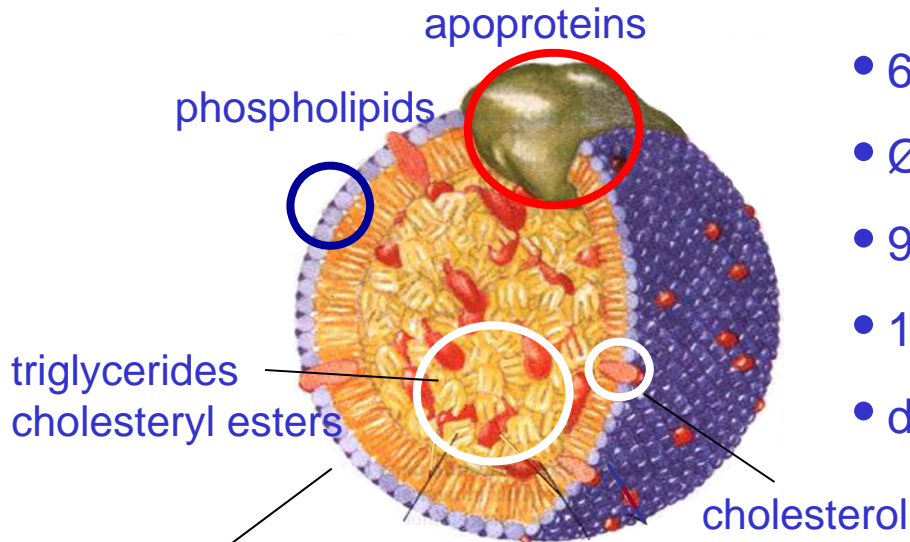
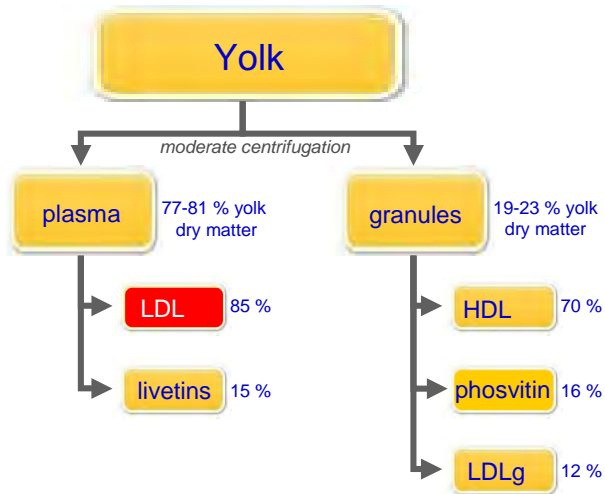


# Yolk: a multi-scale structure

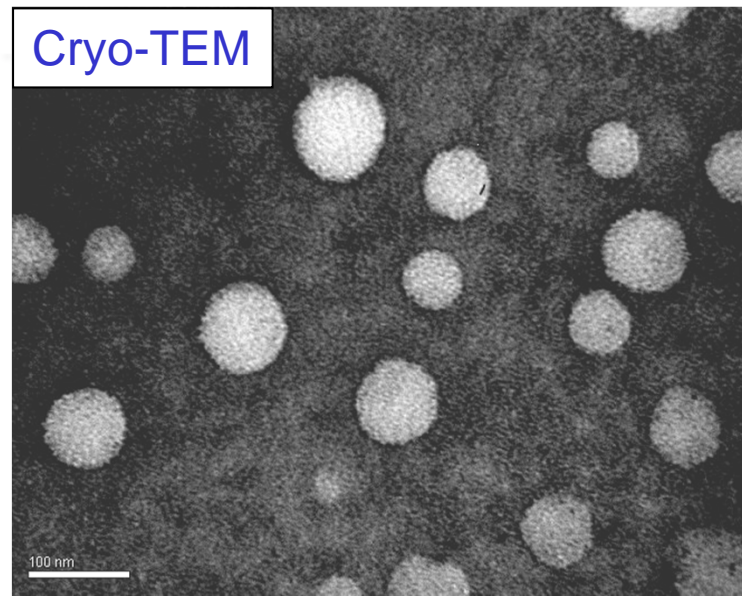
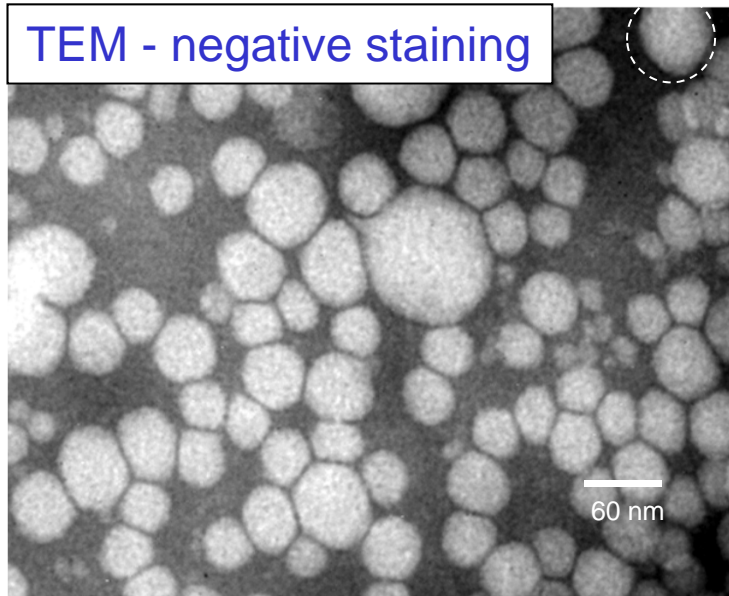


- ❑ a new point of view: yolk is a nanoemulsion of LDL structured by granules (network)
- ❑ natural nano- and micro- assemblies

# LDL nanostructure



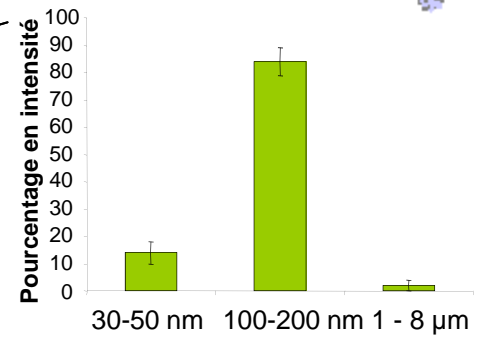
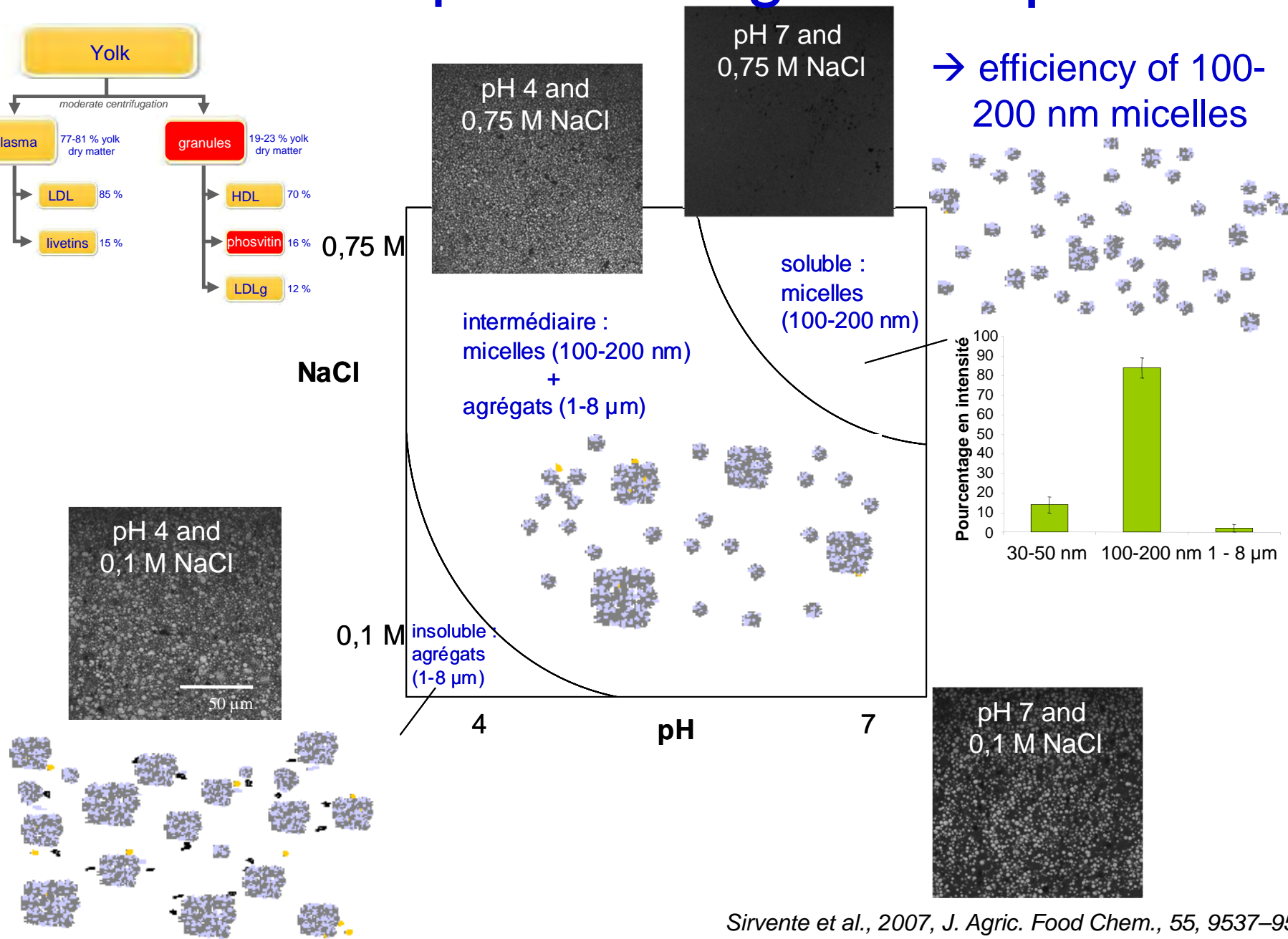
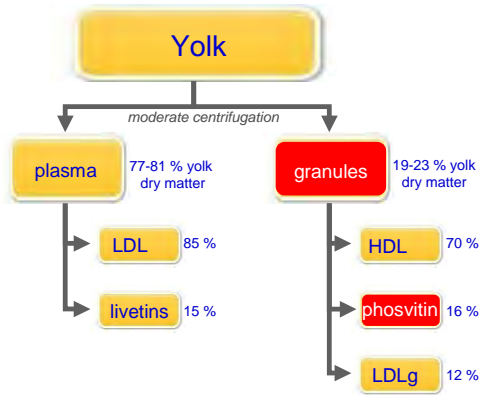
- 66% yolk DM
- Ø 17-60 nm
- 90% lipids
- 10% proteins
- $d = 0.98 \text{ g/cm}^3$



