NIZO
FOR BETTER FOOD & HEALTH

Neutron scattering and food science

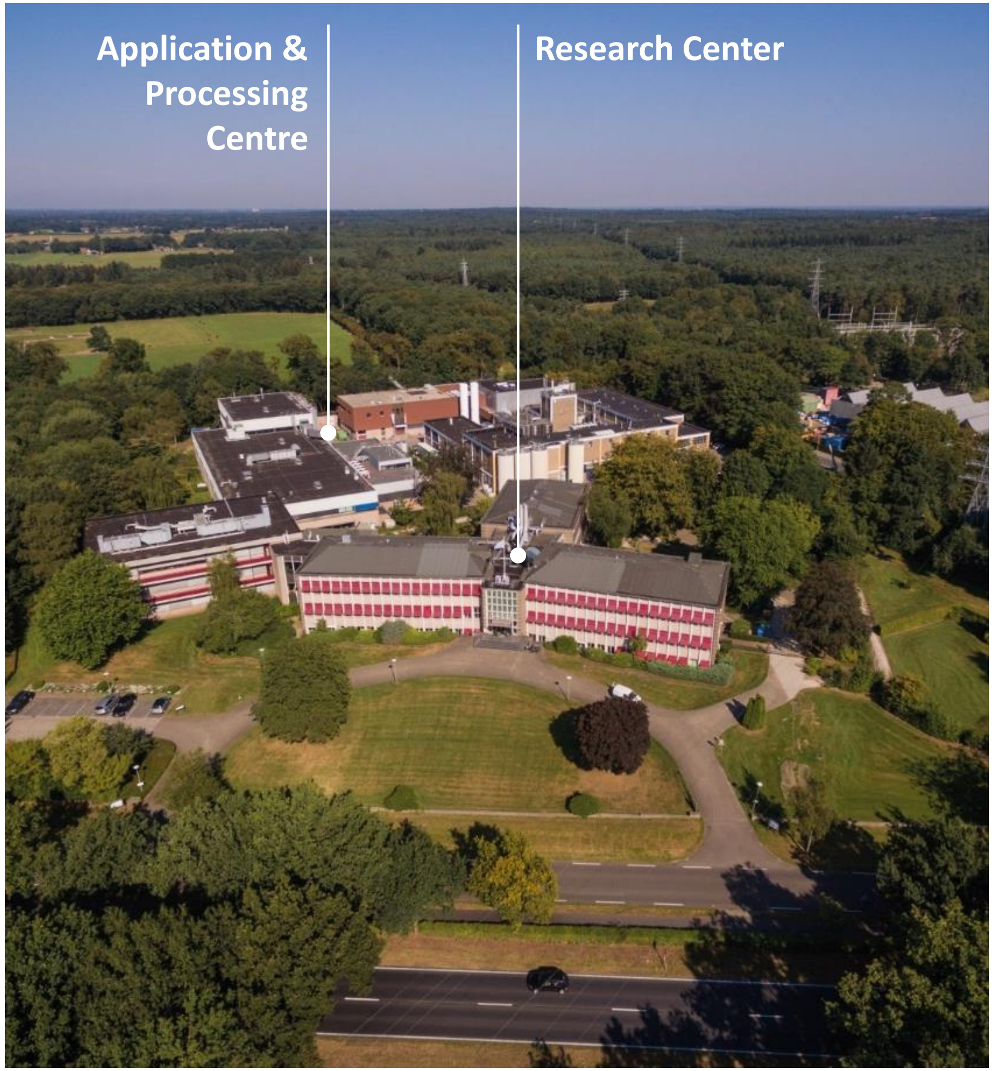
Ideas and results

Hans Tromp (Hans.Tromp@NIZO.com)

18 juni 2021

NIZO food research

- Independent, privately owned Contract Research Organisation for food and health
- Located in Ede (near Wageningen), in the Netherlands
- Founded in 1948, as dairy research institute
- 100 professionals
- From lab to market
  - Labs for physical and chemical analyses
  - Food grade facilities for testing and preparation
  - Food-grade pilot plant
  - In silico and vitro models



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  → Opportunities for neutron scattering in insight/monitoring food processing

