NEW APPROACH FOR THE CHARACTERISATION OF DAIRY PROTEIN FOAMS STABILITY

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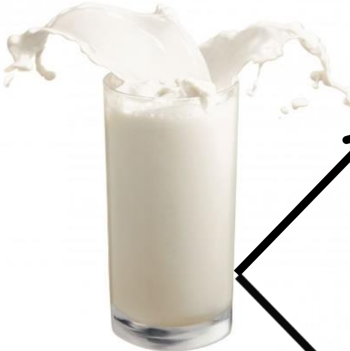
Dairy foams

- ✓ mechanical properties
- ✓ low density
- ✓ high surface area


example of food foams



bovine milk

whey

cheese

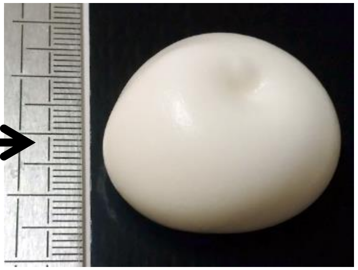
WPI powder

≈ 90 % of proteins

Whey Protein Isolate

deionised water

air



model foam

≈ 50 g/L protein

pH 7.0

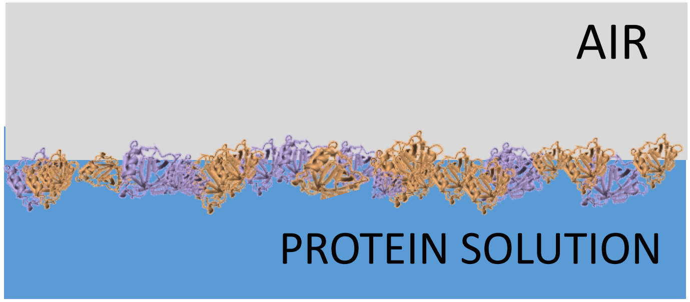
processed

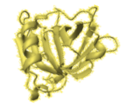
by dry-heating (70 °C)

≠ *pH* and dry-heating time (powder state)

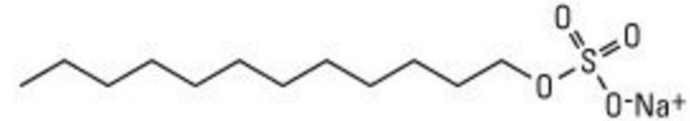
= as a way to change surface properties

LMW surfactants vs proteins

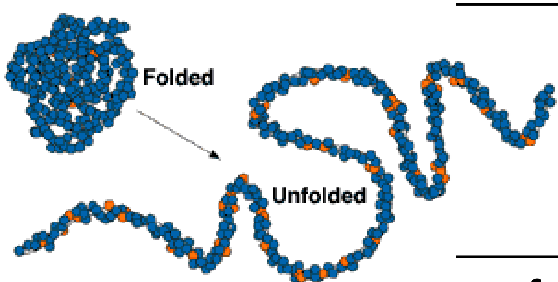




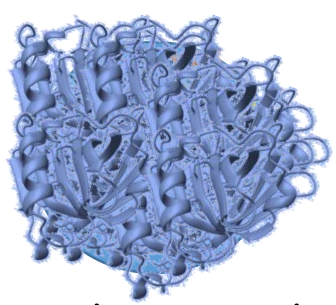
β-lactoglobulin
M = 18 000 g/mol



Sodium docecyl sulfate SDS
M = 288 g/mol



protein unfolding



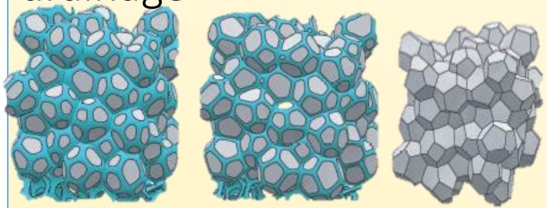
protein aggregation

Proteins	Low Molecular Weight LMW surfactants
unfolding self association (interface + bulk)	no conformational changes upon adsorption
high surface visco-elasticity	low or 0 surface visco-elasticity
adsorption ≈ irreversible	adsorption reversible

(Bos and van Vliet, 2001)