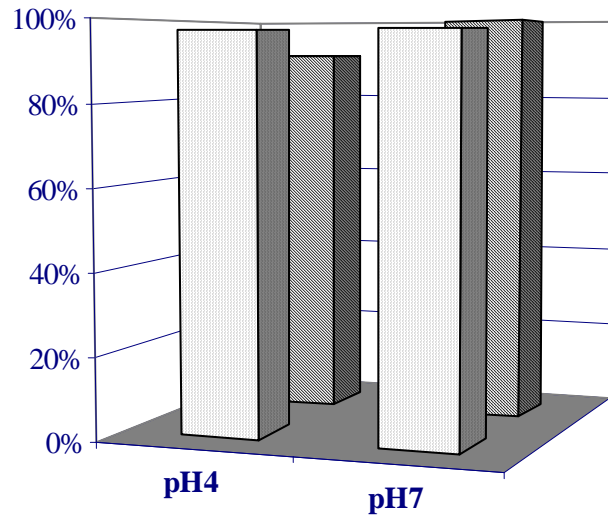
→ soluble nanoemulsions



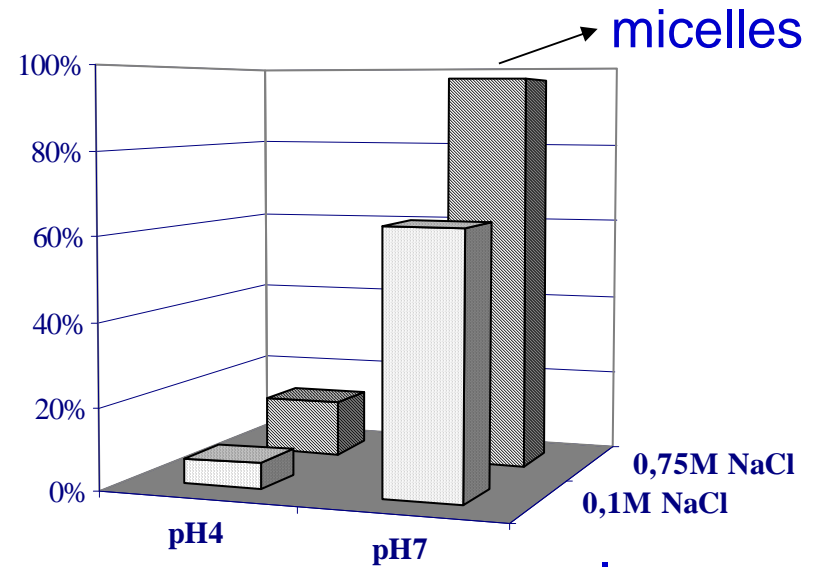
# Granules: phase diagram vs pH/salts



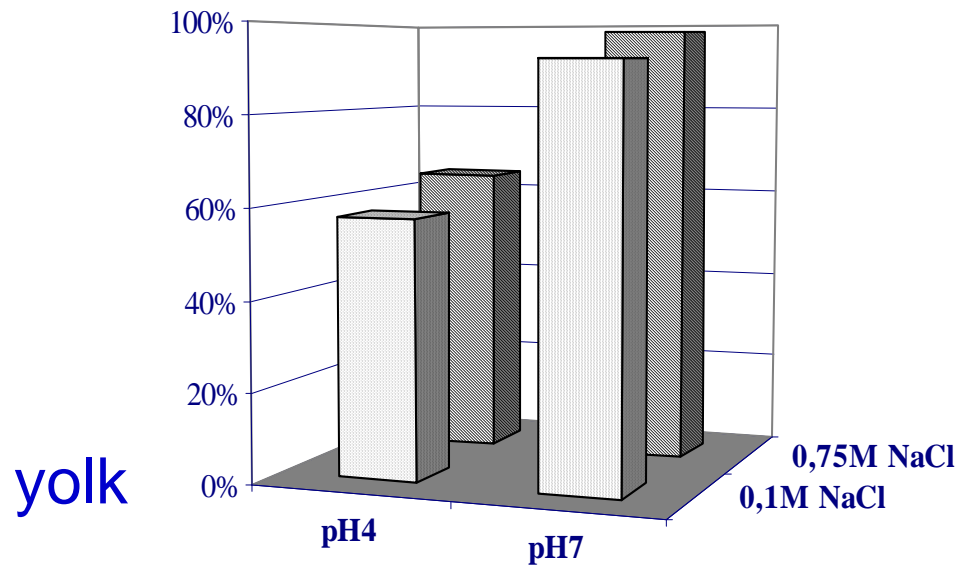
# Protein solubility



plasma

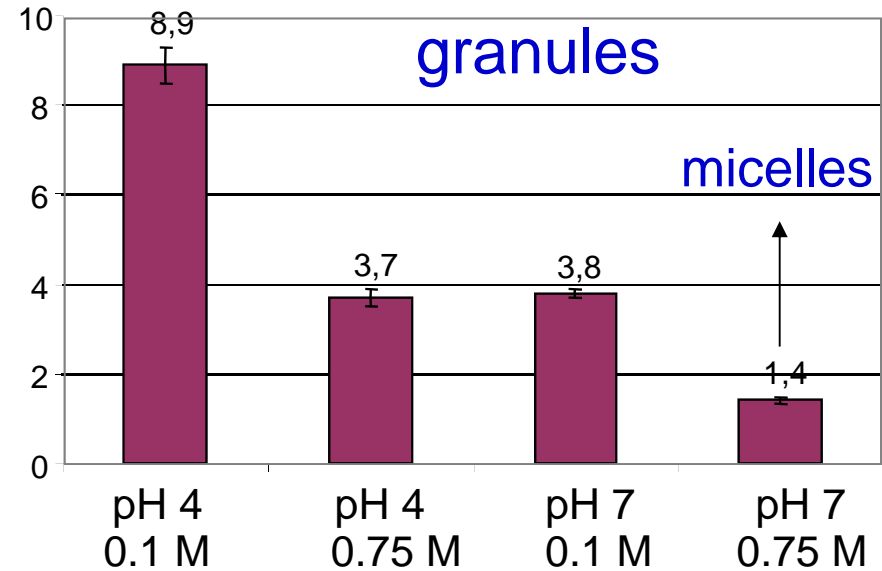
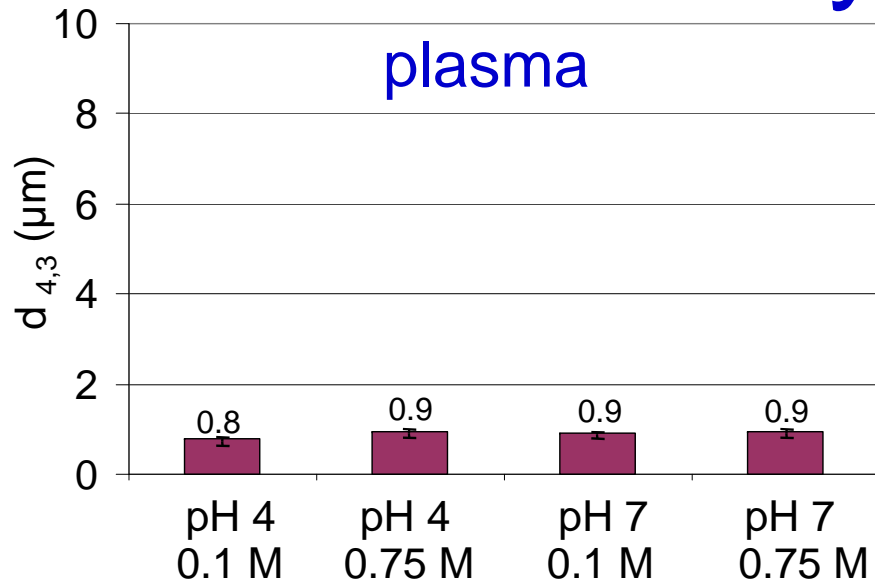


granules

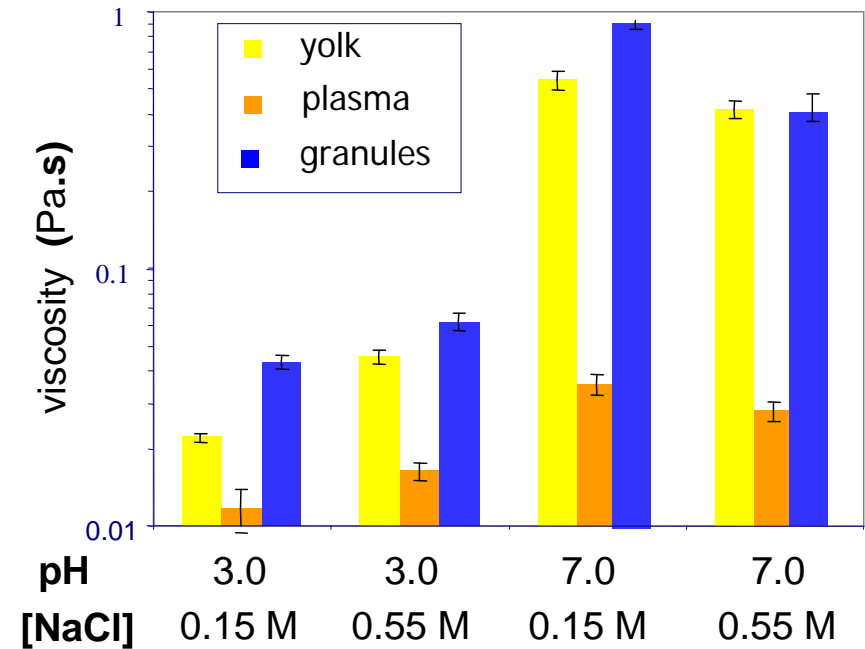


yolk

# Emulsifying properties



	Plasma proteins	Granules proteins
Yolk	52	48
pH3 / 0.15 M	61	39
pH3 / 0.55 M	63	37
pH7 / 0.15 M	47	53
pH7 / 0.55 M	49	51



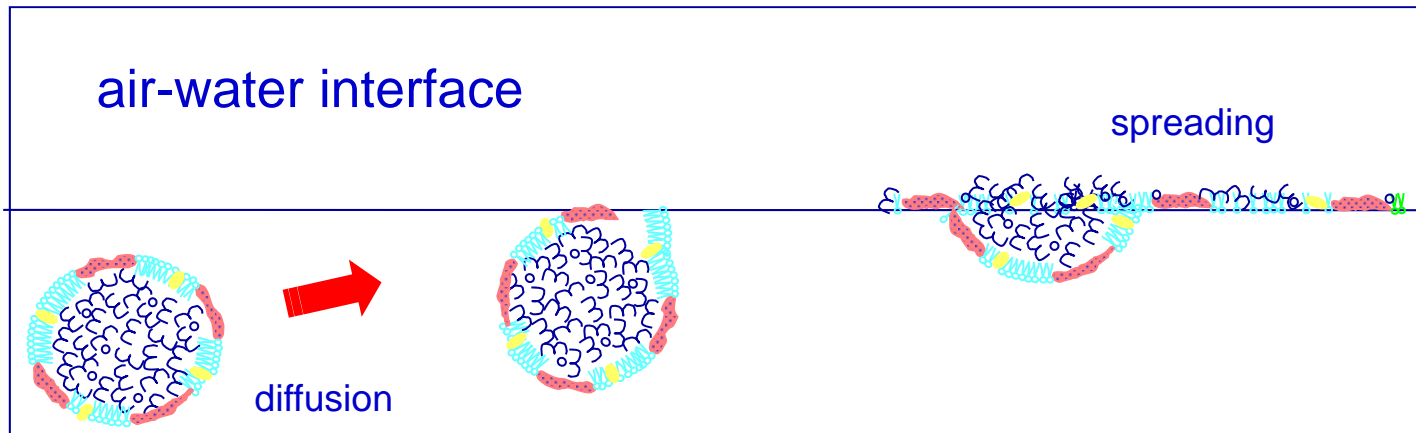
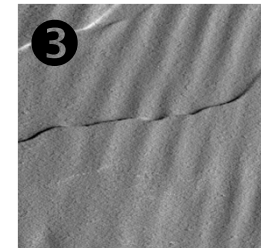
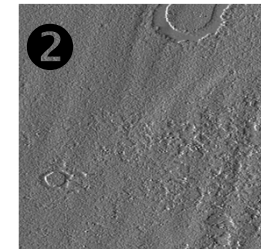
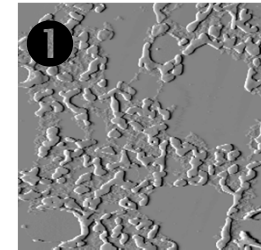
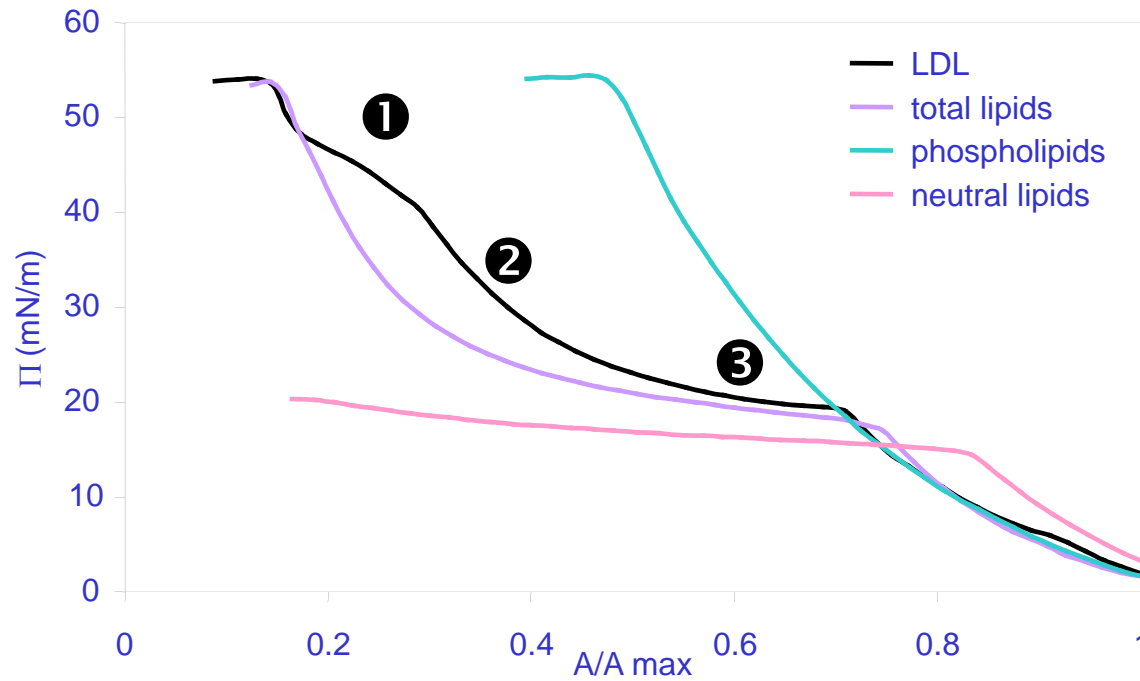
# Highlights

- yolk structures are governed by natural nano- (LDL) and micro- to nano- (granules) assemblies with specific properties
  - when soluble granules are in form of micelles
  
- $\forall$  conditions, plasma constituents are more efficient than granules to stabilise oil-in-water emulsions
  - granules constituents contribute to the rheological behaviour of yolk and yolk emulsions
  - competition between granules constituents and LDL at the interface: main contribution of LDL but pH- $\Gamma/2$  dependent

# Yolk constituent adsorption at interfaces

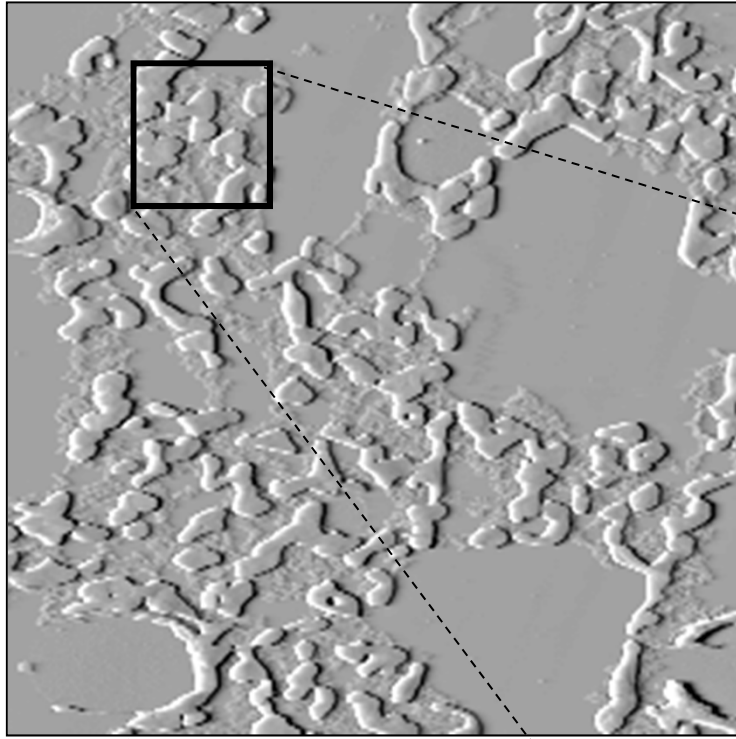
# LDL at an interface

pH 7



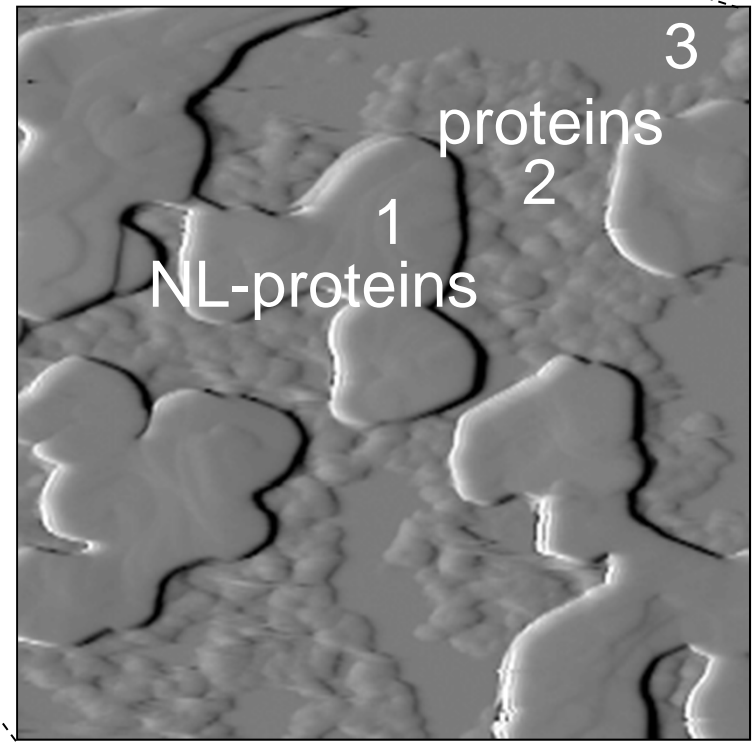
Martinet et al., 2003, *Colloids and Surfaces B: Biointerfaces*, 31, 185-194  
 Dauphas et al., 2006, *J. Agric. Food Chem.*, 54, 3733-3737  
 Dauphas et al., 2007, *Colloids and Surfaces B: Biointerfaces*, 54, 241-248