- Some examples from food science

Unique applicability of neutrons in food science

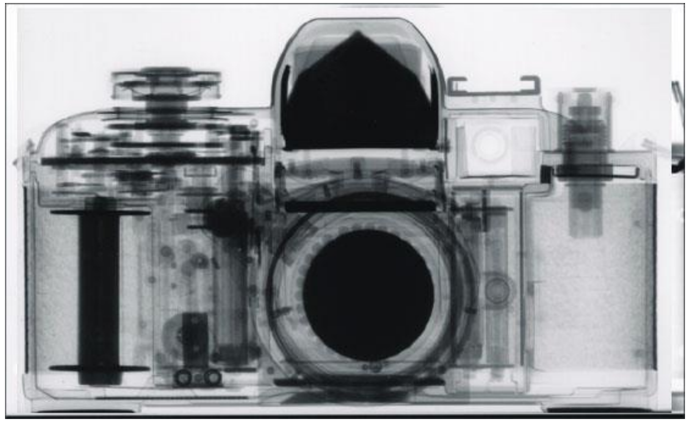
- H/D subsitution
  - Makes hydrogen bonding visible

- Turbid systems relatively accessible (substitution of H_2O with D_2O helps)

- Transparency of steel for neutrons

  - effect of high pressure
  - buid up of food structure under shear
  - *fouling in heating equipment*
  - *processes inside a homogenizer*
  - *flow inside nozzles of drying equipment: spray drying, electrospinning*

