



# Soft matter approaches for food proteins: interfacial and foaming properties

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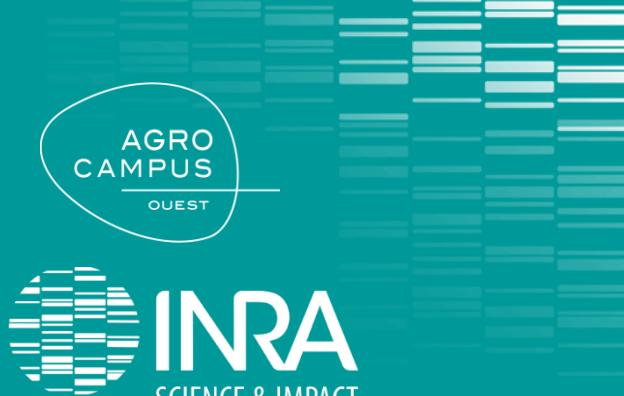
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# Soft matter approaches for food proteins: interfacial and foaming properties



STLOpen Days  
19-21 March 2019



Valérie Lechevalier & Stéphane Pezennec



# Protein functionality

- relation of technological aptitudes to intrinsic features
- ‘biochemical’ viewpoint  
(amino-acid composition, sequence, structure...)
- *colloidal* viewpoint  
(size, charge, anisotropy, pressure, transport, concentration...)
- the two worlds meet at interfaces

*Boire et al., 2019 ([doi:10/c3jt](https://doi.org/10/c3jt))*

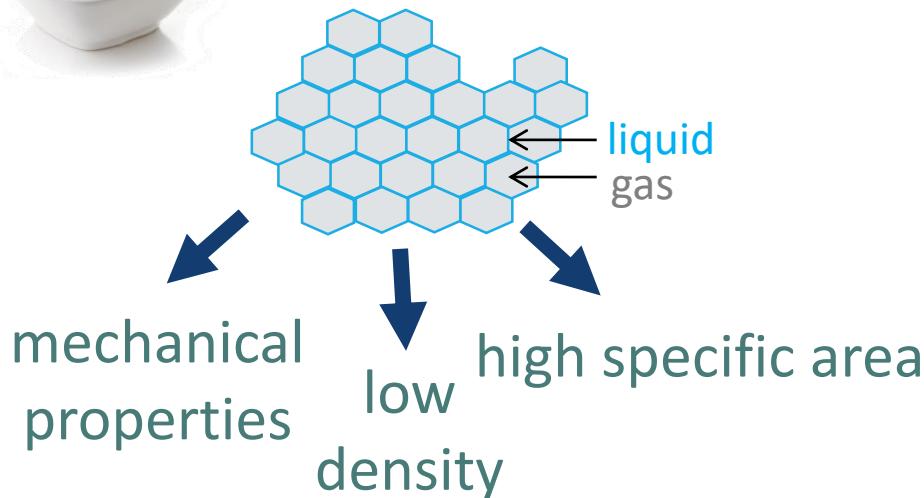
# Interfacial properties of proteins

- proteins as surfactants: adsorption to hydrophobic interfaces
- irreversible adsorption
- unwanted consequences  
(loss of enzymatic activity, fouling...)
- target effects: stabilization of dispersed systems
- our focus: air—water interface, foams

# Outline

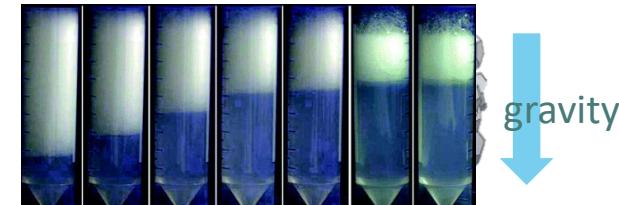
- approach & tools
- proteins at the air—water interface
- (interfacial) crowding
- properties of protein foams