pH 7

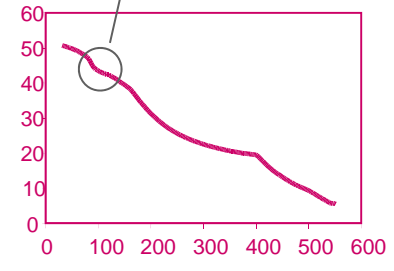


3 layers

PL or proteins-PL

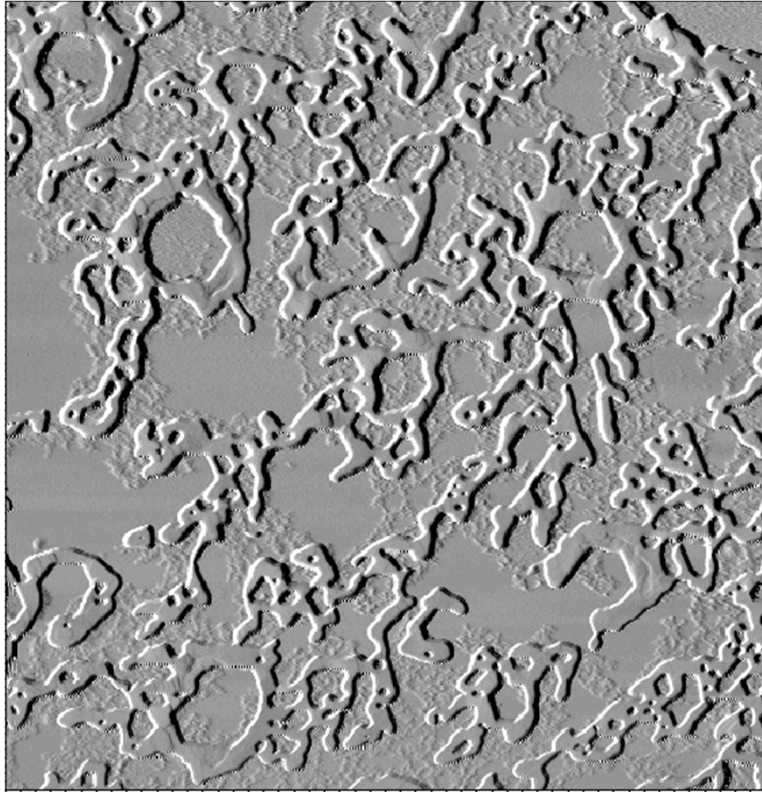


10 x 10  $\mu\text{m}$



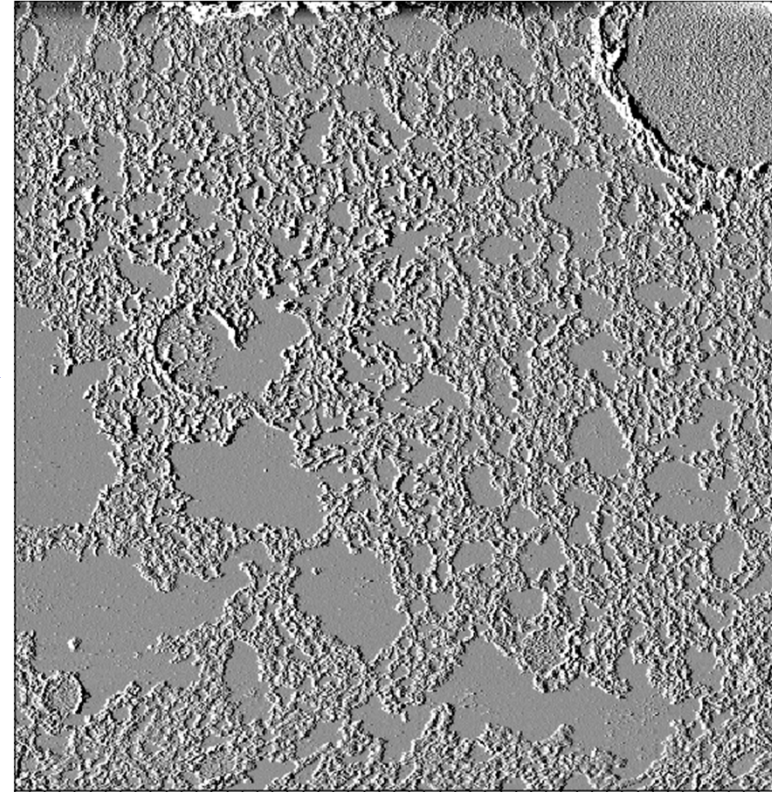
2 x 2  $\mu\text{m}$

Air



10 x 10  $\mu\text{m}$

Butanol

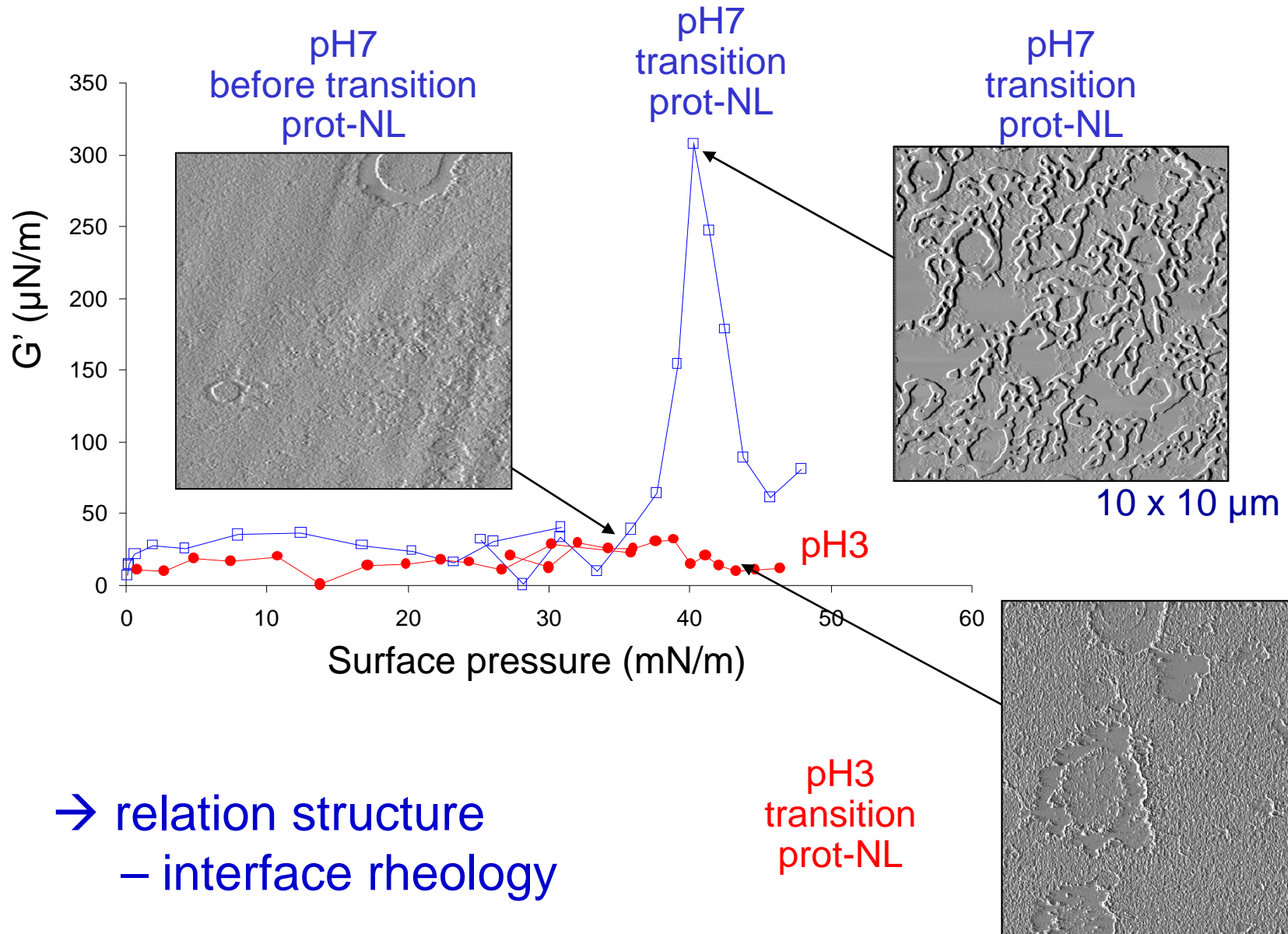


10 x 10  $\mu\text{m}$

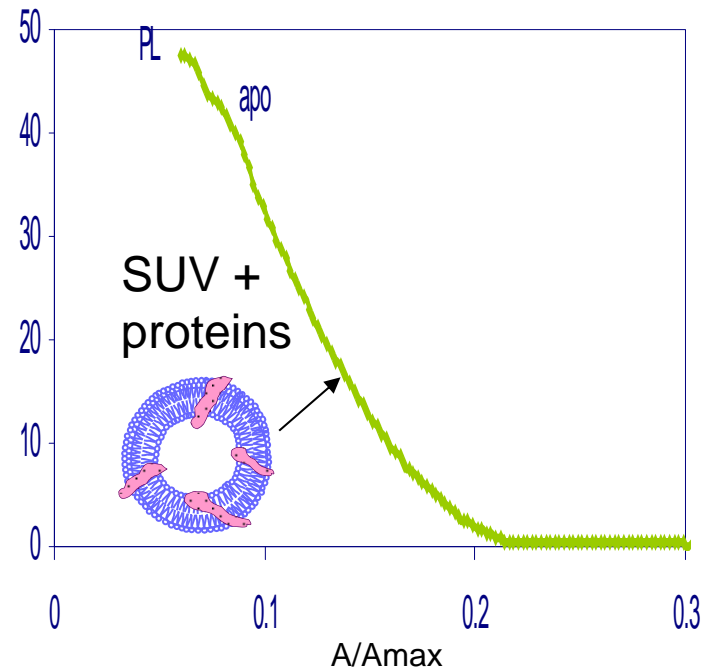
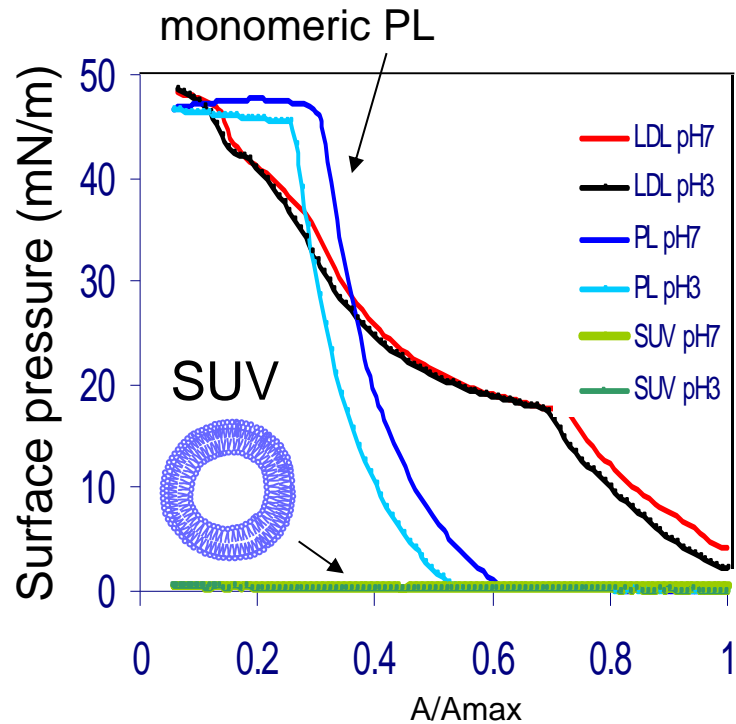
- ➔ blocks: presence of lipids
- ➔ rough: proteins



# Shear rheology



# Biomimetic study

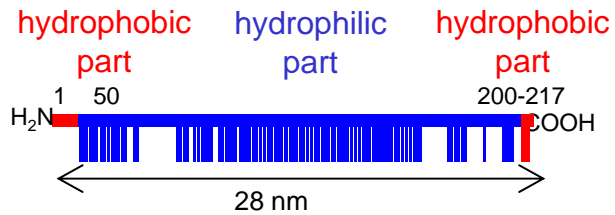


- monomeric PL give the same transition than that observed with LDL
- PL organized in SUV do not spread at the interface

- the biomimetic model (with inserted proteins) spread very rapidly

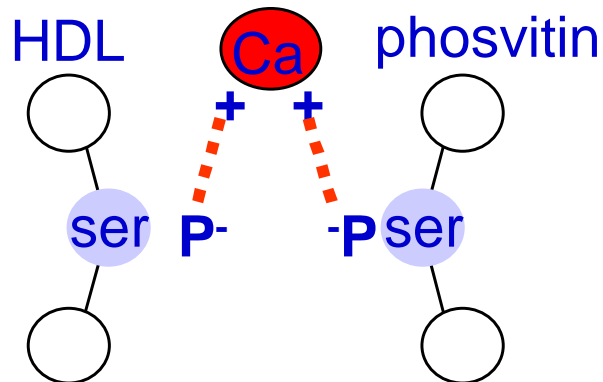
- proteins serve as an anchorage point before denaturation and then LDL spreading at the interface

# Phosvitin characteristics

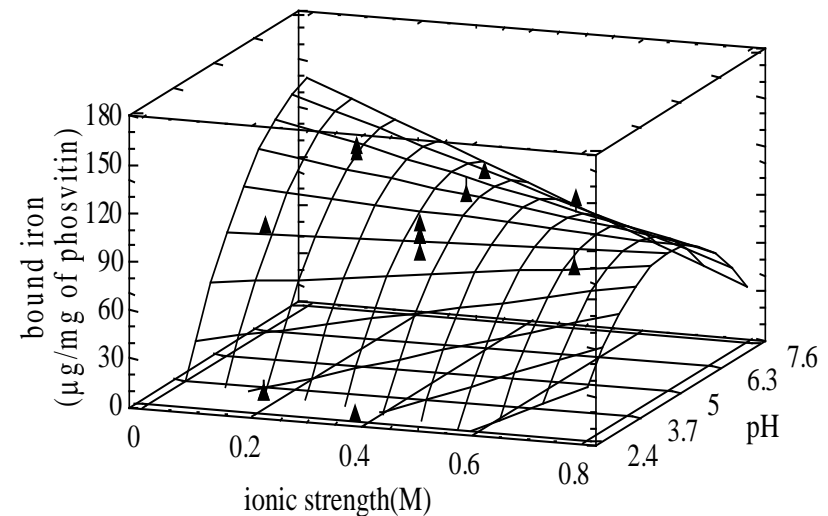


50% phosphorylated serines  
 8% hydrophobic a.a at the two extremities  
 Highly charged tribloc model (-220 mv)

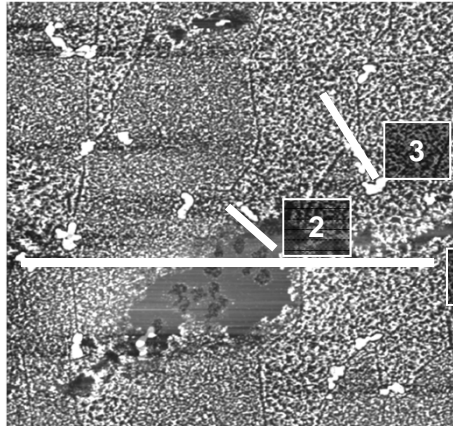
## Granular structure



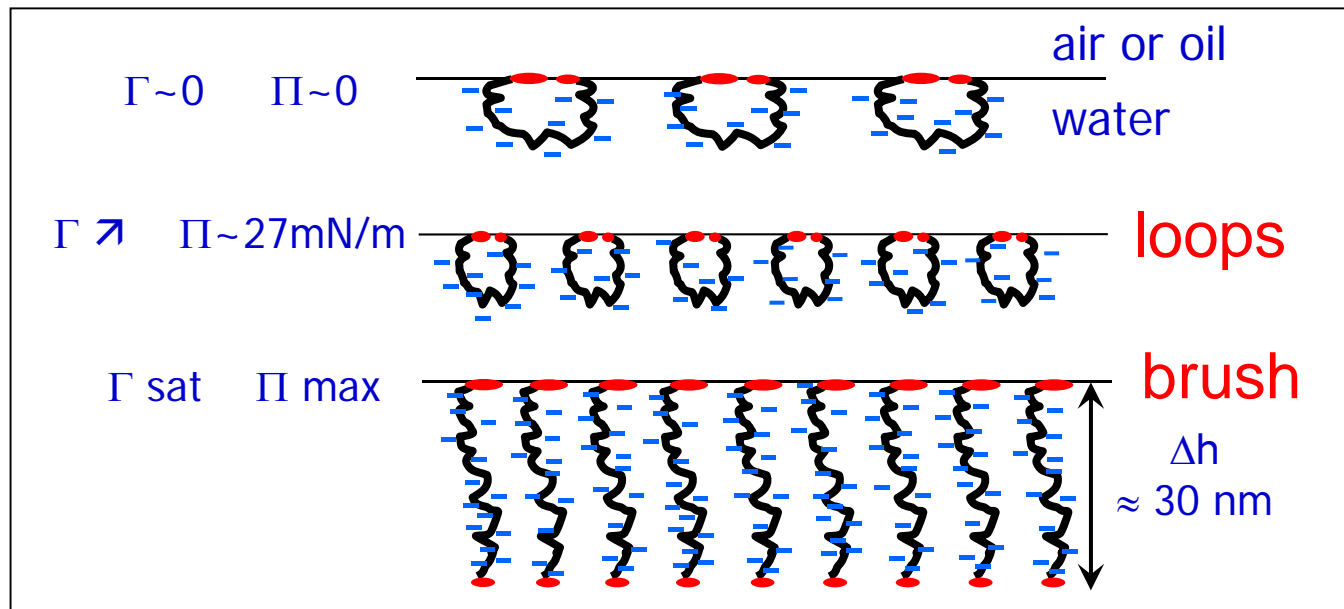
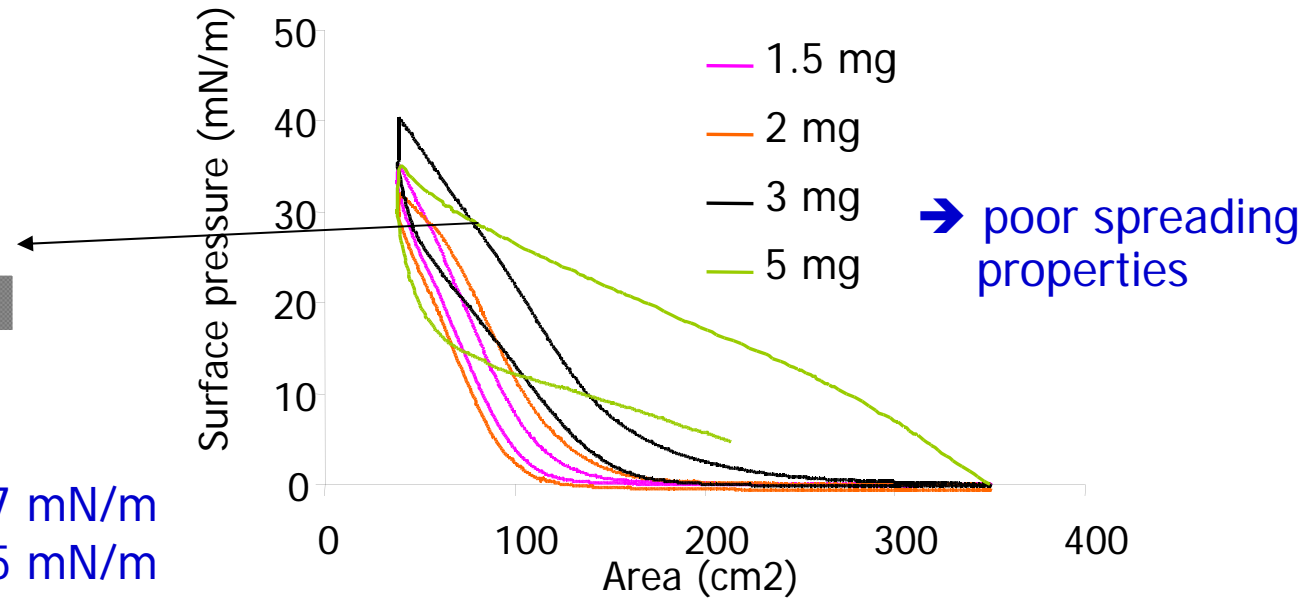
## Metal chelation