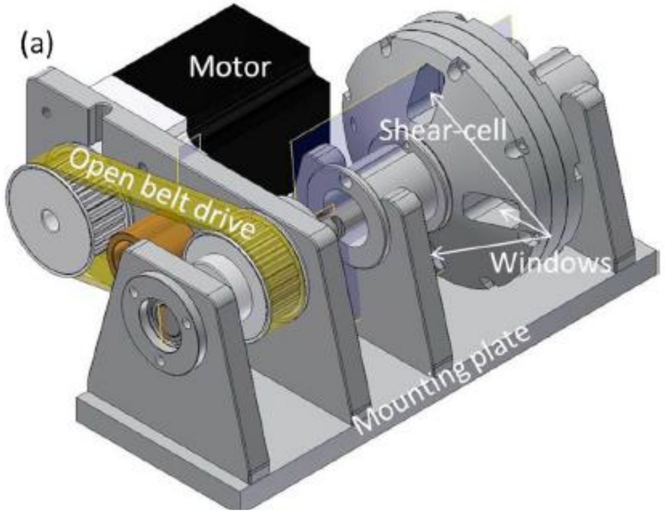
Neutron imaging

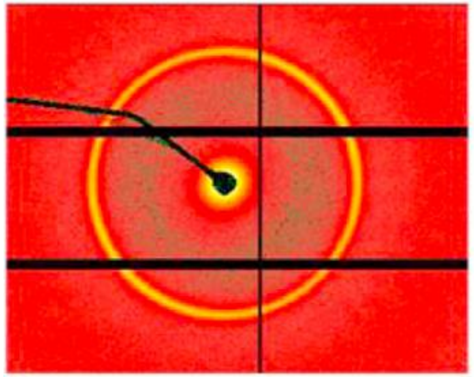


The McClellan Nuclear Research Center, UC Davis

Unique applicability of neutrons in food science
Presently available

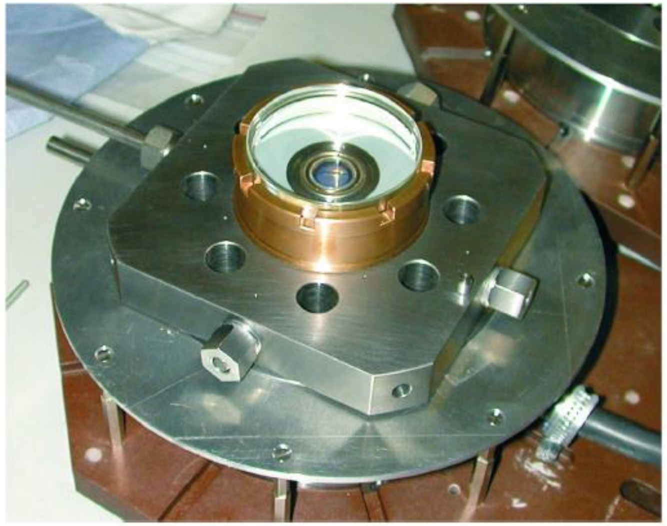
Shear cell for neutron scattering





From: TU Delft, E. Velichko et al. Coll.Surf.A (2019) 566,21

High pressure cell for neutron scattering

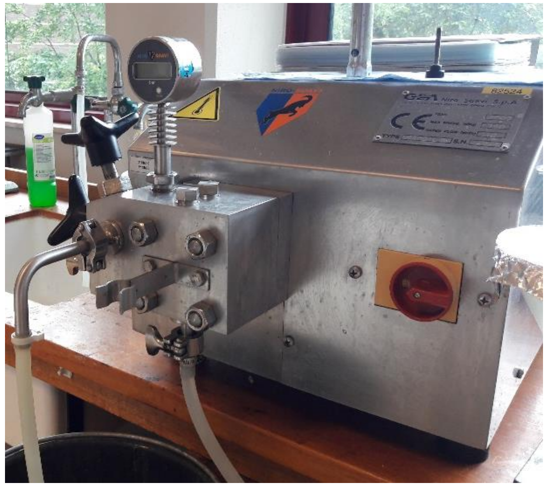


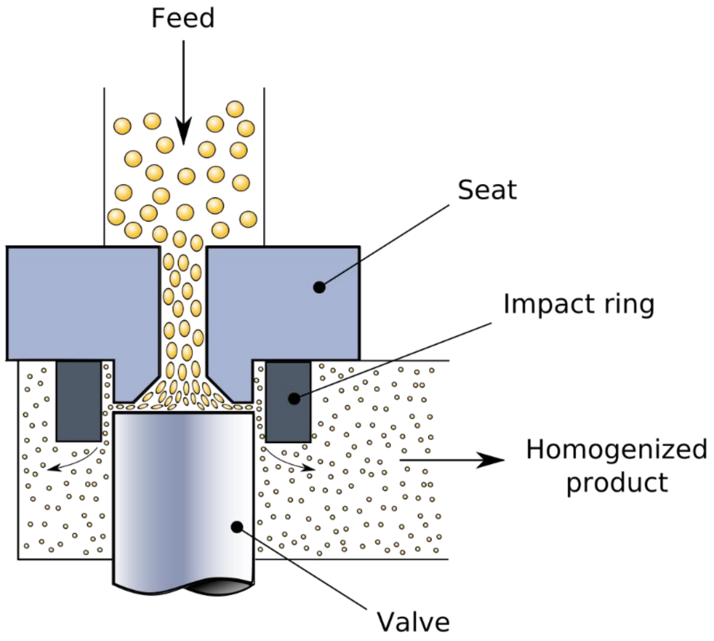
From: Kohlbrecher et al, Rev.Sci.Instr. (2007), 78, 125101

Unique applicability of neutrons in food science
Not yet available (?)

Observing protein and mineral fouling in food processing equipment, real time and *in situ*
→ When/where does fouling start?

Observing what happens inside a homogenizer
→what is the optimal pressure and gap size for optimal emulsification?
→what is the state of emulsified droplets during homogenization?