# Liquid foams are unstable systems



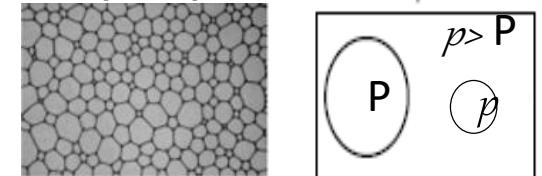
energy content:  $A \cdot \sigma$

drainage



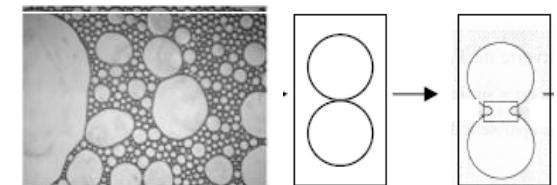
volume, liquid fraction  $\downarrow$

disproportionation



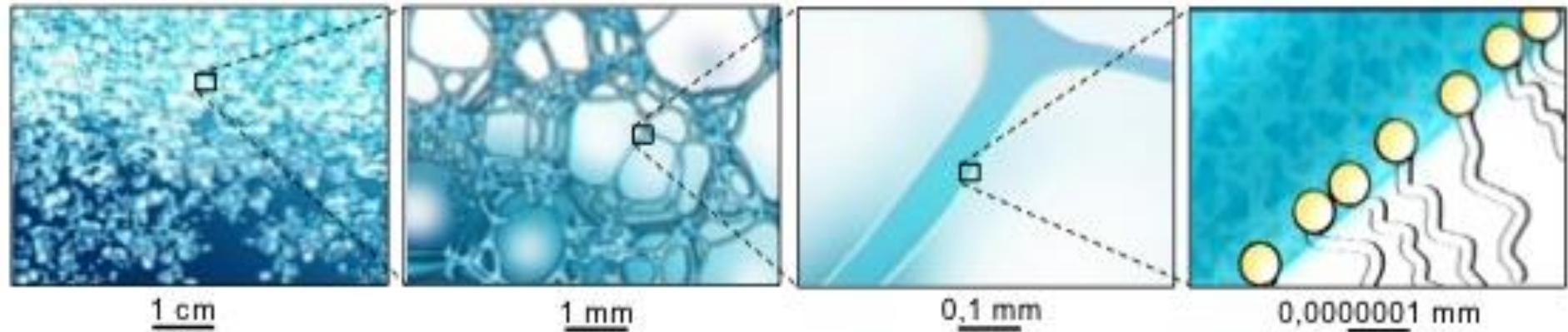
bubble size  $\nearrow$

coalescence



bubble size  $\nearrow$

# Multiscale approach from foam to adsorption layer



**foam:** density, stability, **bubble:** size, shape, rheology surface pressure

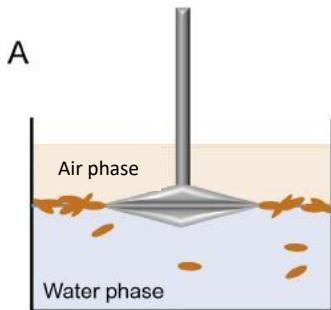
**film:** thickness, visco-elasticity, roughness

**adsorption layer:** adsorption kinetics, surface concentration, protein conformation and orientation, visco-elasticity, surface pressure

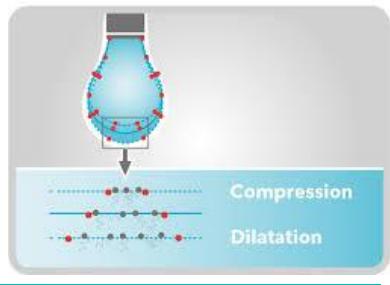
# Interfacial measurements



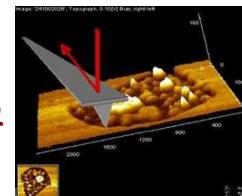
surface tension  
shear rheology



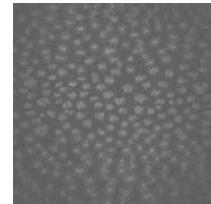
dilatational rheology



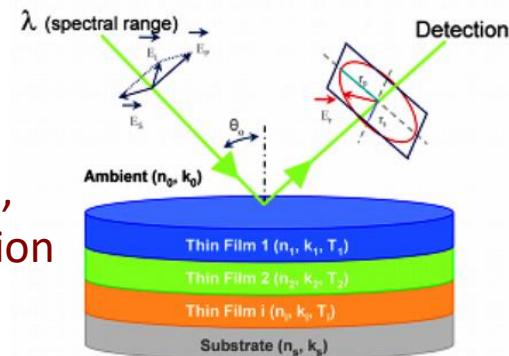
atomic force  
microscopy  
film thickness &  
roughness