Stability in food sciences

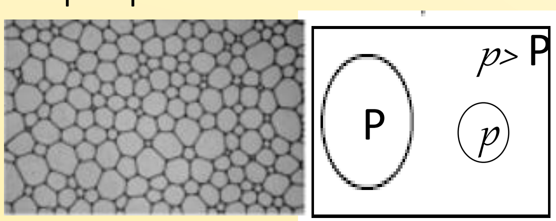
drainage



* flow of liquid under the gravity through PB

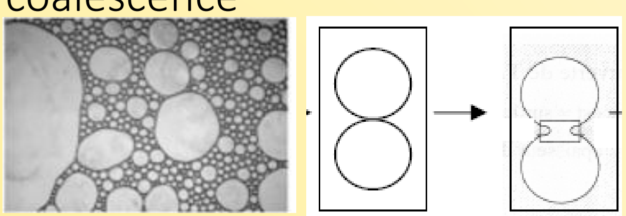
↘ foam liquid fraction Ø

disproportionation



* transfer of gas (Laplace's law)

coalescence



* fusion after liquid film rupture

↗ bubble coarsening R

instability mechanisms

In food sciences :
global stability = integrative of all of them

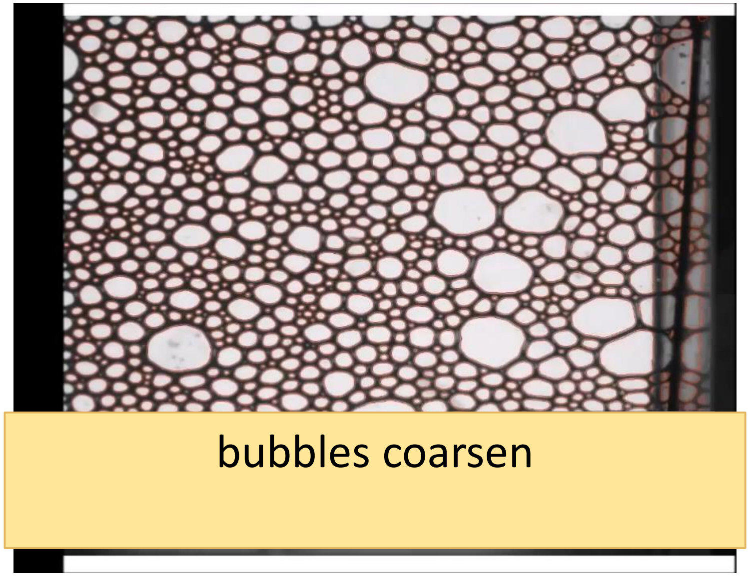
**the time at which the first drop drained*
**the cumulative weight of drained liquid as a function of time*

- ❑ improvement of protein foam characterisation by **transposition of foam physics**
- ❑ understanding the respective relation of these instability mechanisms with **surface properties** may help to understand **protein foam stability**
- ❑ surface properties : planar, semi-static conditions

What about the protein foam dynamics ?

Foam dynamics for proteins

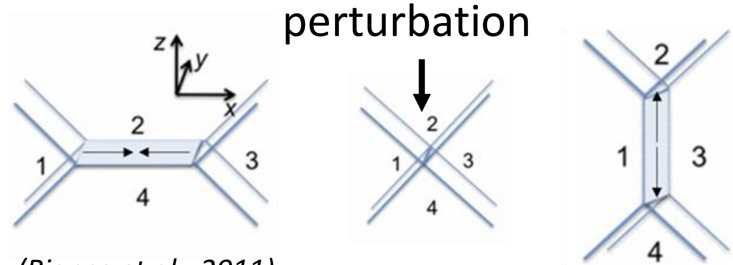
(*Krüss*)



bubbles coarsen

T1 topological rearrangements

= bubbles neighbour switching



(*Biance et al., 2011*)

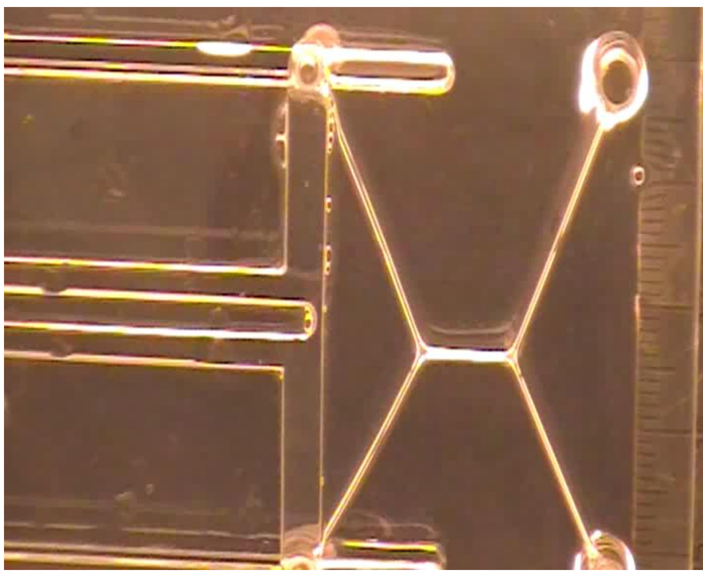
T1 duration

during relaxation process

↘ disproportionation :↘ T1 probability to occur

if T1 occurs : ↗ T1 duration ↘ risk of film rupture (coalescence events) (*Cantat et al., 2013; Biance et al., 2011; Carrier and Colin, 2003; Drenckhan and Langevin, 2010*)

What about protein foams ?