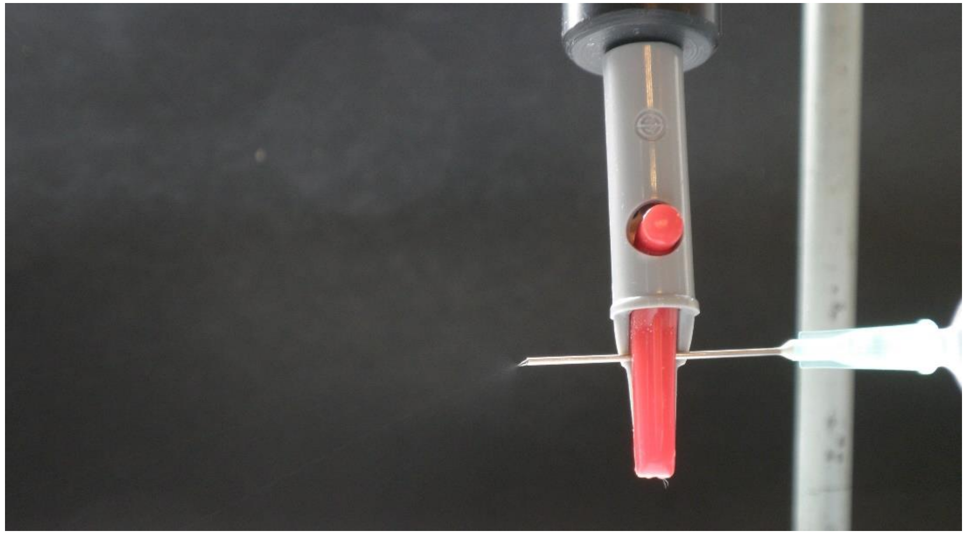


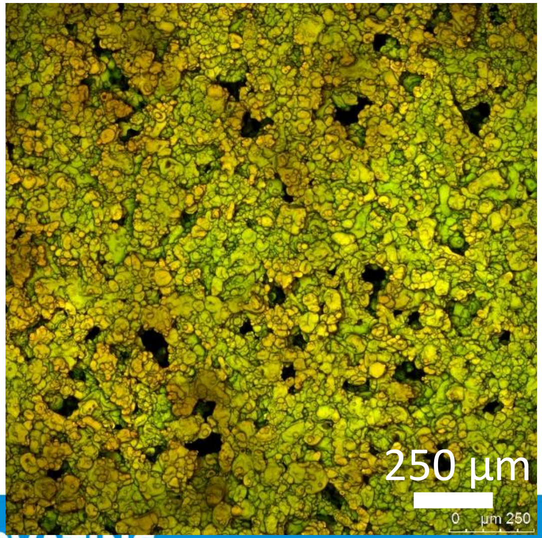


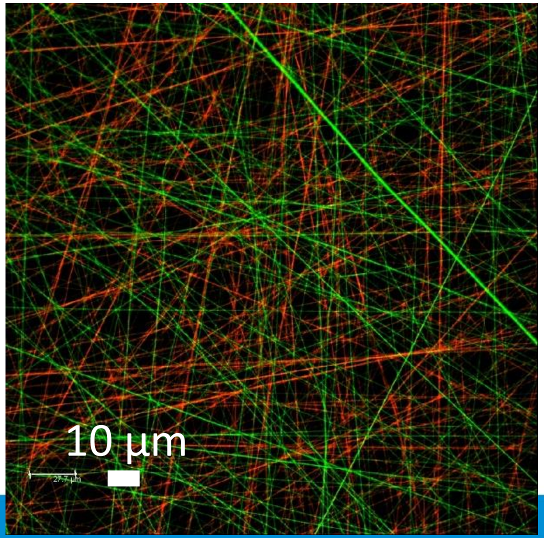
Unique applicability of neutrons in food science
Not yet available (?): looking inside a spraying nozzle

Spray drying

Electrospinning







- What is the shear profile in the nozzle?
- Is there shear banding?
- Does this affect the stability of the process?
- Does this affect the morphology of the product?

Some examples from food science

Wide angle neutron scattering:

- Hydrogen bonding in sugar glass

Small Angle Neutron Scattering:

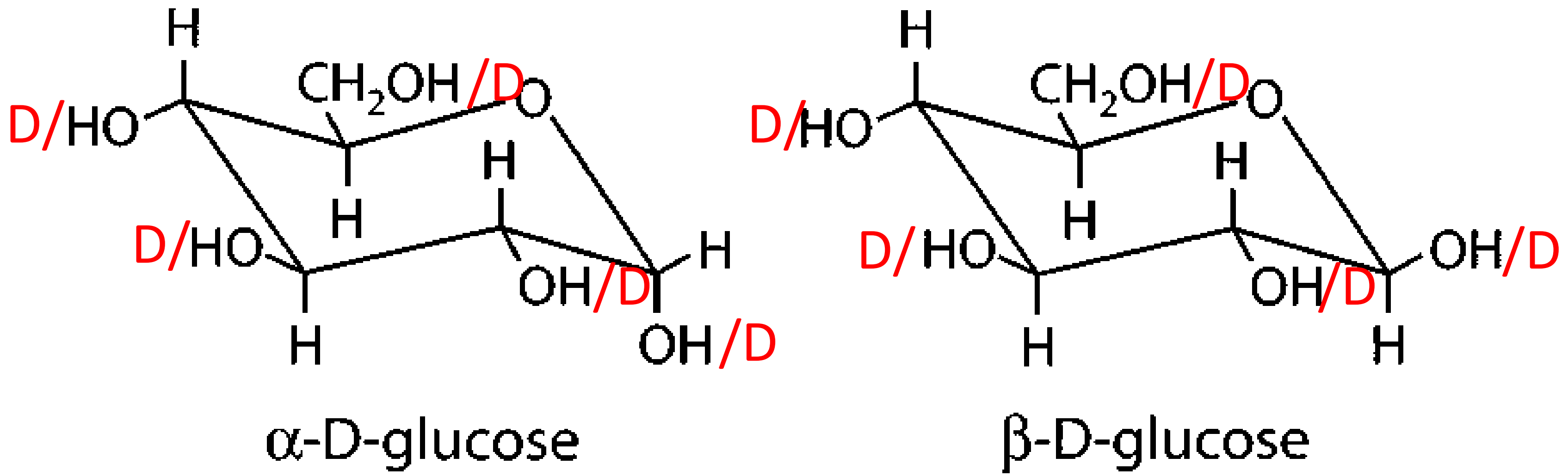
- In situ observation of renneting/curdling (SESANS)
- High pressure effect on casein (SANS)