Brewster angle microscopy  
imaging ellipsometry

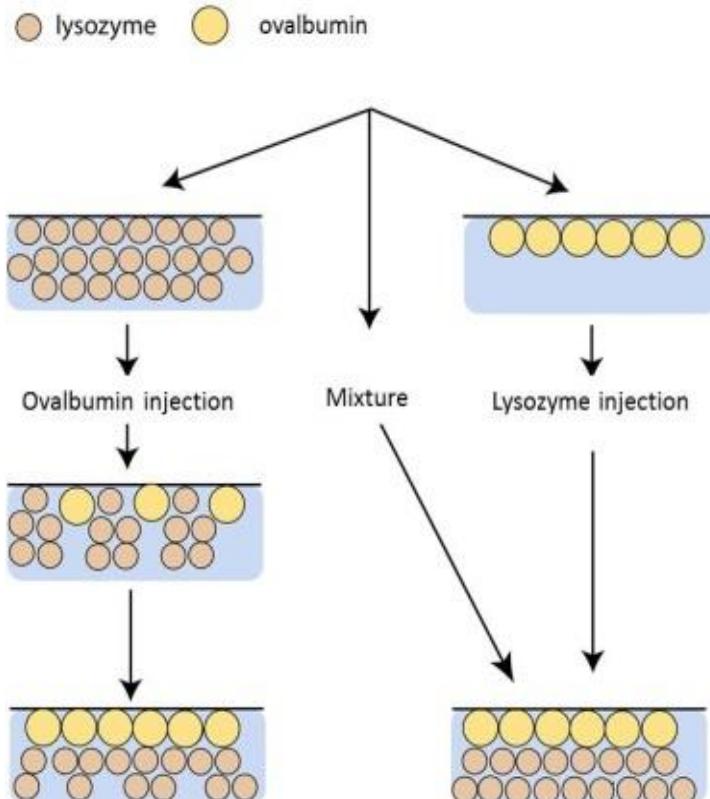


PM-IRRAS  
molecular  
conformation and  
orientation



ellipsometry  
adsorption kinetics,  
surface concentration  
excess

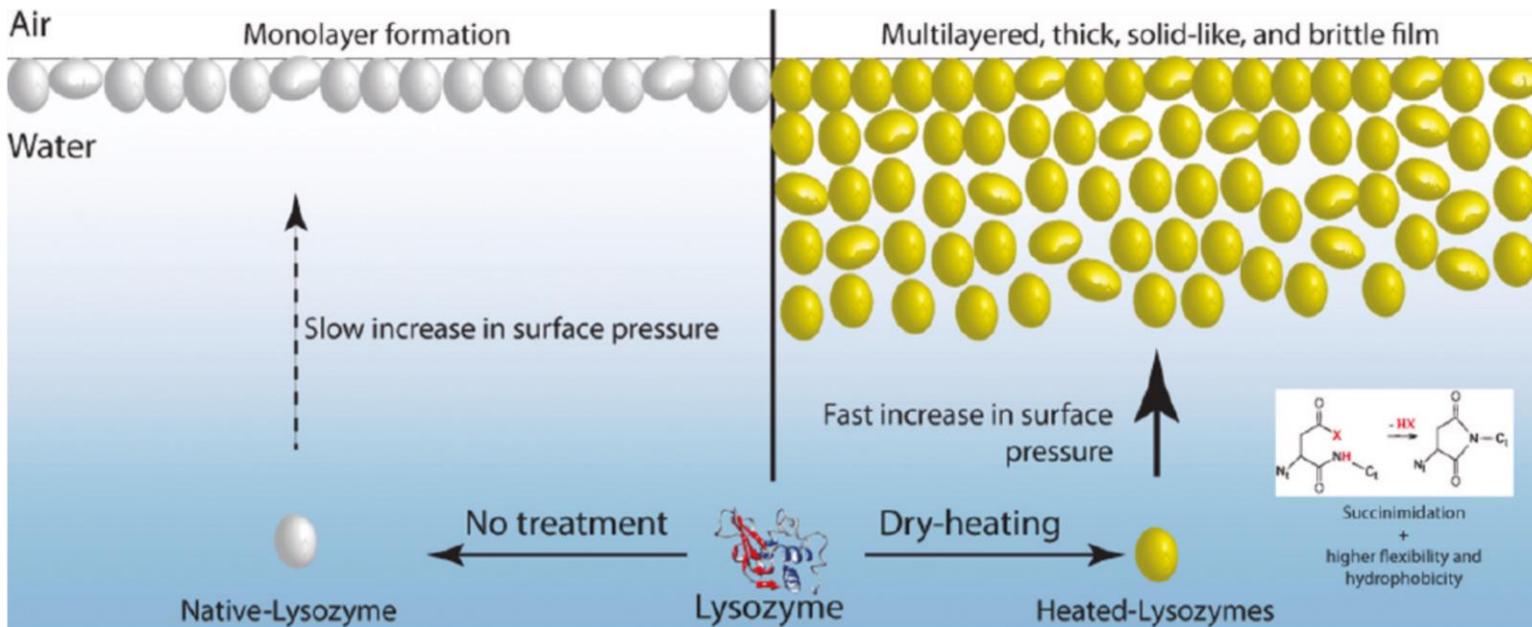
# Interface as a competitive site for protein adsorption



- synergistic co-adsorption
- preferential protein assembly at the air-water interface
- stratified model, surface activity

*Le Floch-Fouéré et al., 2009 ([doi:10/fxdc22](https://doi.org/10/fxdc22)), 2010 ([doi:10/d38gsz](https://doi.org/10/d38gsz))*

# Interface as an indicator of the changes in protein conformation



- minor changes in the protein stability dramatically impact the interfacial behavior
- dry-heating increases aggregation and propensity to self-association at the interface

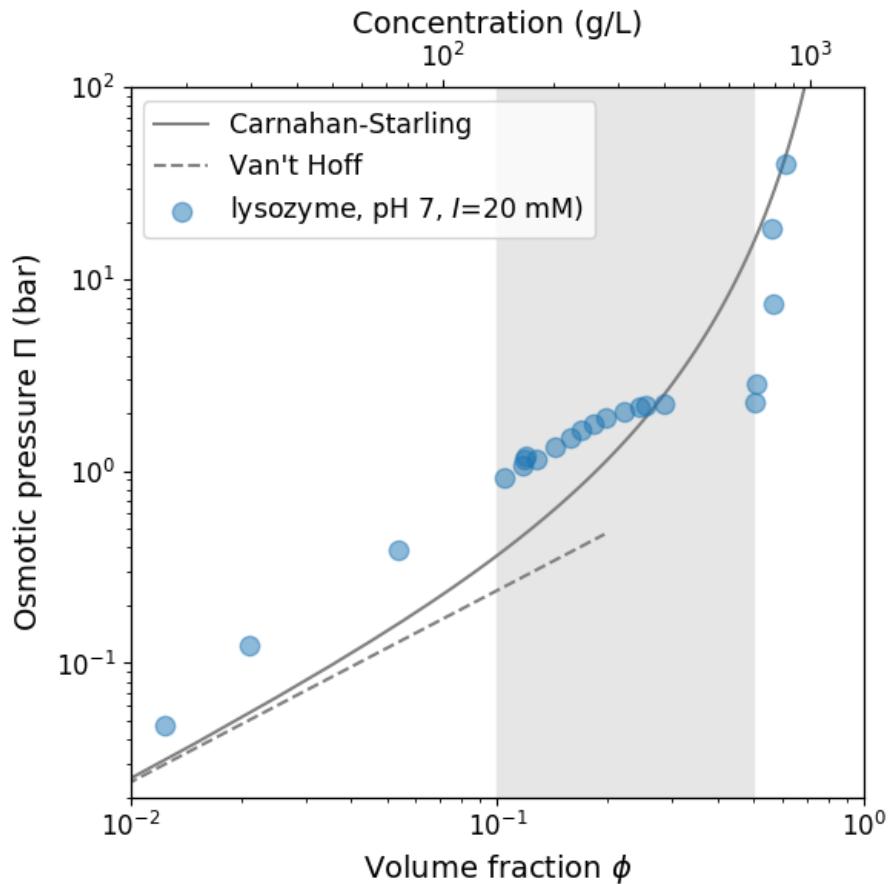
*Desfougères et al., 2008 ([doi:10/ck4w63](https://doi.org/10/ck4w63)), 2011 ([doi:10/bfb25m](https://doi.org/10/bfb25m))*

# Interface as a crowded system

- high local concentration in the interfacial film
- which contribution of crowding?
- osmotic pressure in concentrated solutions?