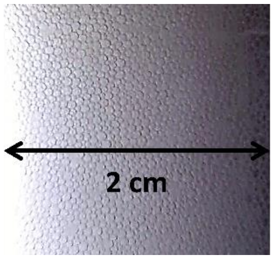


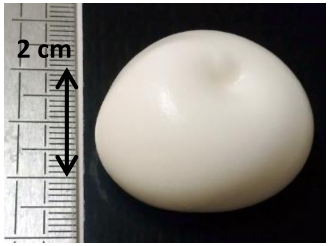
protein T1 relaxation

without co-surfactants

Multi-scale approach

foam stability

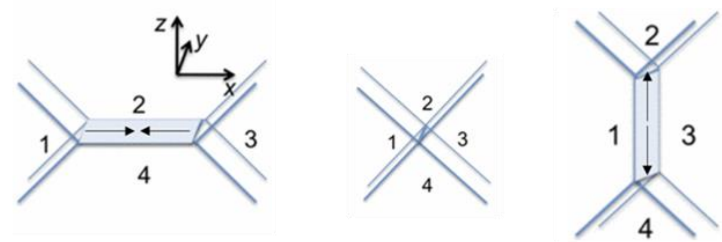




foams by bubbling → drainage exponent

foams by two-syringe → disproportionation coefficient

T1 topological rearrangements

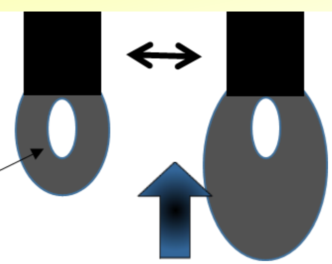


duration of T1 relaxation

50 g/L proteins for all experiments

visco-elasticity

surface rheology



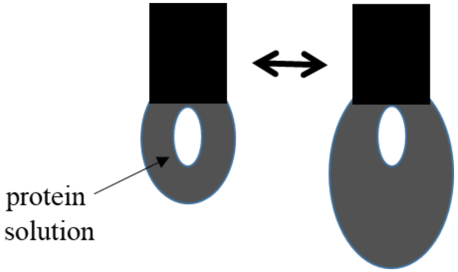
protein solution

proteins (WPI)