# Phosvitin at an interface



$\Delta h = 25\text{-}30 \text{ nm}$  at  $\Pi \sim 27 \text{ mN/m}$   
 $\Delta h = 12\text{-}14 \text{ nm}$  at  $\Pi \sim 15 \text{ mN/m}$



Belhomme et al., 2007, *Food Hydrocolloids*, 21, 896–905

Belhomme et al. 2008, *Colloids and Surfaces B: Biointerfaces*, 63, 12–20

# Highlights

- relevance of supramolecular organisation LDL through interactions between amphiphilic apoproteins and phospholipids
  - this structure allows the transport through the aqueous phase until the interface of these non soluble amphiphilic species where they spread
  - proteins are essential for the initial adsorption and disruption of LDL at the interface, allowing the adsorption of proteins and phospholipids in different mixed layers
  
- surface active soluble granules are in reality constituted by micelle-like aggregates of 100-200 nm
  - in purified form phospholipin constitutes loops or brushes depending on environmental conditions

# Impact of various processes on structures and functionalities

1 dynamic high-pressure

2 static high-pressure

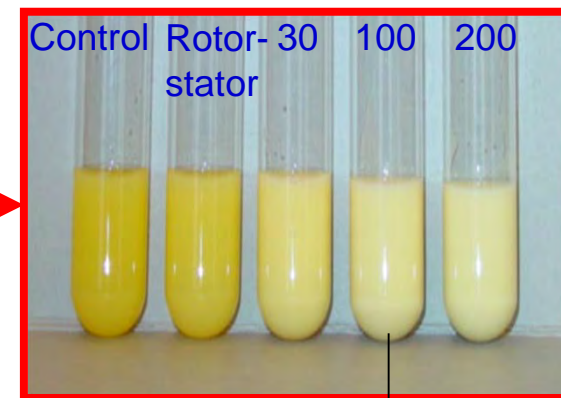
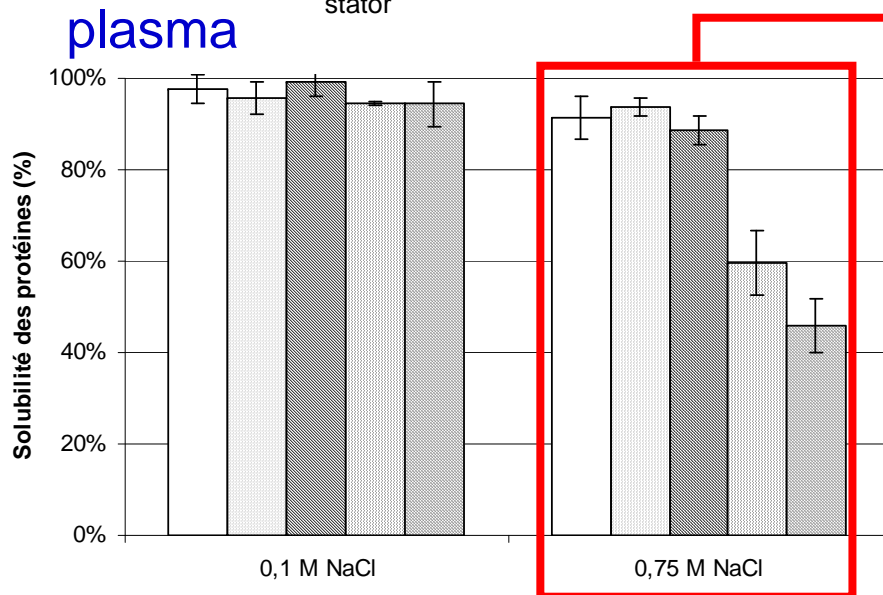
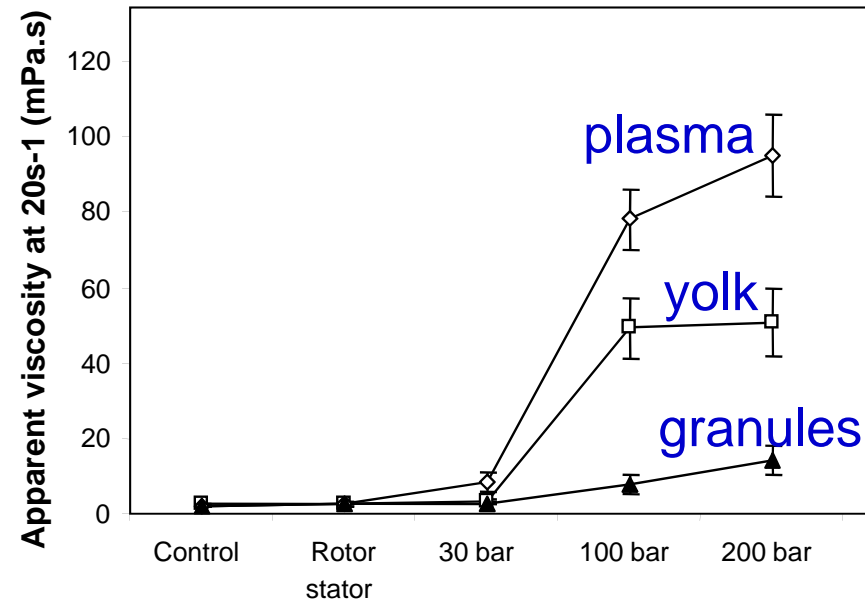
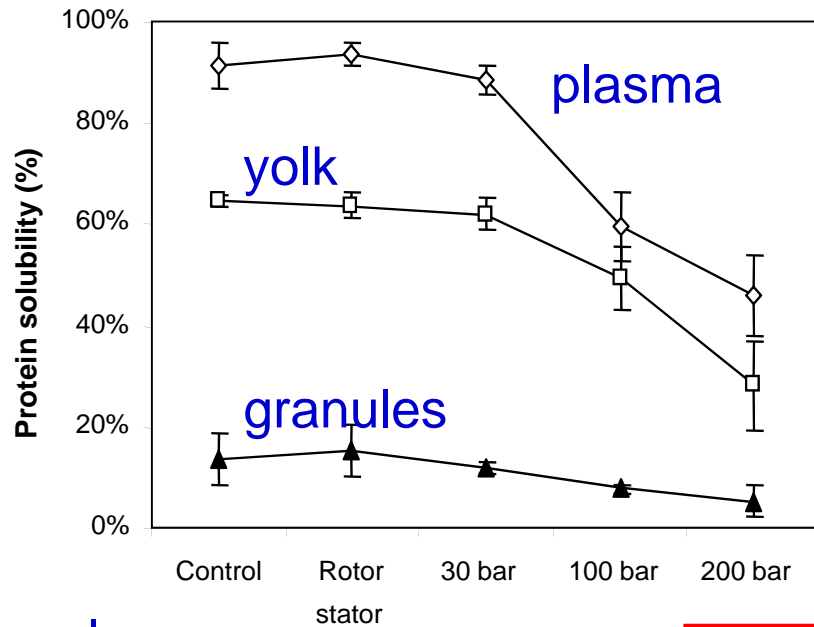
3 heat treatments

4 mechanical treatments

5 gastro-intestinal tract

# 1 Dynamic high-pressure treatments

pH 4 and 0,75 M NaCl

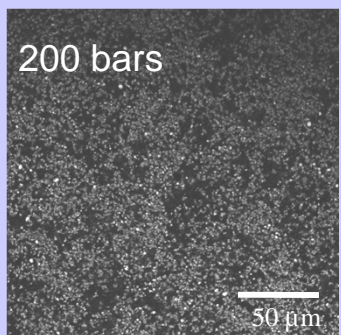
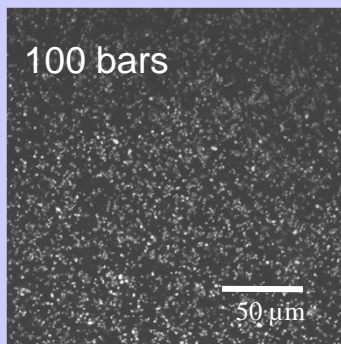
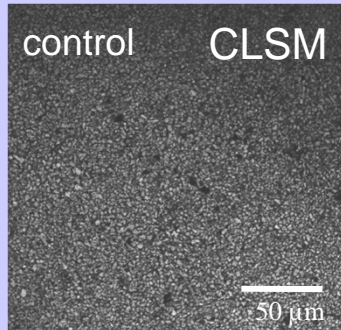


pseudo-gel !

# Dynamic high-pressure treatments

## Granules

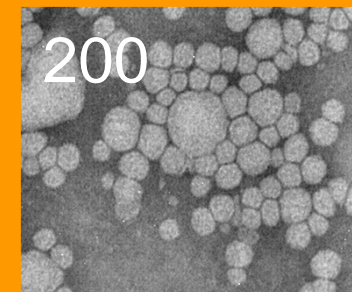
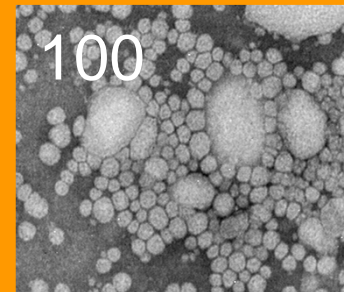
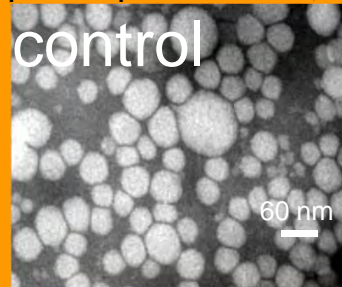
pH 4 and 0,75 M NaCl



→ structuration of granules under HP

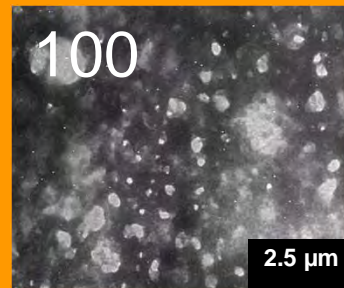
## Plasma → LDL

pH 7 / pH 4 and 0,1 M NaCl



→ intact structures

pH 4 and 0,75 M NaCl

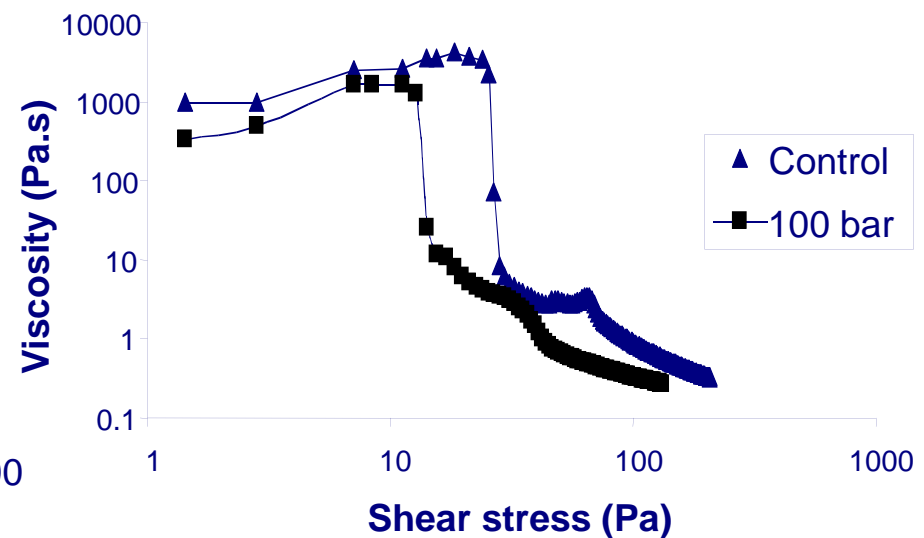
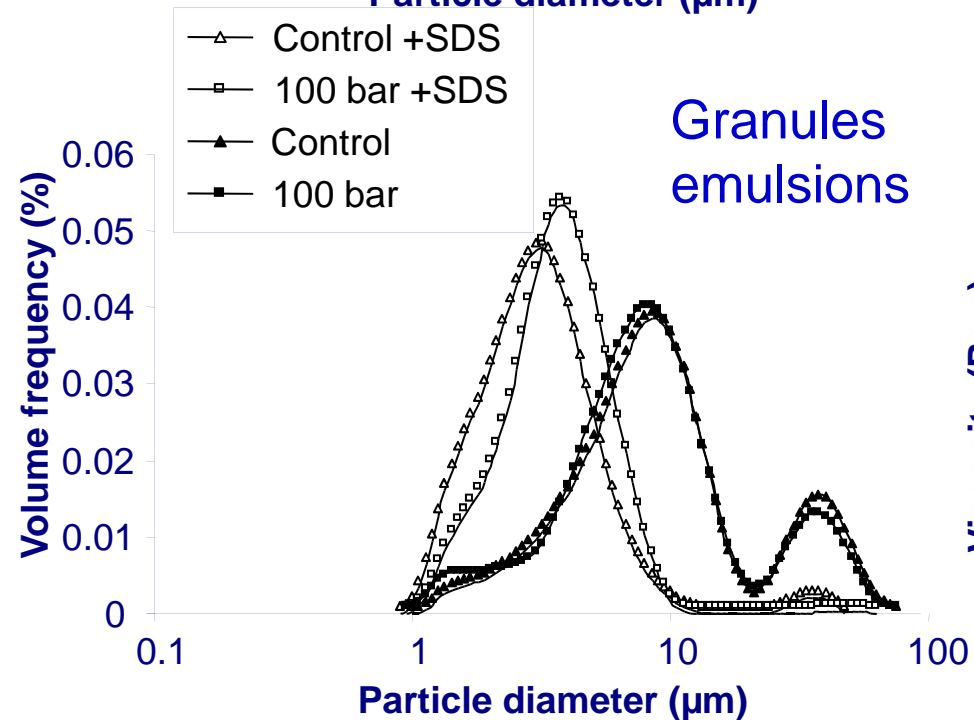
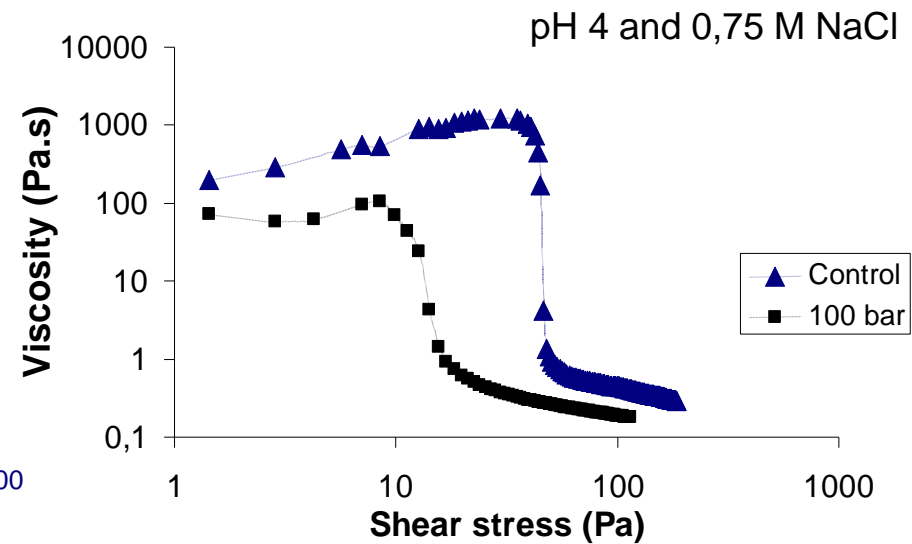
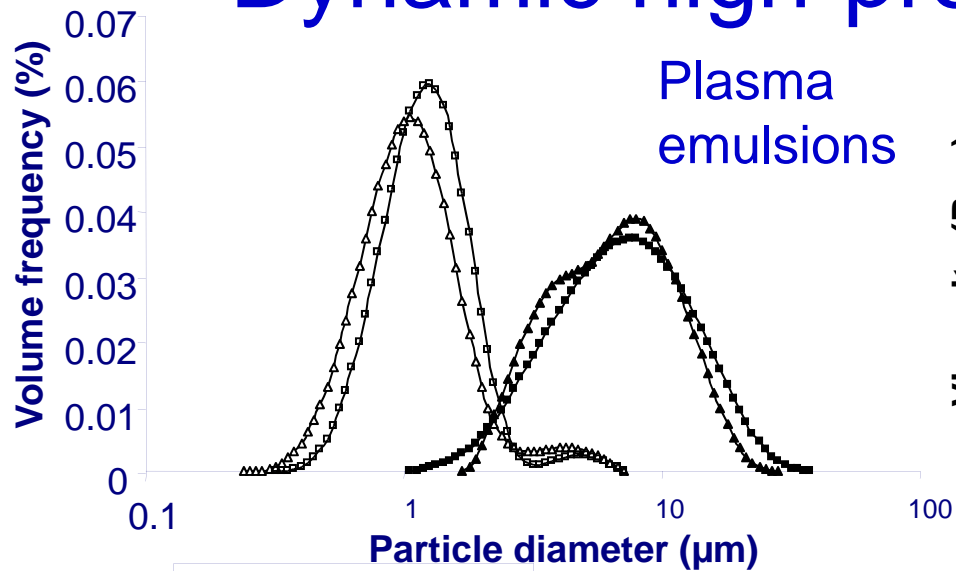