# Interface as a crowded system

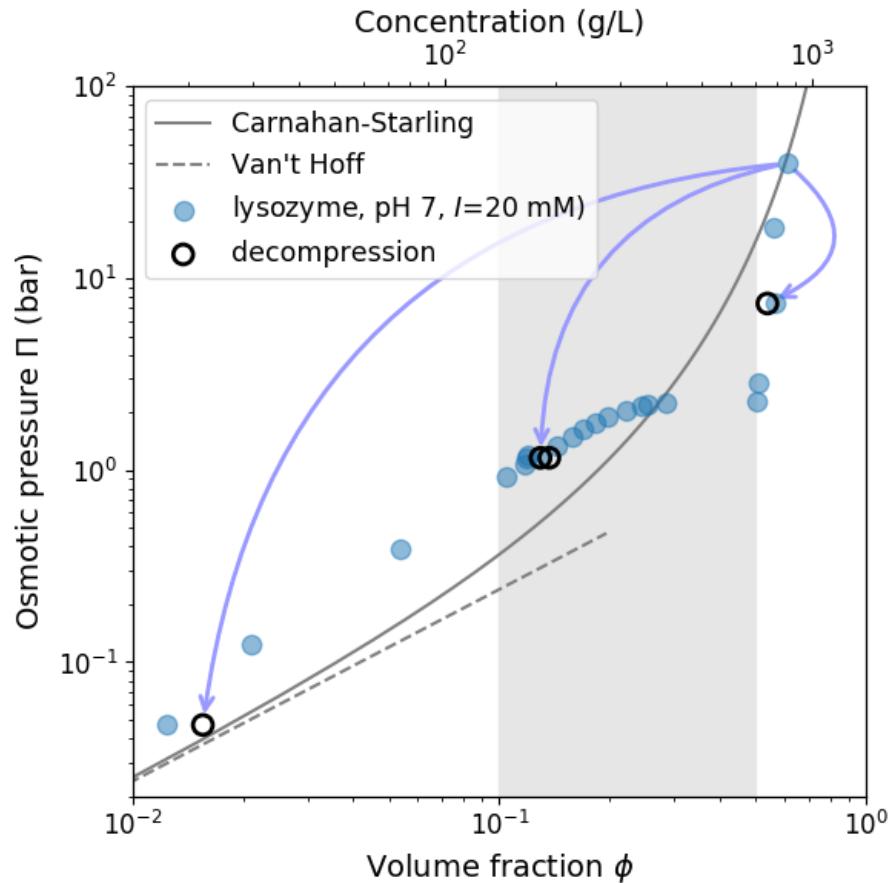
- phase transition:  
crystallisation



Pasquier et al., 2016 ([doi:10/bqrz](https://doi.org/10/bqrz))

# Interface as a crowded system

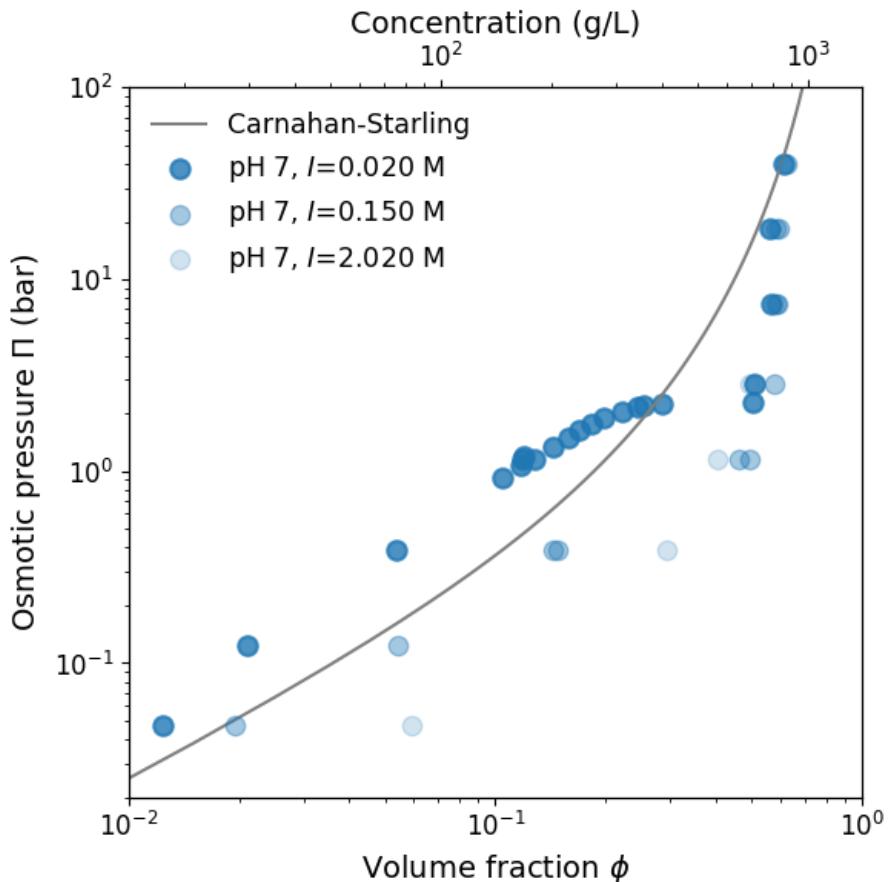
- phase transition:  
crystallisation
- reversibility,  
therm. equilibrium



Pasquier et al., 2016 ([doi:10/bqrz](https://doi.org/10/bqrz))

# Interface as a crowded system

- phase transition:  
crystallisation
- reversibility,  
therm. equilibrium
- electrostatic  
interactions



Pasquier et al., 2016 ([doi:10/bqrz](https://doi.org/10/bqrz))

# Interface as a crowded system

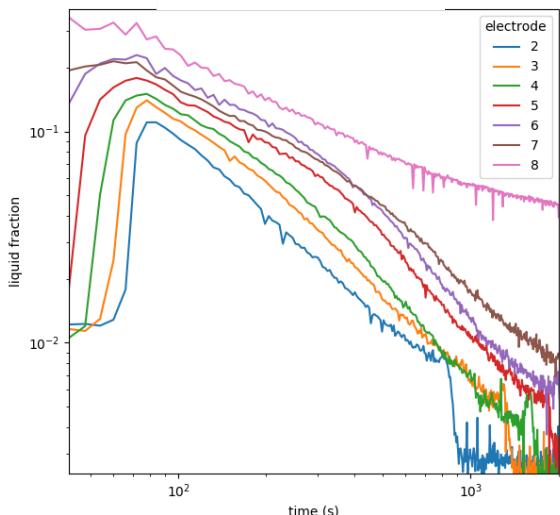
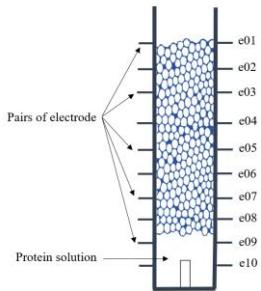
- correlation between EOS and interfacial behavior
- coupling between osmotic pressure gradients and transport
- advection
- ionic effects