Aims of our study
- ❑ new approach for proteins
- ❑ **any correlations ?**

no comments about WPI process effects

Surface properties



area changes by dilatation/compression
frequency = 0.2 Hz
Drop 7 µl ± 0.75 µl

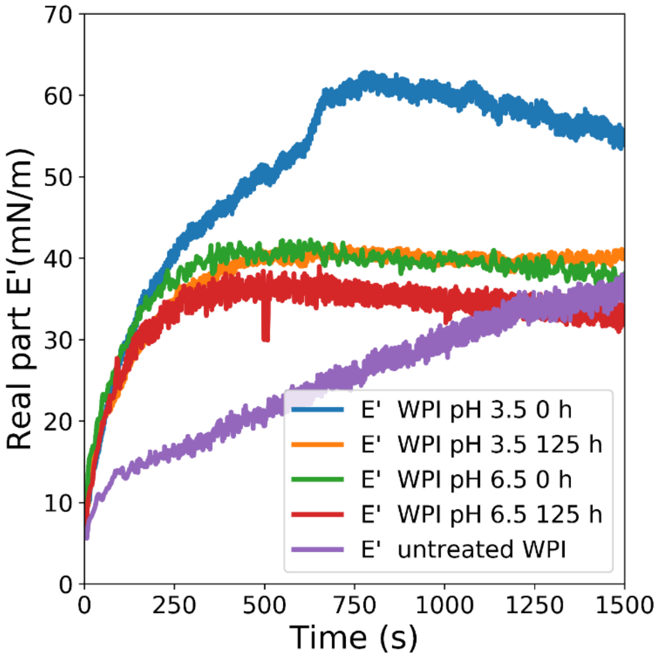
pendant drop method

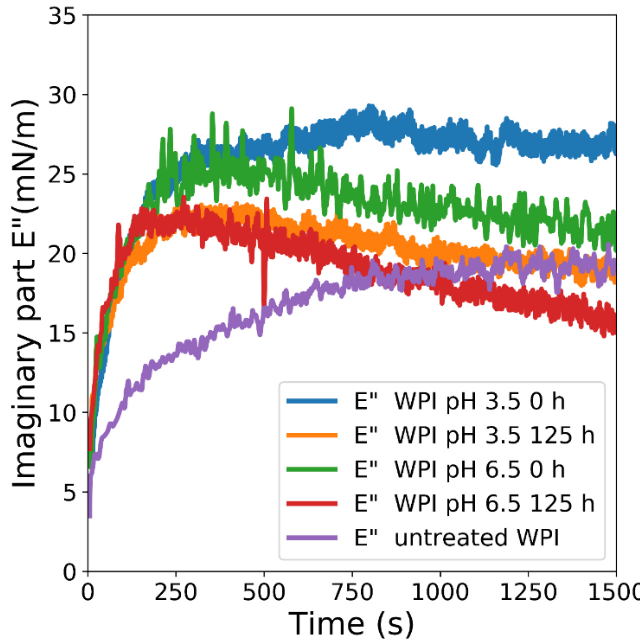
surface tension (drop shape)

Samples	$\sigma_{(250\ s)}$ mN/m		$\sigma_{(1600\ s)}$ mN/m	
untreated WPI	$49,35_{\pm0,81}$	bd	$45,62_{\pm0,89}$	ab
WPI pH 3.5 0 h	$51,57_{\pm0,02}$	e	$49,00_{\pm0,24}$	fg
WPI pH 3.5 125 h	$49,07_{\pm0,39}$	bc	$46,53_{\pm0,17}$	bc
WPI pH 6.5 0 h	$50,17_{\pm0,37}$	d	$47,76_{\pm0,18}$	de
WPI pH 6.5 125 h	$49,91_{\pm0,32}$	cd	$47,08_{\pm0,24}$	cd

- ❑ **no equilibrium state for proteins**
- ❑ broad variety of surface visco-elasticity **kinetics**

surface dilatational modulus E’ E’’ (oscillation drop method)



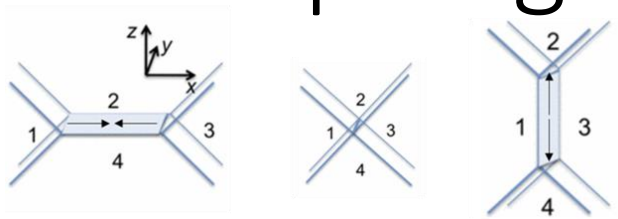


parameters for correlations :

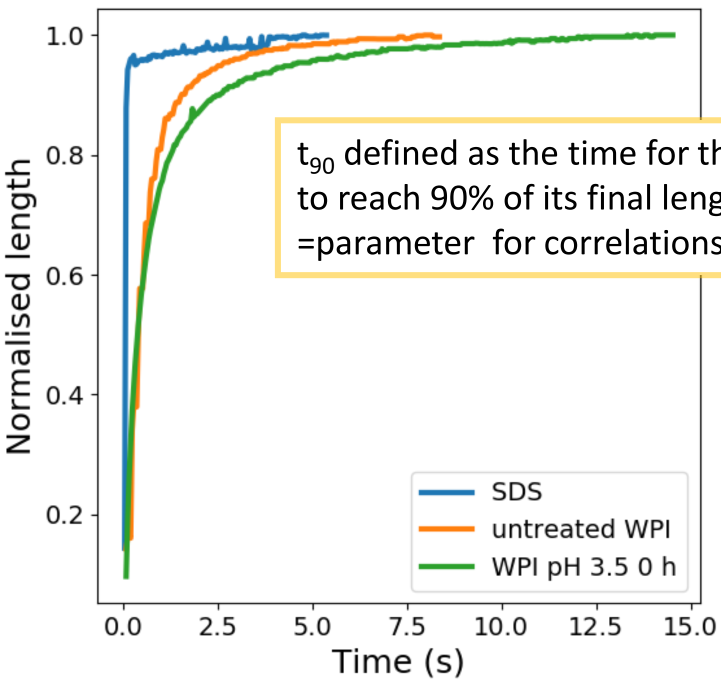
E’ elastic modulus
E’’ viscous modulus
σ surface tension