→ disruption, re-organisation, gelation

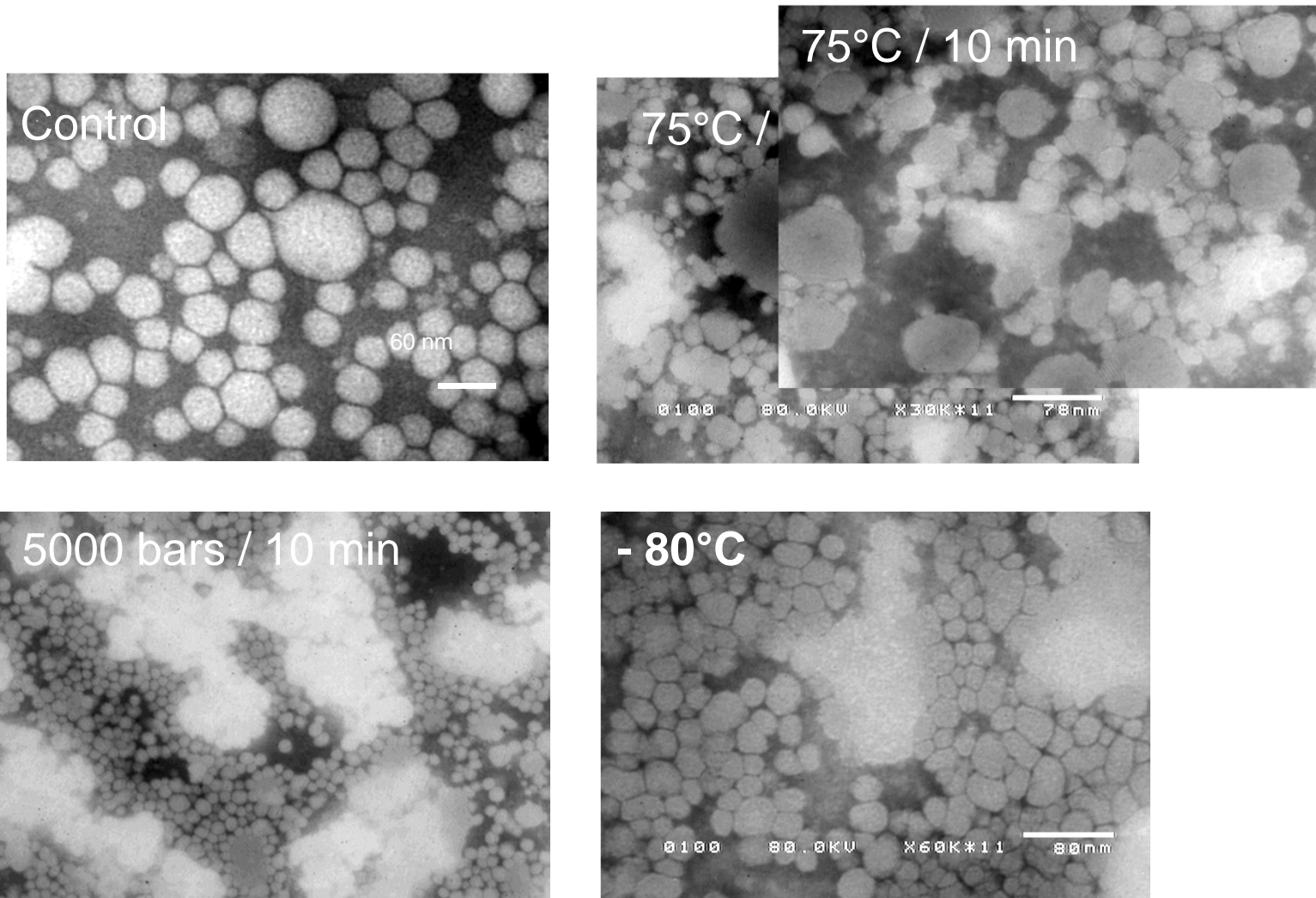
└─→ environment dependent



# Dynamic high-pressure treatments

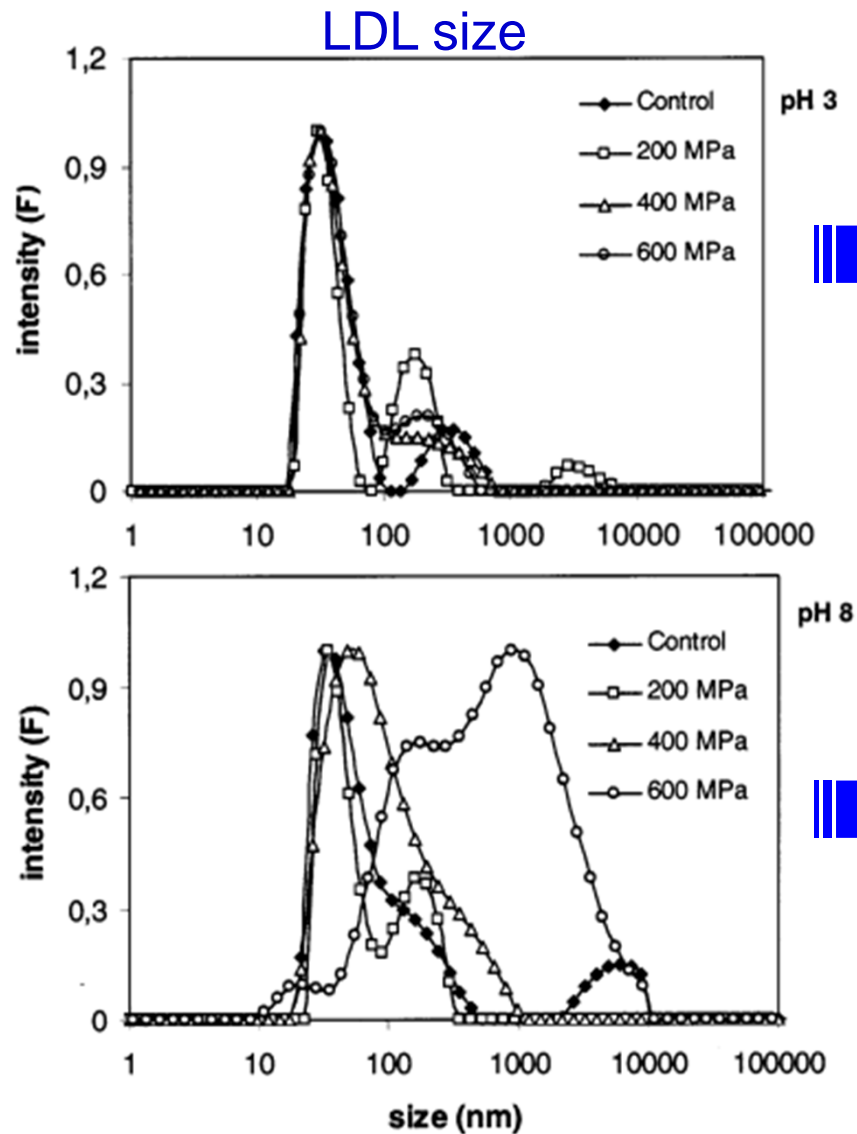


# Different treatments on LDL

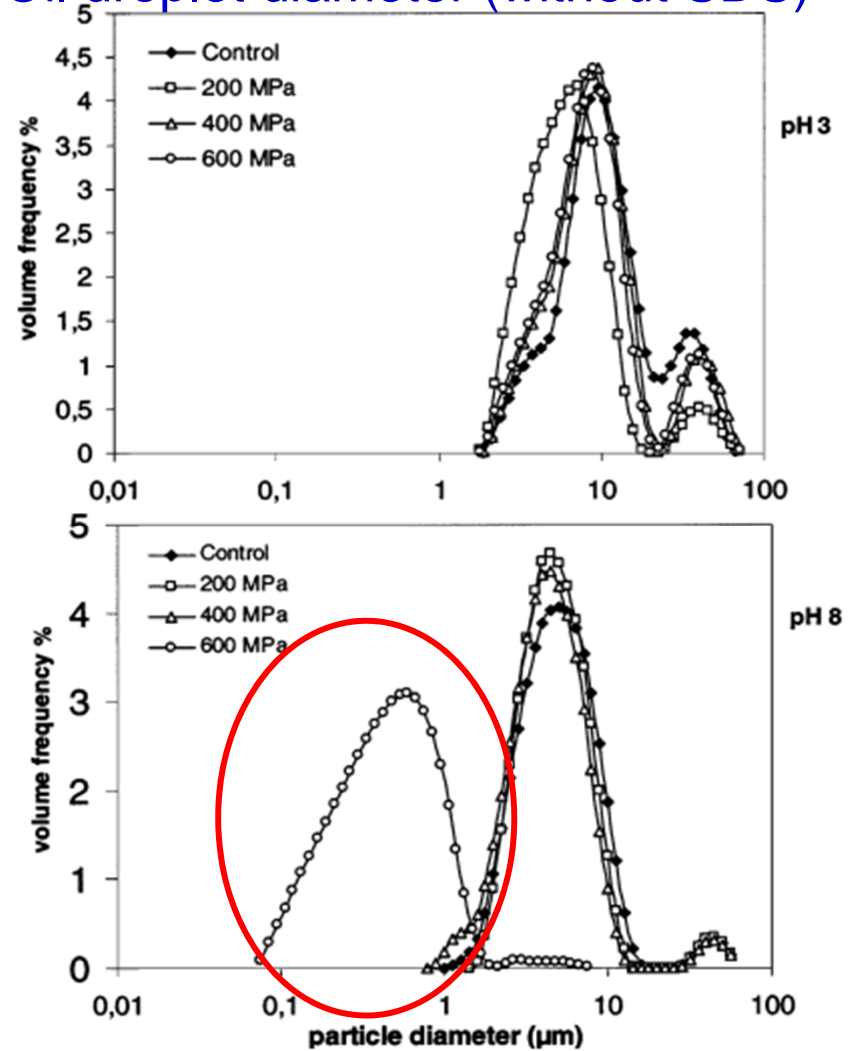


→ disruption and re-arrangements under these different treatments

## 2 Static high-pressure on LDL



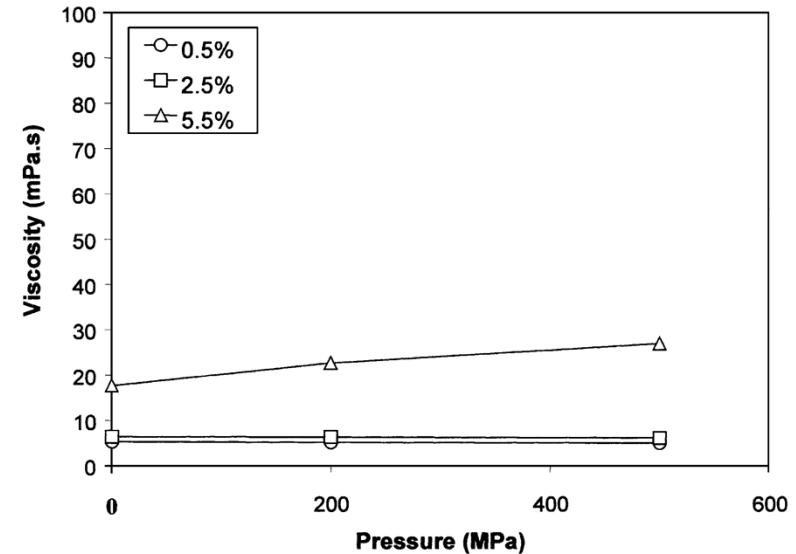
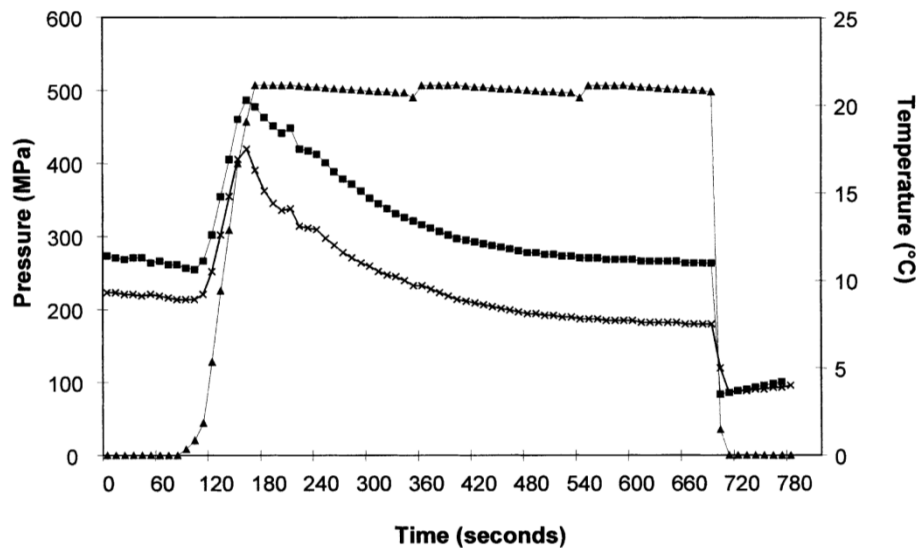
Oil droplet diameter (without SDS)