# From the interface to the foam

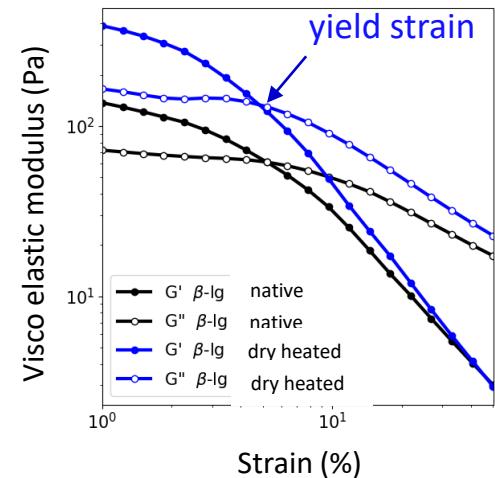
- relation of foaming properties to interfacial behavior?

# Foam measurements

liquid volume fraction, drainage



foam rheology

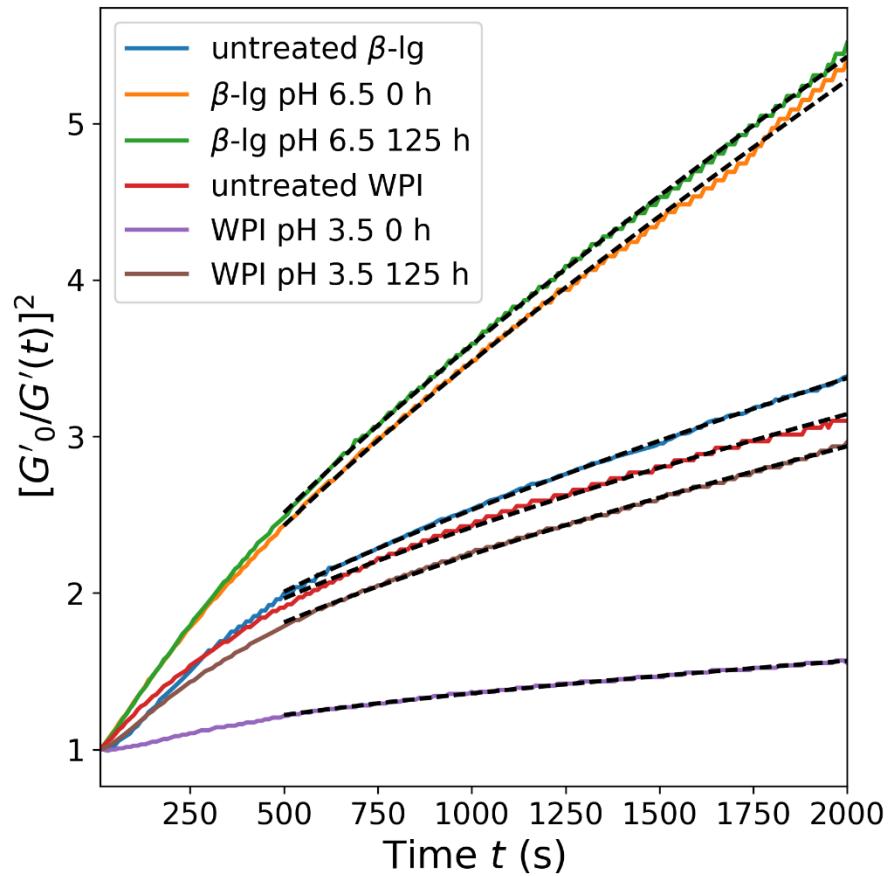


disproportionation

Audebert et al., 2019a ([doi:10/ctf8](https://doi.org/10.1016/j.ctf.2019.01.001)), 2019b ([doi:10/cz9w](https://doi.org/10.1016/j.cza.2019.01.001))

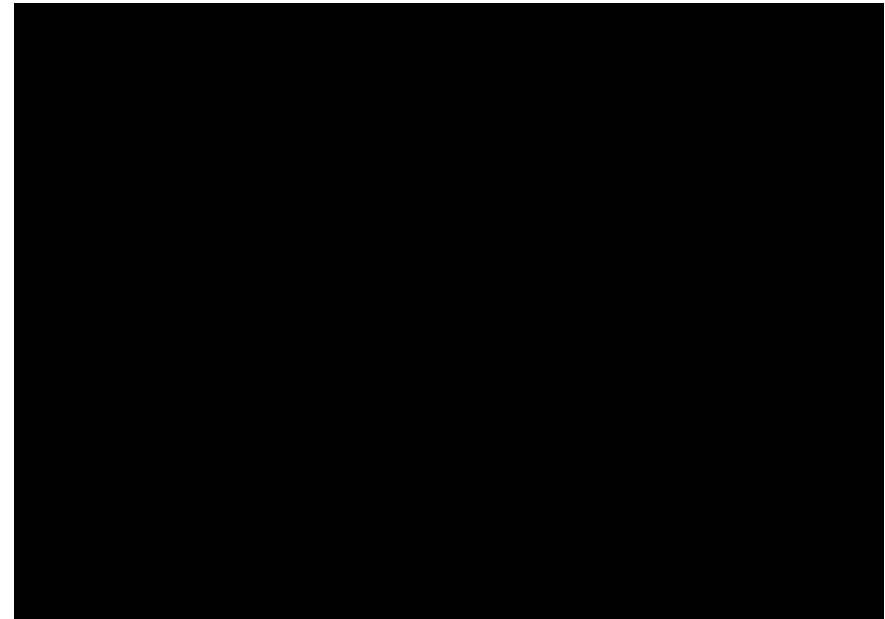
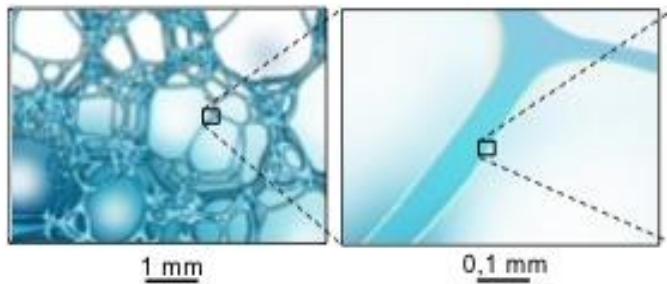
# Foam rheology & disproportionation