250 s
1600 s

T1 topological rearrangements

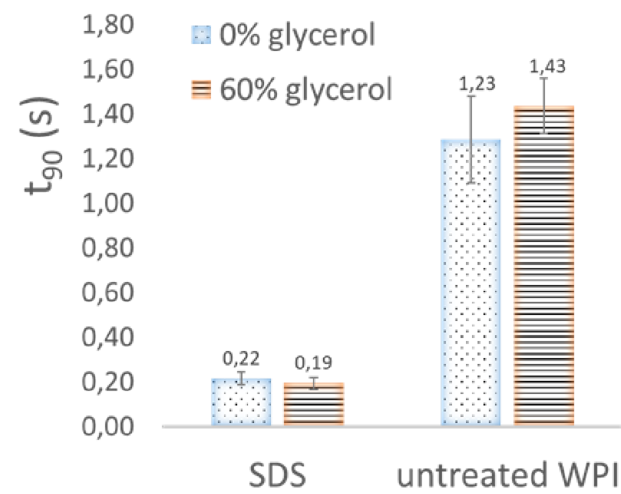


T1 duration
relaxation process



t_{90} defined as the time for the film to reach 90% of its final length =parameter for correlations

stretching film during the T1 relaxation for different samples



effect of bulk viscosity on T1 duration

- ❑ no effect of bulk viscosity

- ❑ **protein film relaxation without co-surfactants** by increasing protein concentration ≈ 50 g/L
- ❑ protein discrimination

T1 duration depends on surface rheology

spearman correlations between dimensionlesss ratio and T1 duration t_{90}

where E' elastic modulus; E'' viscous modulus ; σ surface tension

	t_{90}
$(E'/\sigma)_{250s}$	0.72**
$(E'/\sigma)_{1600s}$	0.58 *
$(E''/\sigma)_{250s}$	0.70 **
$(E''/\sigma)_{1600s}$	0.66 **

*NS no significant, * p-value < 0.05*

significant correlations :
between surface visco-elasticity E' E'' and T1 duration

Foam stability especially against disproportionation

foams by double syringe
control liquid fraction = 0.16
bubble size R ≈ 30 µm

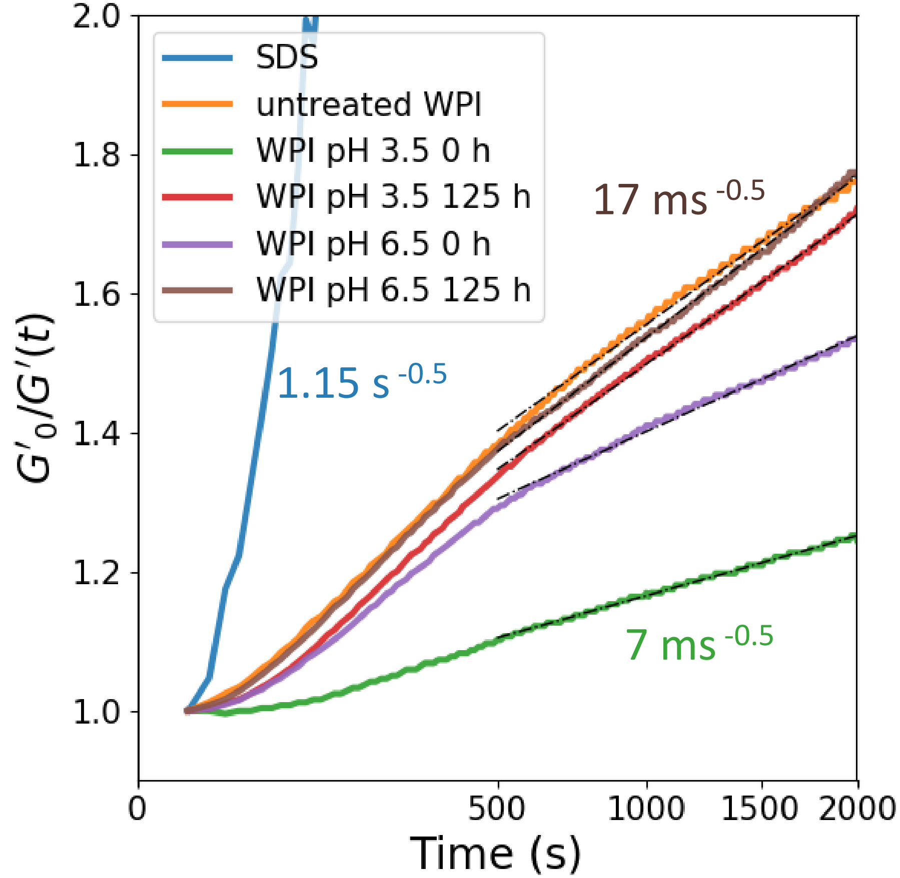
$$G' \propto \frac{\sigma}{R}\, g(\emptyset)$$

where $g(\emptyset)$ decreasing function
(Saint-Jalmes and Durian, 1999 ; Marze et al., 2009)

drainage : ↘ liquid fraction Ø : ↗ G'
disproportionation :↗ bubble size R : ↘ G'
= indirect access to foam stability

disproportionation : ↗ bubble size vs $\sqrt{t}$
(Hutzler and Weaire, 2000)