→ modifications of LDL increase functionality from 600 MPa

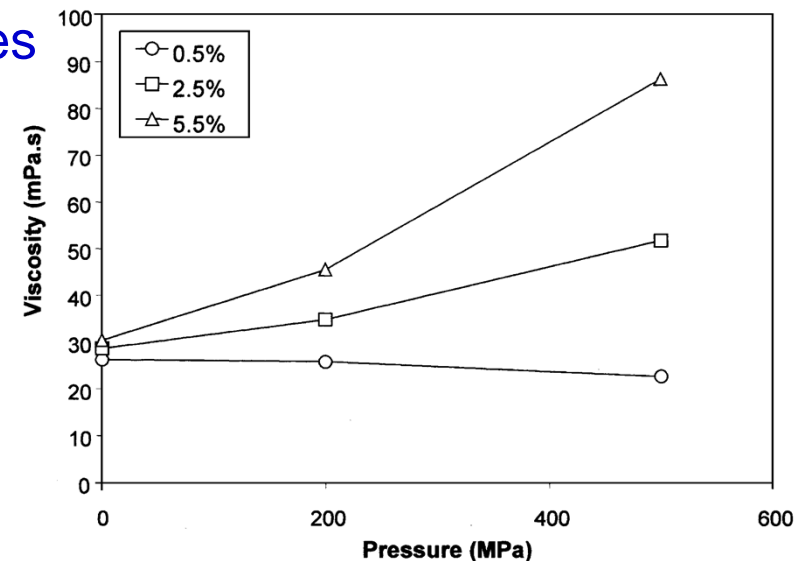
# Static high-pressure on LDL emulsions

pH 3



- HP treatment of yolk emulsions provides suitable elimination of total microbial flora
- no change of physicochemical properties at pH 3
- increase of viscosity at pH 7 → droplet flocculation

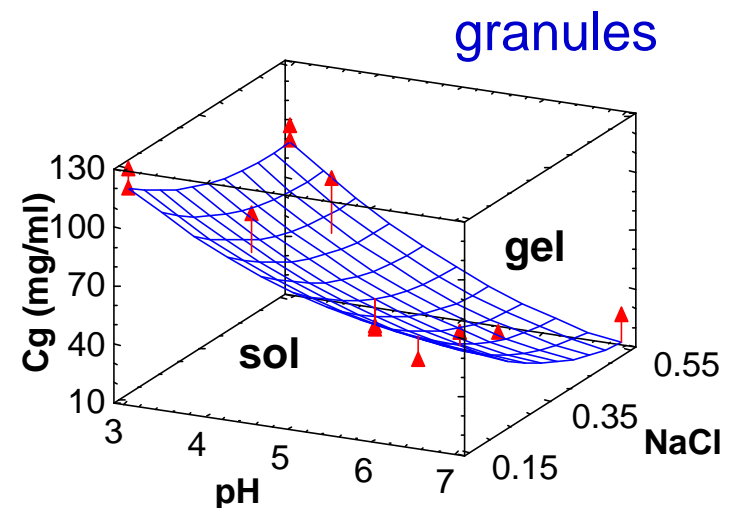
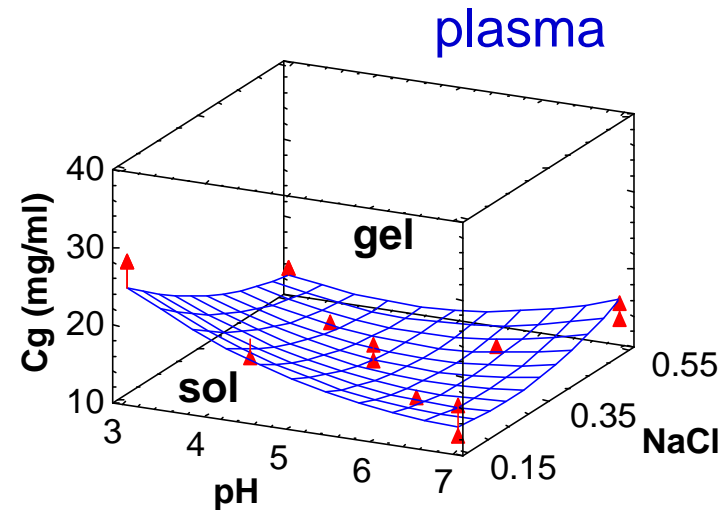
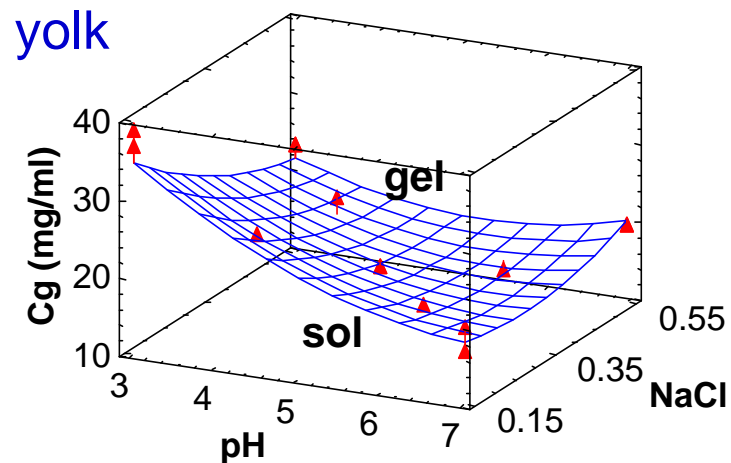
pH 7



### 3 Thermal treatment

Heating solutions of yolk, plasma and granules at 80°C

→ phase diagrams



- plasma much more sensitive
- depends on conditions for granules

Ledenmat et al., 1999, *J. Food Sci.*, 64, 194-197

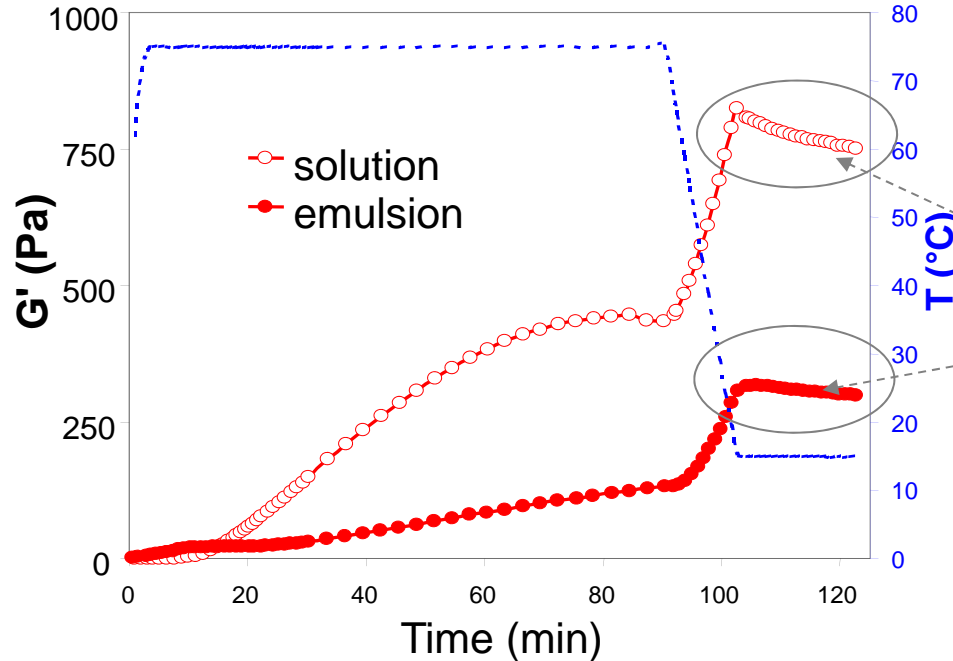
Ledenmat et al., 2000, *J. Food Sci.*, 65, 581-584

pH 7,0  
NaCl 0,55 M  
protéines 55 mg/ml

# In solution or in emulsion ?

emulsions H/E 30:70  
 $d_{3,2} \sim 1 \mu\text{m}$

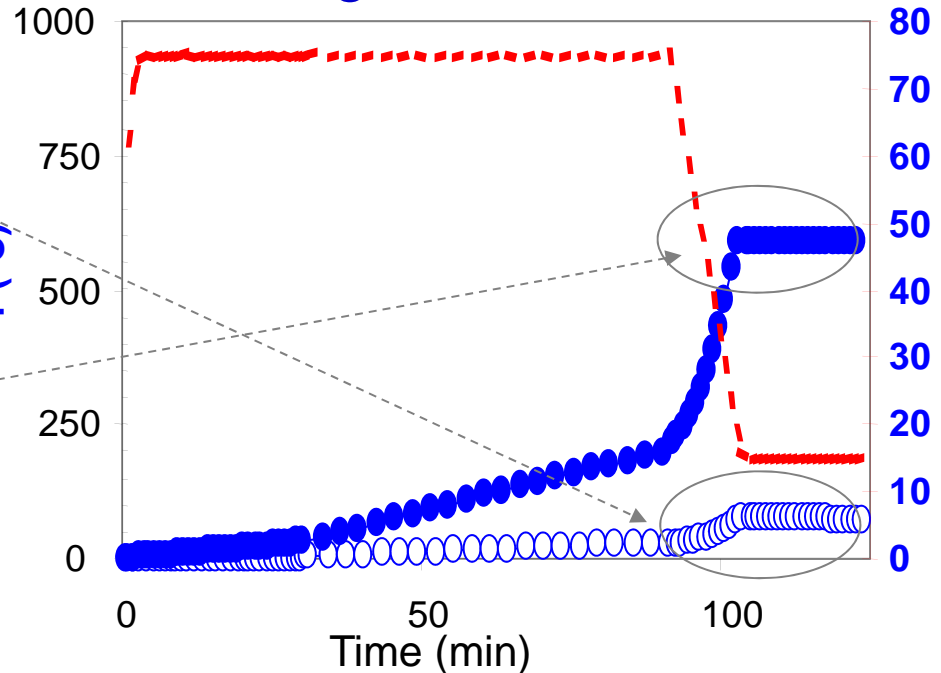
plasma (or yolk)



inactive fillers

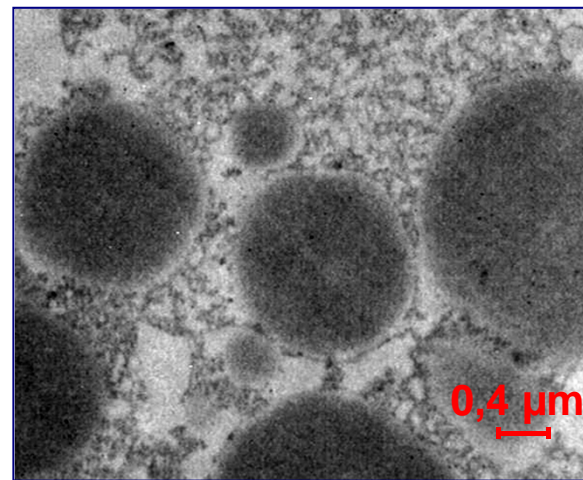
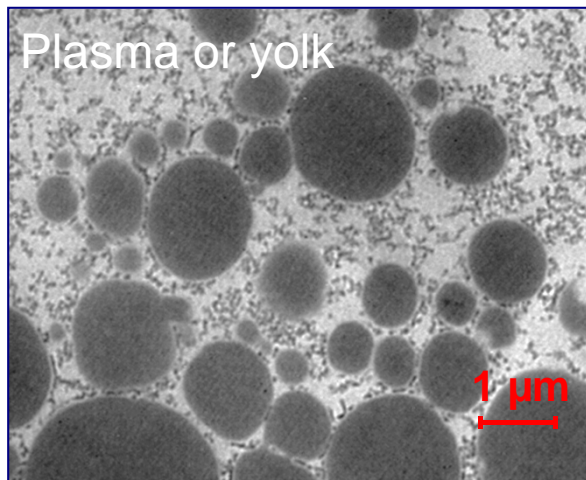
- weakening of gel due to  
↳ prot. conc. and lack of droplet-droplet interactions with plasma constituents

granules

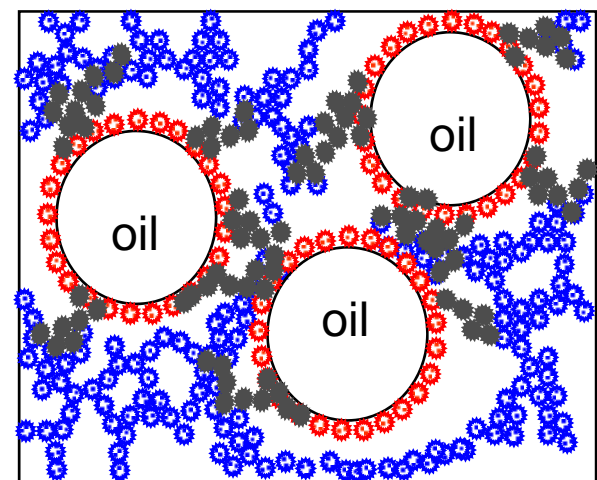
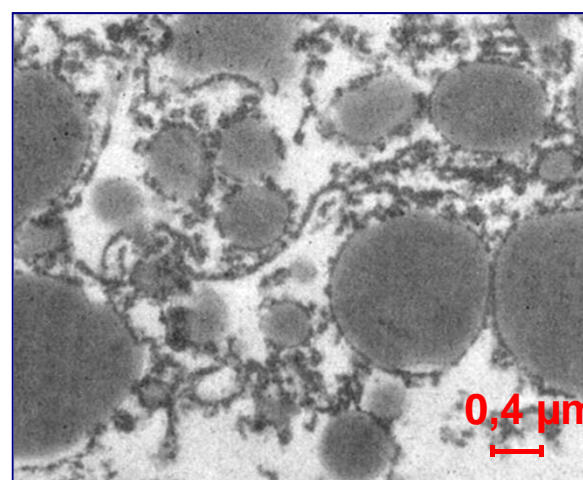
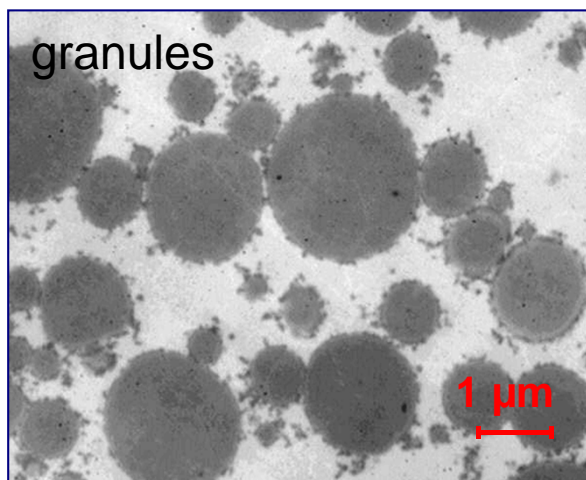
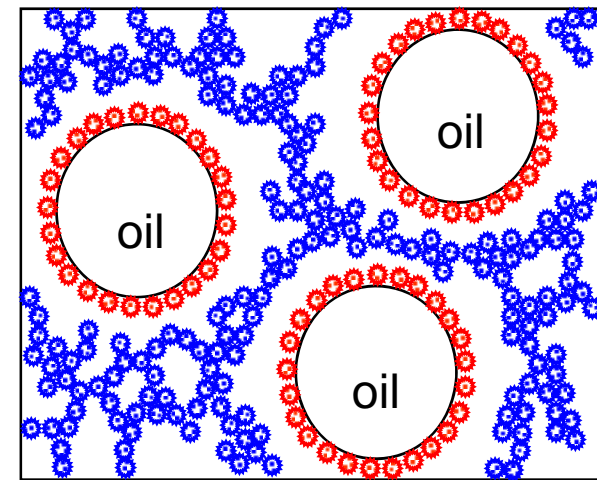


active fillers

- re-inforcement of gels due to droplet-droplet interactions through granules proteins