- $G' = \frac{\sigma}{R} g(\Phi_l)$
- $R \sim \sqrt{t}$



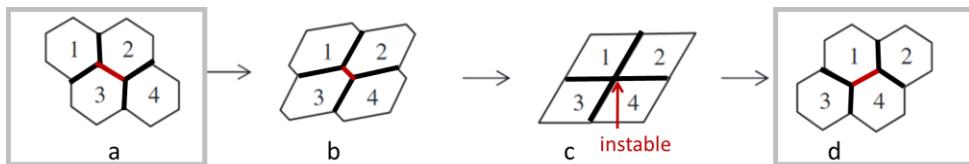
Audebert et al., 2019b ([doi:10/cz9w](https://doi.org/10/cz9w))

# Bubble film dynamics

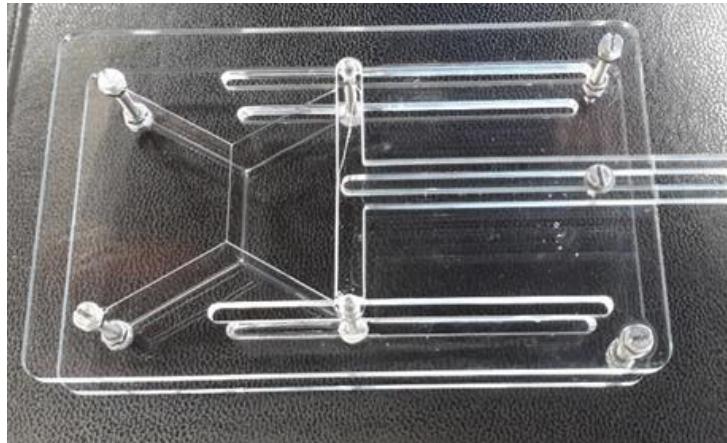


T1 topological  
rearrangements

Krüss GmbH



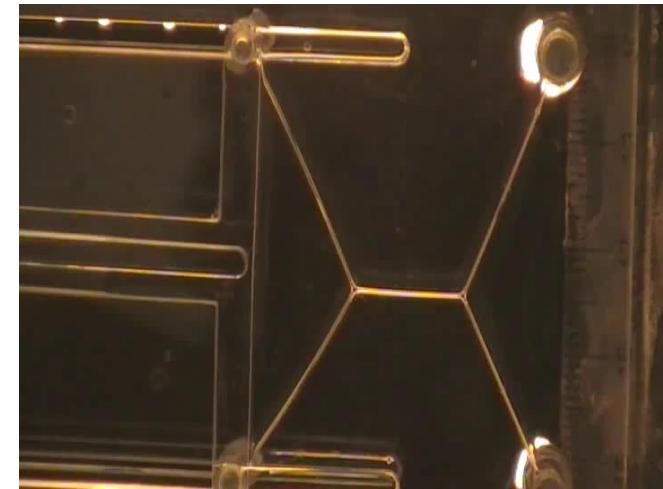
# Bubble film dynamics



native  $\beta$ -Ig

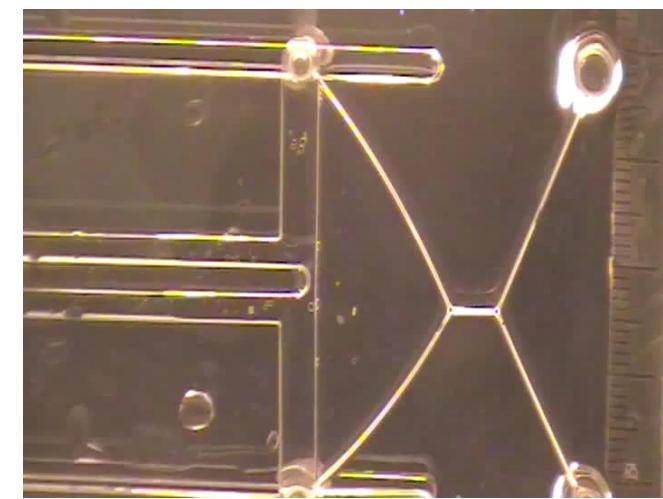
1.5 s

time for 90%  