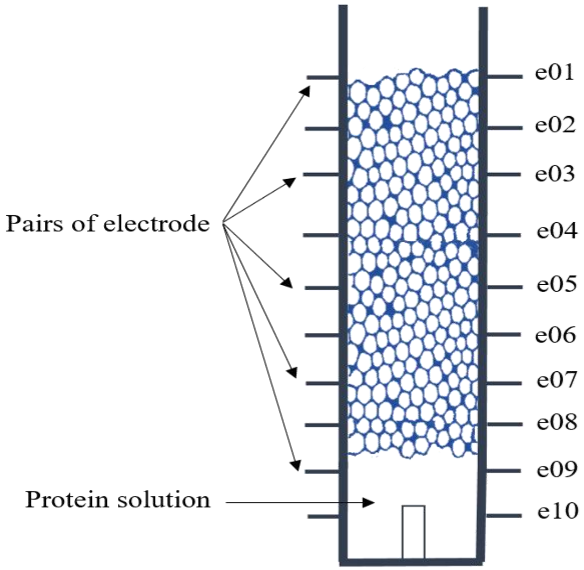
disproportionation coefficient
=parameter for correlations



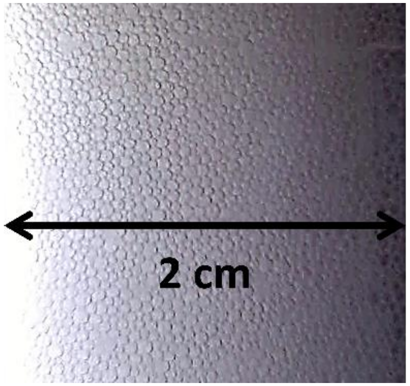
foam shear elastic moduli G'
(1 Hz, 1 % déformation)

different disproportionation coefficients

Foam stability especially against drainage



device



foam with milimetric bubbles

bubbling method

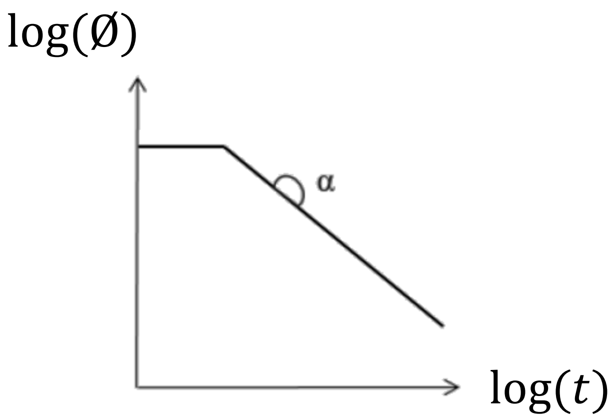
conductivity measurements ≠ heights

➔ *Liquid fraction Ø*

$$\emptyset = \frac{3\sigma(1+11\sigma)}{1+25\sigma+10\sigma^2}$$

where σ was the relative conductivity $\sigma_{foam}/\sigma_{solution}$

(Feitosa et al., 2005)



$\emptyset \propto t^{-\alpha}$

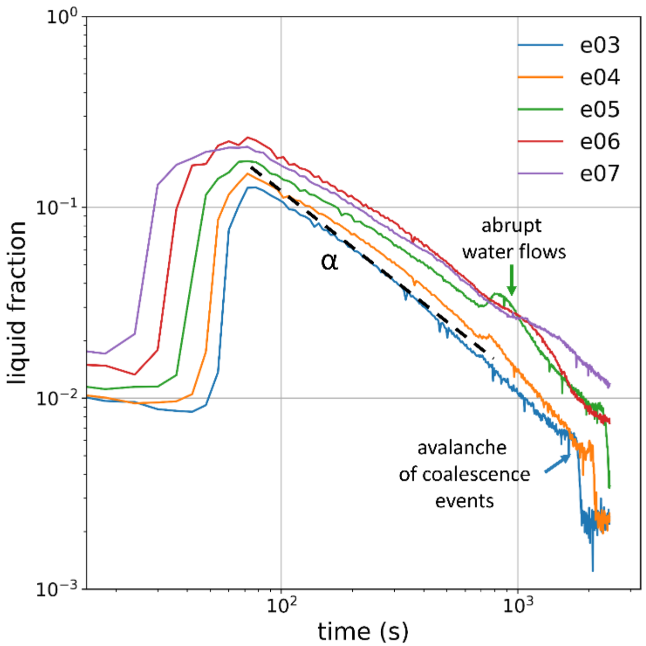
where α is the free-drainage exponent

(Koehler et al., 2000; Saint-Jalmes and Langevin, 2002)