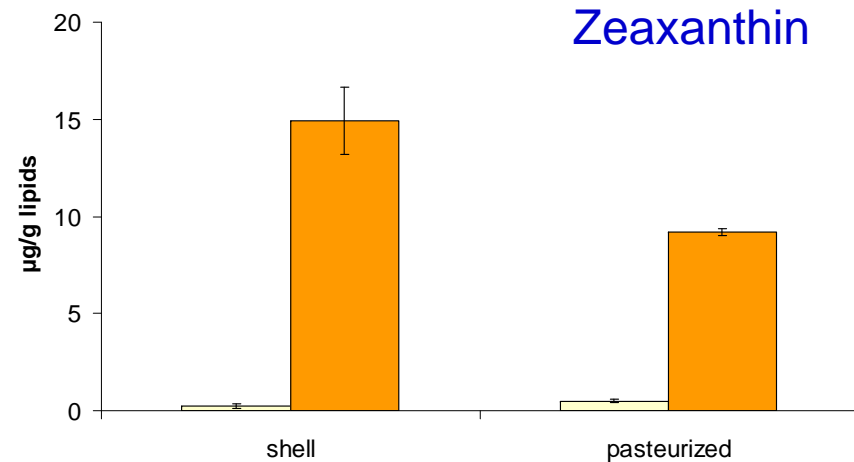
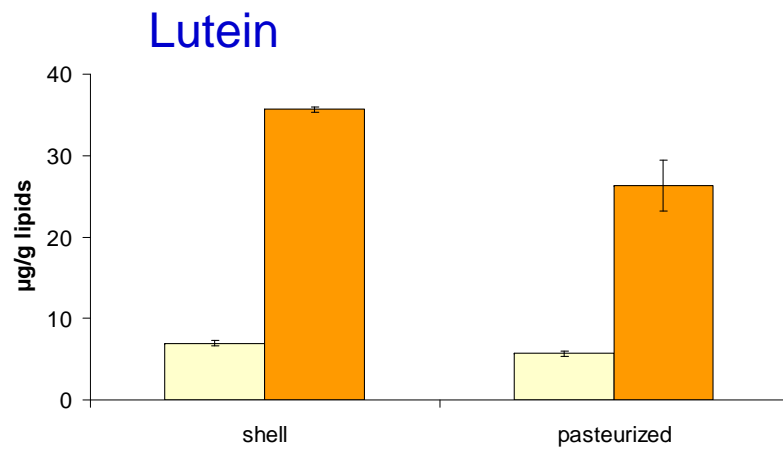
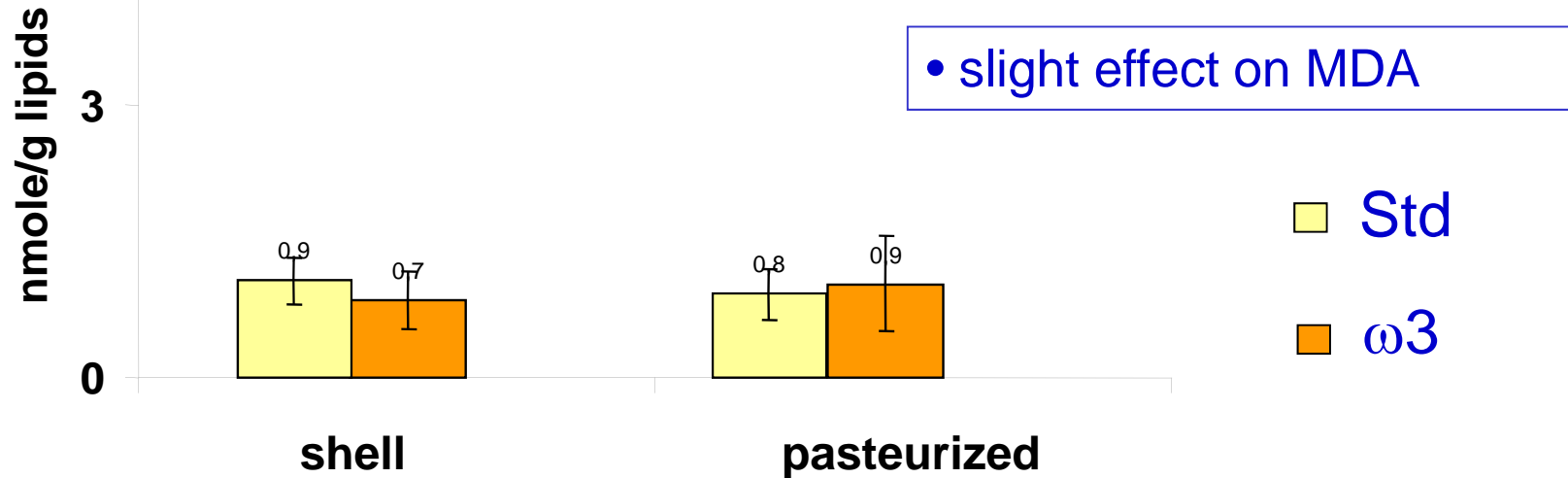
## Inactive fillers



## Active fillers

# Pasteurisation and lipid oxidation

Secondary products: malondialdehydes (MDA)

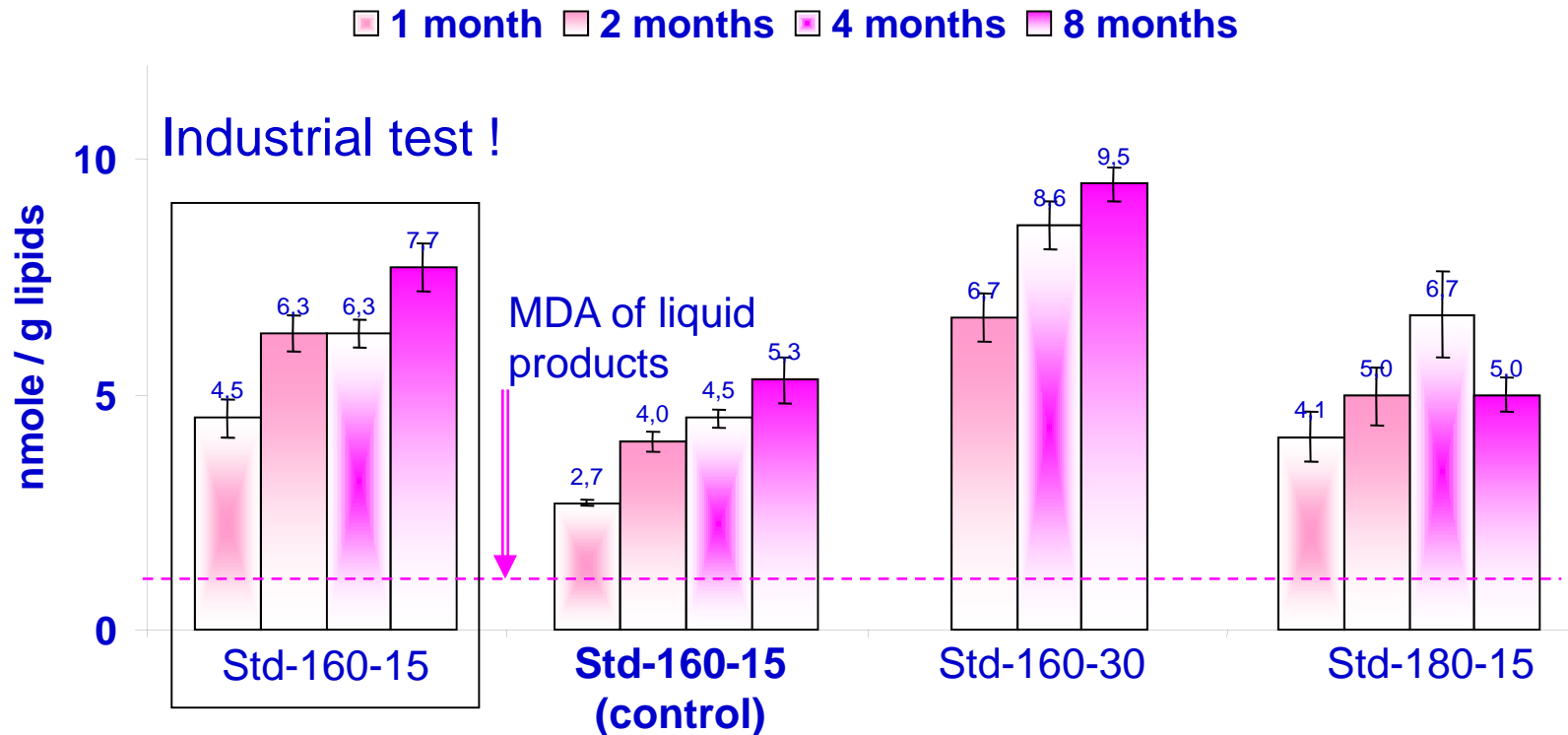


• pasteurization:  $\searrow$  carotenoids  $\rightarrow$  protective effect



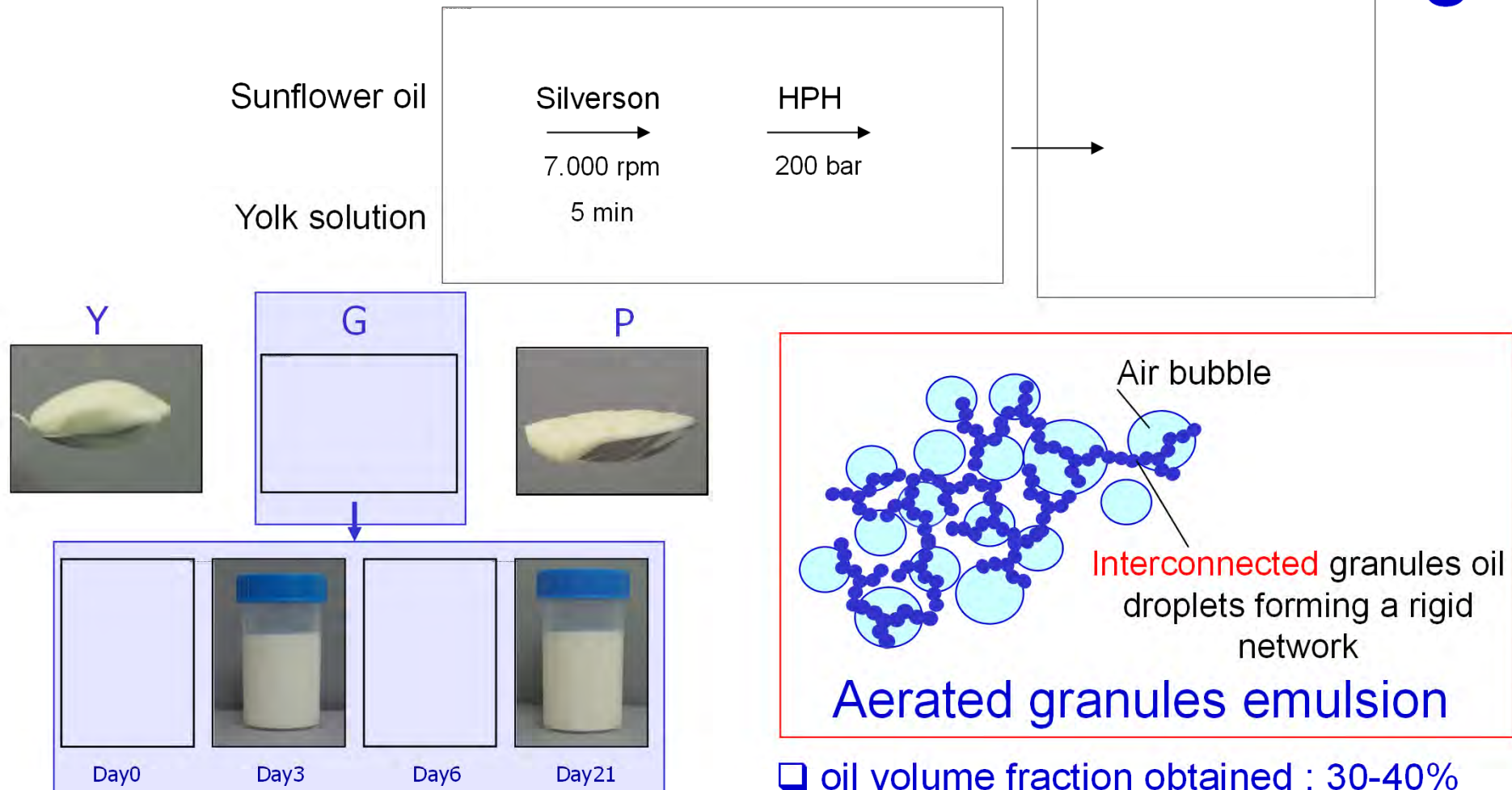
# Spray-drying and lipid oxidation

## Secondary products (MDA)



- ↗ MDA / liquid → ↗ of oxidation due to spray-drying
- ↗ MDA with T° spray-drying
- important ↗ MDA with storage T° and storage time
- differences between pilot and industrial processes
- levels “reasonable” ! → no sensorial degradation

# 4 Mechanical treatment: foaming



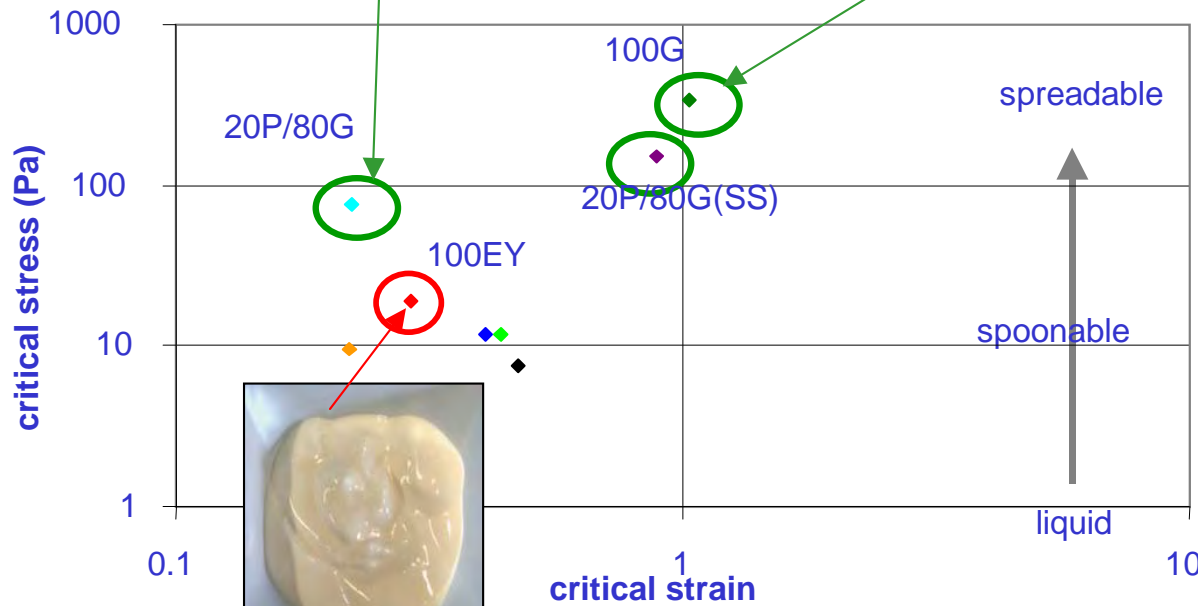
- ❑ foams made with granules emulsions are the most promising (texture and stability)
- ❑ no coalescence observed after foaming

- ❑ oil volume fraction obtained : 30-40% for mayonnaise-like texture → low-fat mayonnaise
- ❑ foam stability favored by high elastic modulus and high critical stress of emulsions