of final length



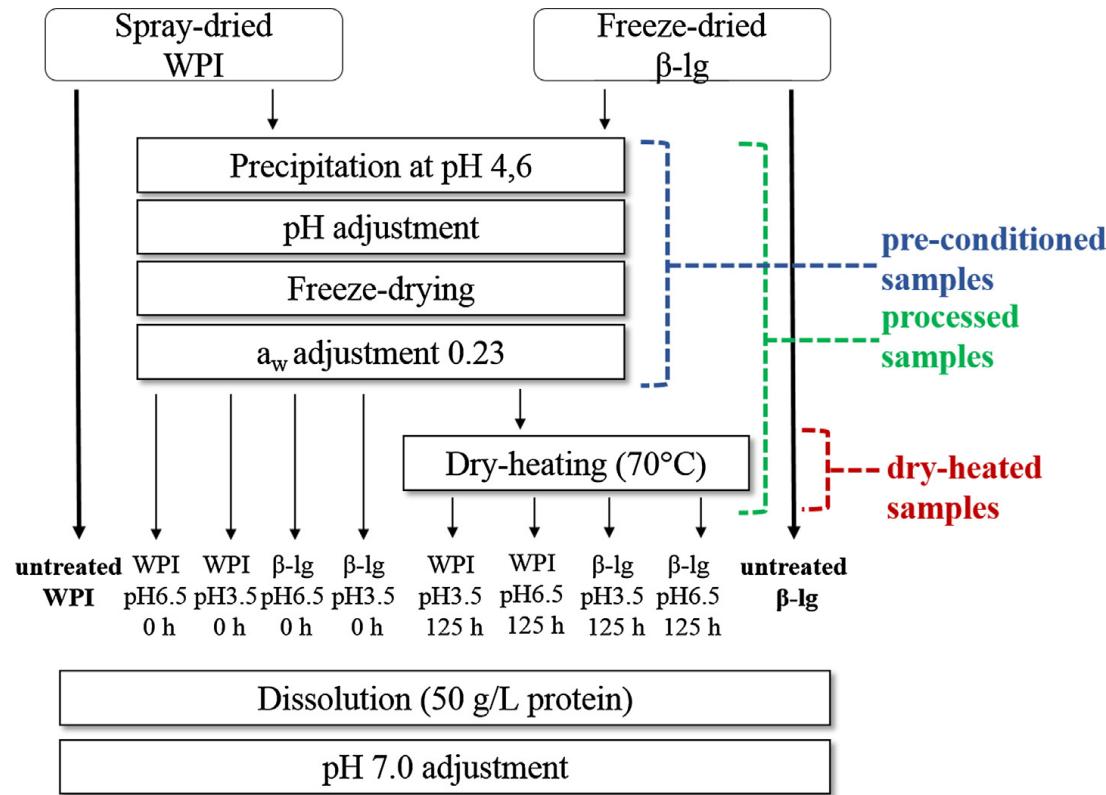
dry heated  $\beta$ -Ig

4.6 s



Audebert et al., 2019 ([doi:10/cz9w](https://doi.org/10/cz9w))

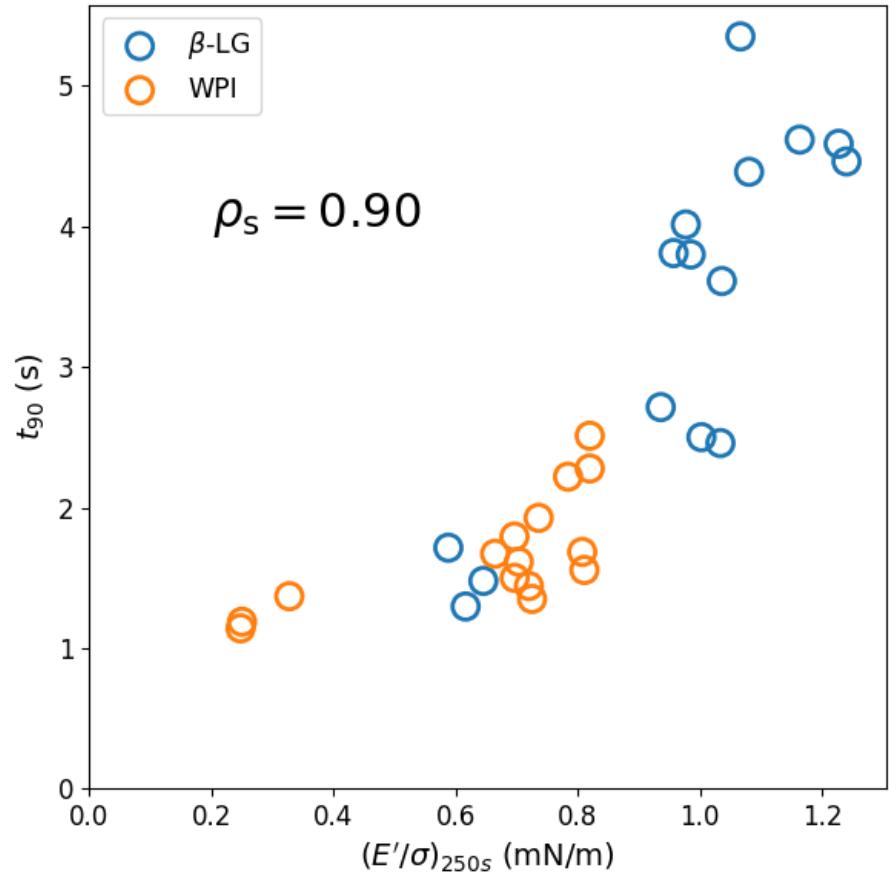
# Protein modification



Audebert et al., 2019a ([doi:10.1016/j.foodcont.2019.01.018](https://doi.org/10.1016/j.foodcont.2019.01.018)), 2019b ([doi:10.1016/j.foodcont.2019.01.019](https://doi.org/10.1016/j.foodcont.2019.01.019))