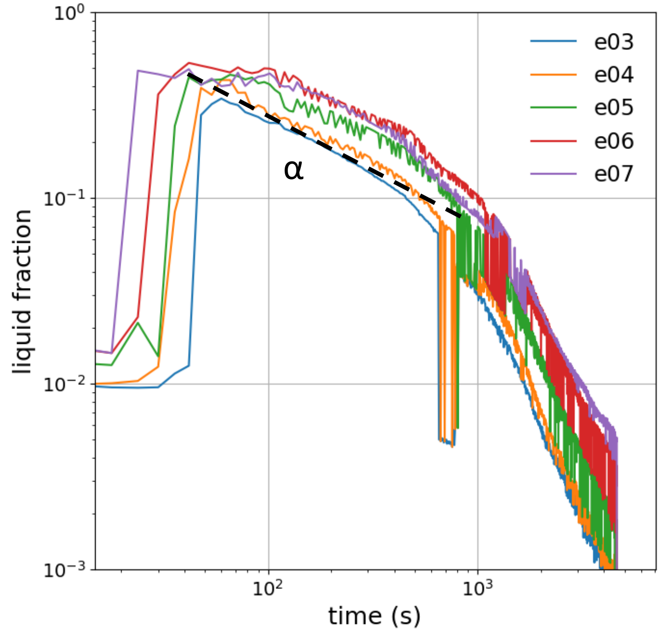
when drainage is the only instability phenomena occurring in the foam

Foam stability especially against drainage

Typical results



2 g/L proteins



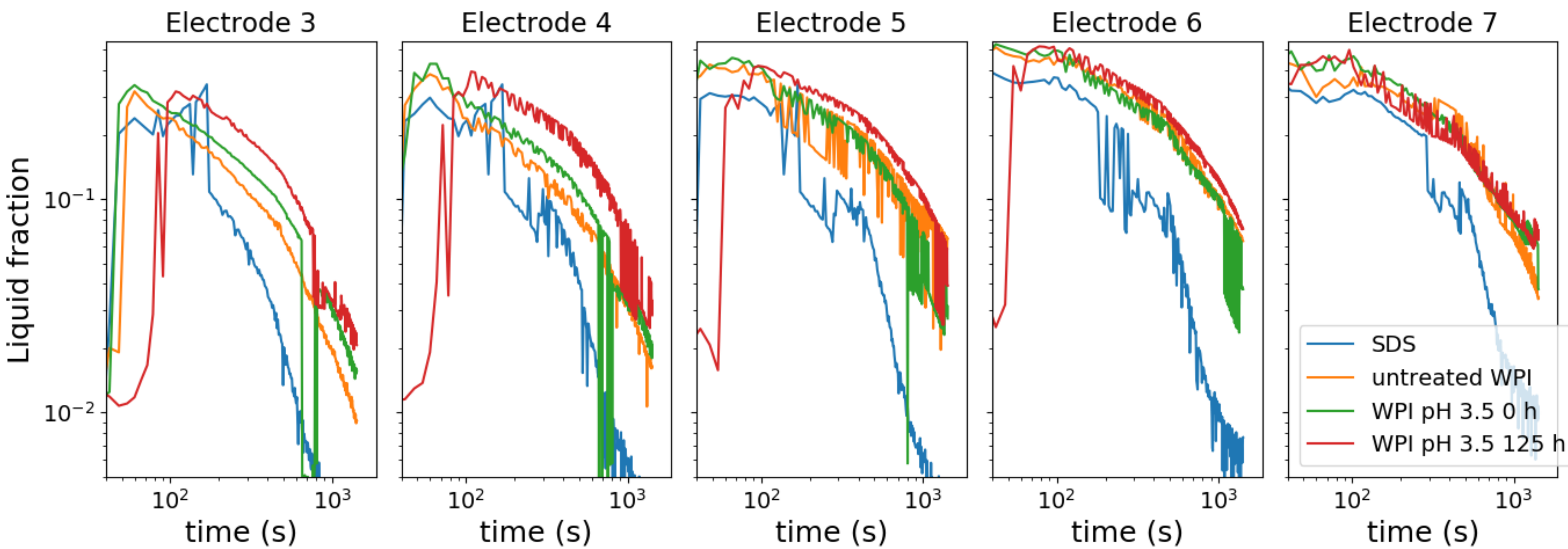
50 g/L proteins
(for all experiments)