# Sequential re-incorporation of treated granules and plasma



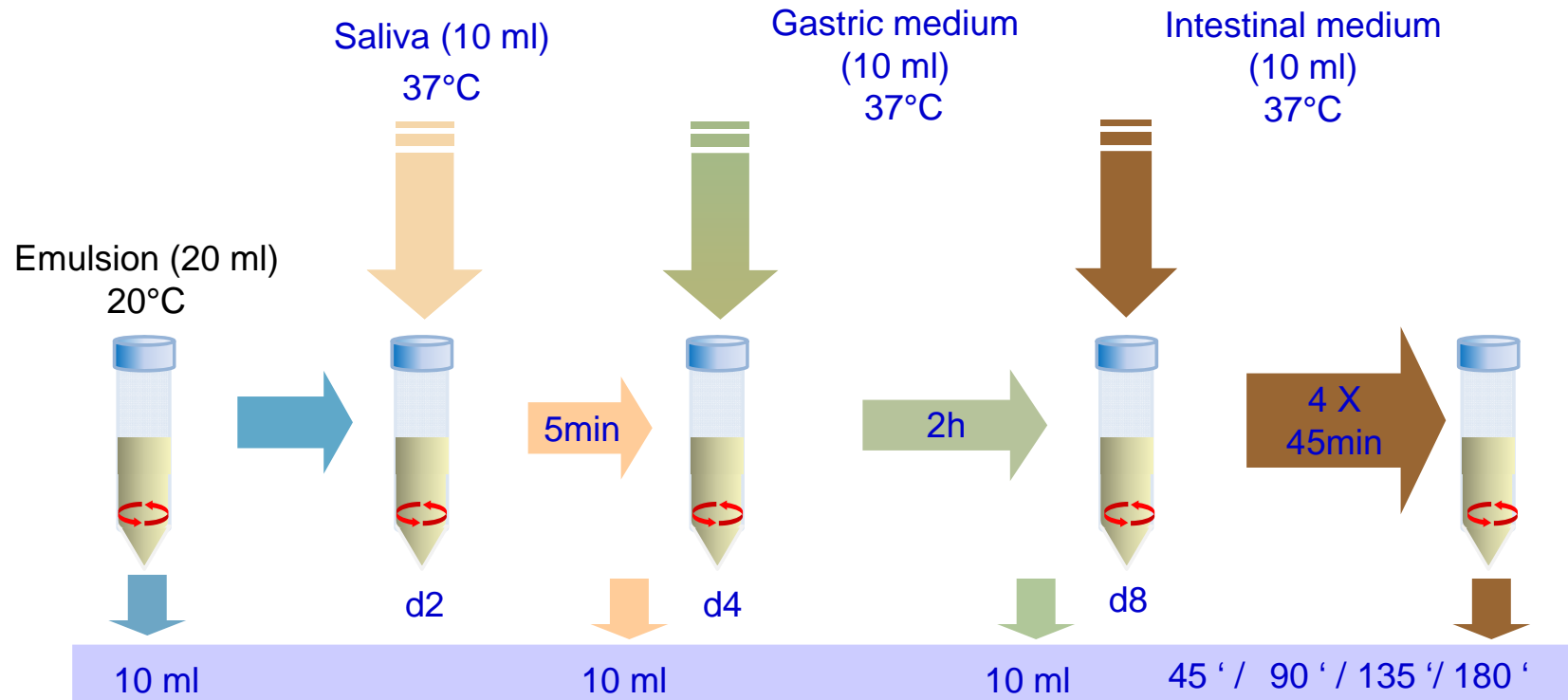
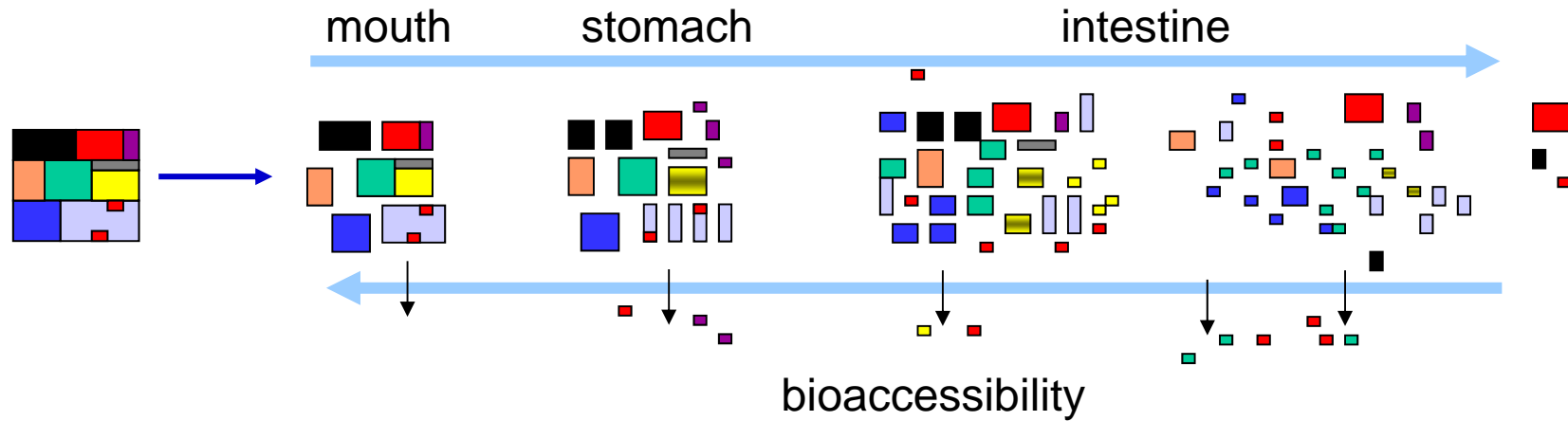
Stress sweep in oscillatory flow  
 ⇒ Cross over point  $G'' = G'$  ( $\tan \delta = 1$ )



⇒ oil fraction: 60 %  
 ⇒ granules are forming a remarkable strong network (firmness 275g vs 120g for yolk)  
 ⇒ the higher the level of granules, the more spreadable is the emulsion system

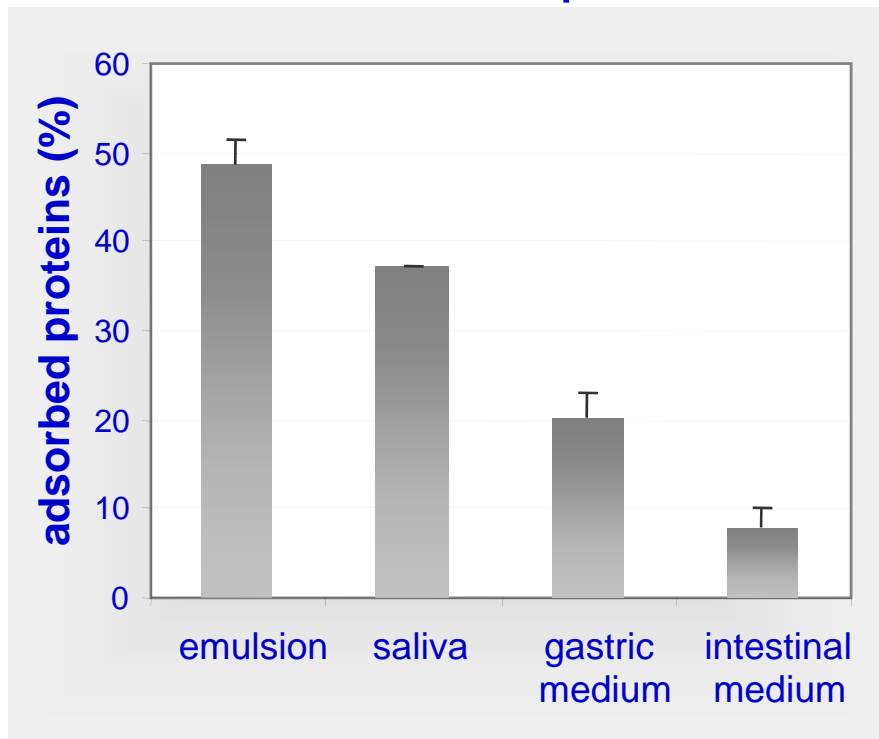
- ◆ 100Ey      ◆ 100P      ◆ 100G      ◆ 20P/80G
- ◆ 20P/80G(SS)    ◆ 80P/20G    ◆ 80P/20G(SS)    ◆ 80P/20G(HPH)

# 5 GIT: Food deconstruction

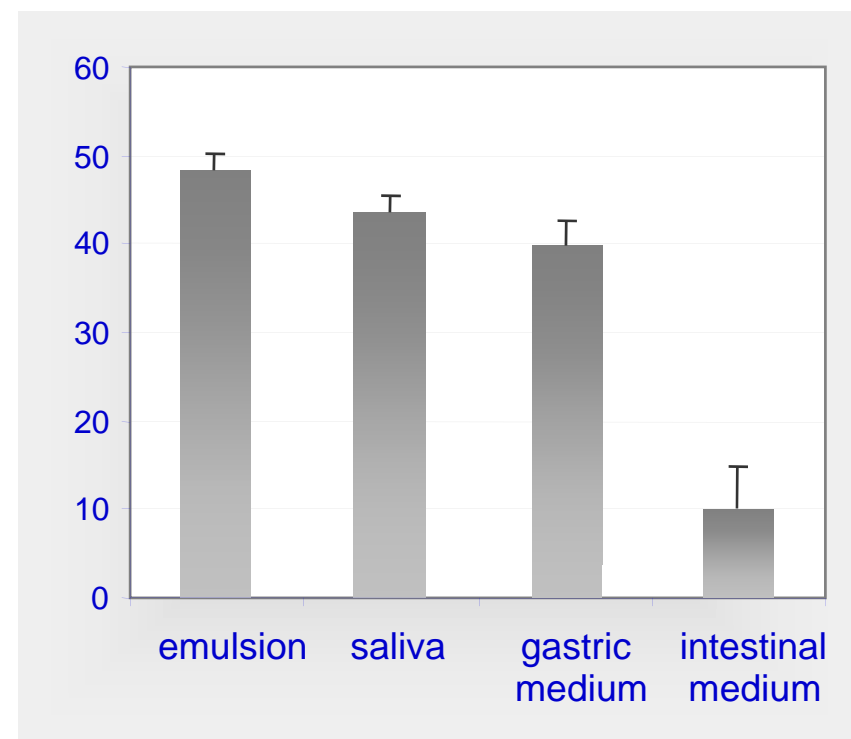


# Adsorbed proteins on the interface along the GIT

amaranth pH2



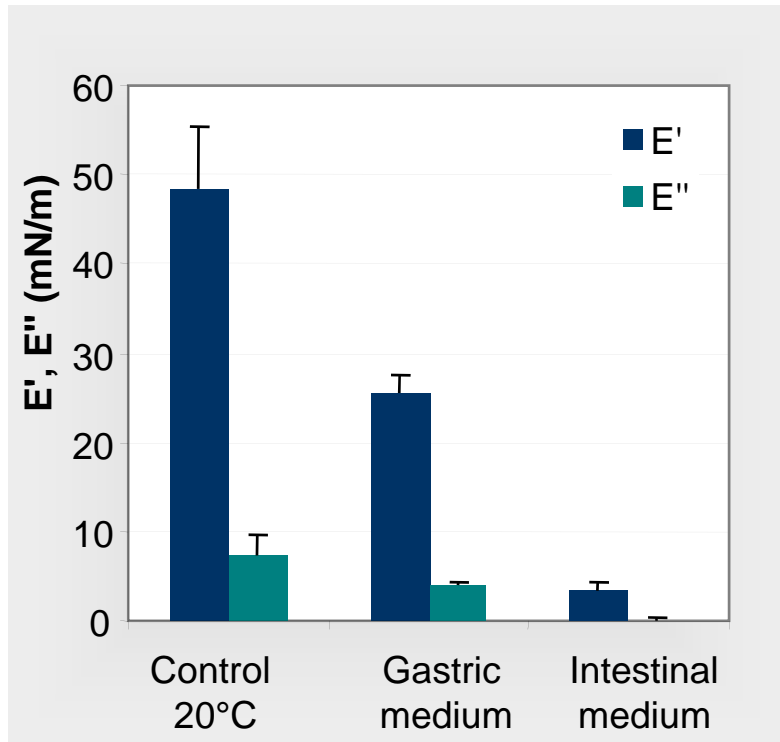
LDL pH3



- amaranth pH2: a regular decrease of adsorbed proteins
- LDL pH3: a delay until intestinal phase

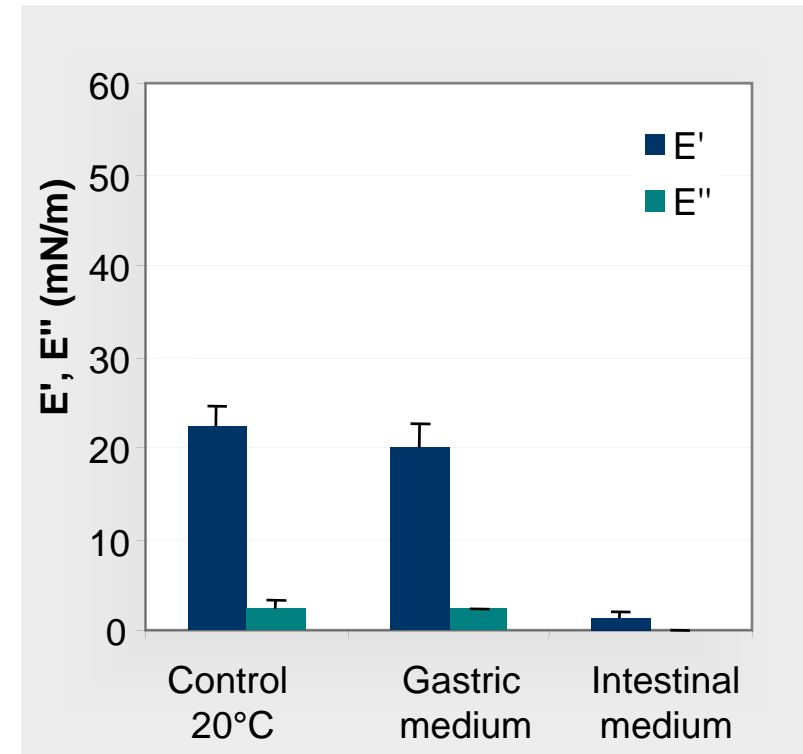
# Dilatational rheology of interface

amaranth proteins pH2



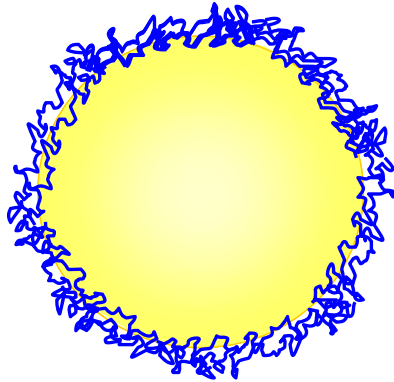
- higher E' for control amaranth interface
- regular decrease of E' for amaranth interface

LDL pH3



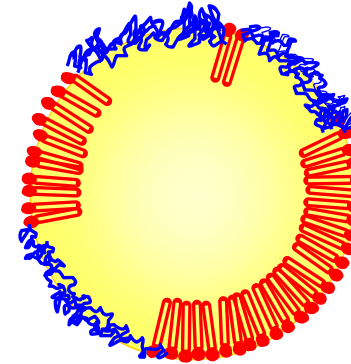
- maintain of E' after gastric medium for LDL interface
- total change of rheology in intestinal medium

film with pure proteins



- ❑ highly elastic film rapidly desorbed/digested and destructured (coalescence from gastric phase)
- ❑ no competition with biliary salts
- ❑ high structuration is not the unique response

proteins and lipids from yolk LDL



- ❑ low viscoelasticity but high resistance to coalescence and delay in film desorption and destructureation (at pH3)
- ❑ combination of charged and mixed film (proteins and surfactants: lecithins)
- ❑ possible competition with biliary salts

# Conclusions

- ❑ importance of natural micro- and nano- structures of egg yolk constituents
  
- ❑ clear (and varied) impacts of processes on physical and chemical properties  
→ influence on functionalities
  
- ❑ understanding of combination structures X medium X treatments is essential
  
- ❑ processes as **tools** to design new properties for food and non food applications
  - protective structures
  - targeted delivery
  - smart interfaces
  - ...