# Multiscale correlations

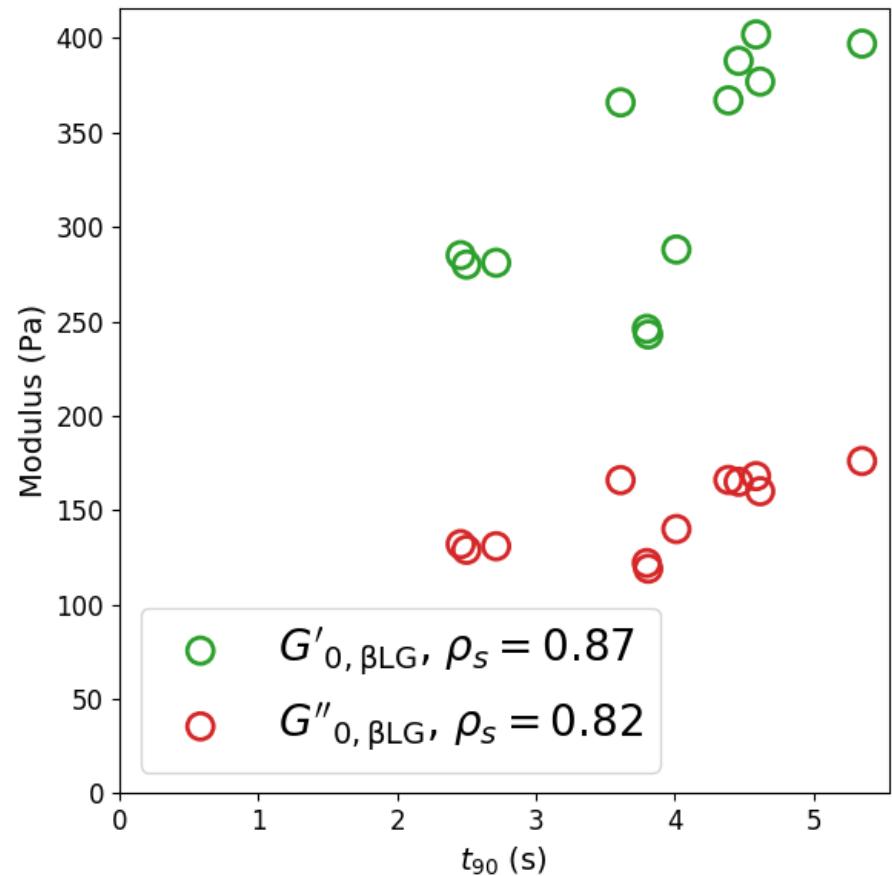
- interfacial rheology & T1



*Audebert et al., 2019b* ([doi:10/cz9w](https://doi.org/10/cz9w))

# Multiscale correlations

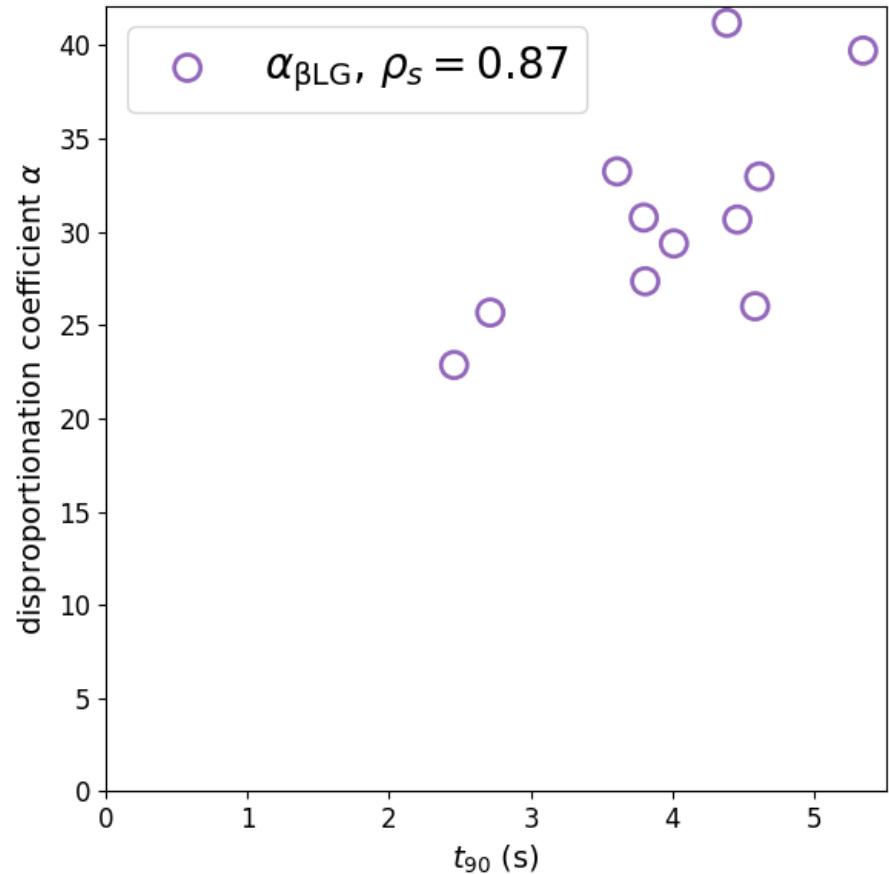
- interfacial rheology & T1
- T1 & foam rheology



Audebert et al., 2019b ([doi:10/cz9w](https://doi.org/10/cz9w))

# Multiscale correlations

- interfacial rheology & T1
- T1 & foam rheology
- T1 &  
foam disproportionation



*Audebert et al., 2019b ([doi:10/cz9w](https://doi.org/10/cz9w))*

# Conclusion

- film dynamics as an intermediate scale between interface and foam
- kinetics, early steps of interfacial film formation
- foam rheology as a functional criterion
- sensitivity to protein structure and stability
- food proteins: open questions in foam / colloid physics
- interdisciplinarity as a necessity

Zaccagnino *et al.*, 2018 ([doi:10/cw2k](https://doi.org/10/cw2k))

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**MERCI**



**THANK YOU FOR  
YOUR ATTENTION**

# Key publications

- Audebert, A. et al. (2019) *J. Food Eng.* 242, 153–162
- Audebert, A. et al. (2019) *J. Colloid Interface Sci.* 542, 222–232
- Boire, A. et al. (2019) *Annu. Rev. Food Sci. Technol.* 10, 14.1–14.19
- Pasquier, C. et al. (2016) *Phys. Chem. Chem. Phys.*, 18, 28458–28465
- Desfougères, Y. et al. (2011) *Biomacromolecules*, 12, 156–166
- Desfougères, Y. et al. (2011) *Langmuir*, 27, 14947–14957
- Le Floch-Fouéré, C. et al. (2010) *Food Hydrocoll.*, 24, 275–284
- Le Floch-Fouéré, C. et al. (2009) *Food Hydrocoll.*, 23, 352–365