$\varnothing \propto t^{-\alpha}$
where α is the free-drainage exponent
(Koehler et al., 2000; Saint-Jalmes and Langevin, 2002)

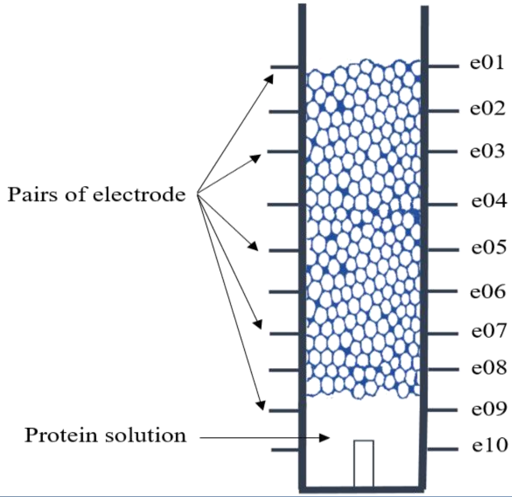
50 g/L proteins drawbacks

- ❑ ≠ liquid fraction profile (wetter foam, lower drainage exponents, others instability mechanisms are coupled
- ❑ noisy signal

Foam stability especially against drainage



- ❑ **local stability** at the top e03 (better discrimination)
- ❑ **general stability** at the bottom e07 integrative from what happens higher
- ❑ protein discrimination



summary of the whole liquid fraction profiles (time + height) by one parameter using Principal Component Analysis (PCA) = informative about *foam stability (parameter for correlations)*

Multiscale correlations

Spearman correlations

where $\eta = E'' \times frequency$ *; E' elastic modulus; E'' viscous modulus ; σ surface tension*

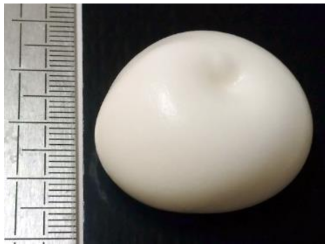
	disproportionation coeficient	foam stability (drainage)
$(E'/\sigma)_{250s}$	-0.85 ***	NS
$(E'/\sigma)_{1600s}$	NS	NS
$(E''/\sigma)_{250s}$	-0.72 **	NS
$(E''/\sigma)_{1600s}$	NS	NS
t_{90}	-0.55 ·	NS

*NS no significant, · p-value < 0.10 ; * p-value < 0.05 ; ** p-value < 0.01, *** p-value < 0.001*

- ❑ correlations only with early surface rheology (250 s)
- ❑ no correlations with foam stability (drainage)
- ❑ **negative correlations**
  - **disproportionation coefficient and dimensionless viscous surface ratio**
  - **disproportionation coefficient and dimensionless elastic surface ratio**

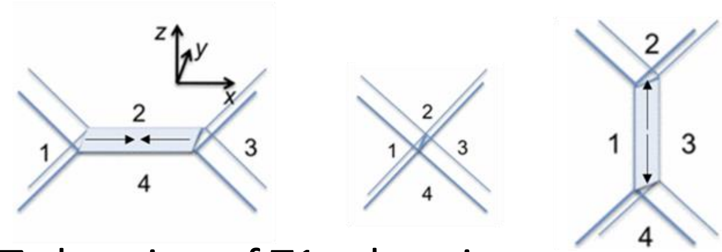
Conclusion

foam stability



↘ disproportionation

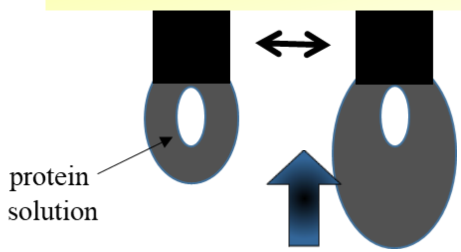
T1 topological rearrangements



↗ duration of T1 relaxation

↗ visco-elastic modulus E' , E''

surface rheology



PROTEINS (WPI)

- ❑ discriminant methods for proteins
- ❑ **protein T1 as a new tool**
- ❑ higher correlations with early surface rheology ; kinetics vs « equilibrium »

Outlooks

no correlation between dilatationnal modulus with foam stability against drainage

surface shear viscosity

bulk properties (protein self-assembly into aggregates, reduced flow by confinement in Plateau border)
(Koehler et al., 2000; Saint-Jalmes and Langevin, 2002)

WPI specificity : multiple proteins, emergent properties due to interactions

Thanks for your attention …

… any questions ?