Hydrogen bonds in liquid and glassy glucose

H/D substitution for exchangeable H atoms

- Glucose-H_5
- Glucose-D_5 (all non-covalent H replaced by D)
- 50/50 Glucose-D_5/ Glucose-H_5

Glass transition:35-39°C

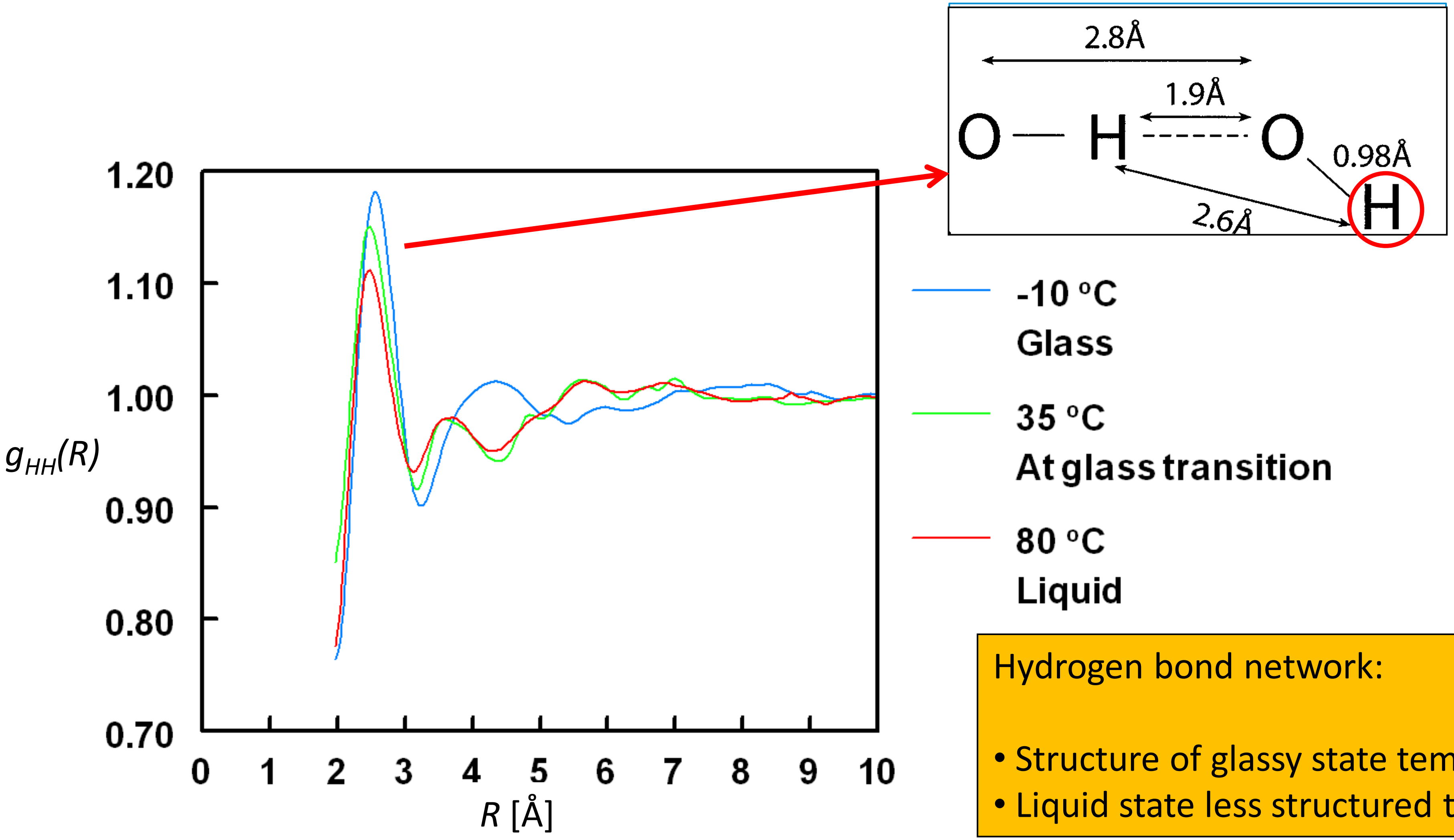


Melting point 146°C

Melting point 150°C

Hydrogen bonds in liquid and glassy glucose

$g_{HH}(R)$ from three H/D ratios; measured at ISIS (SANDALS)

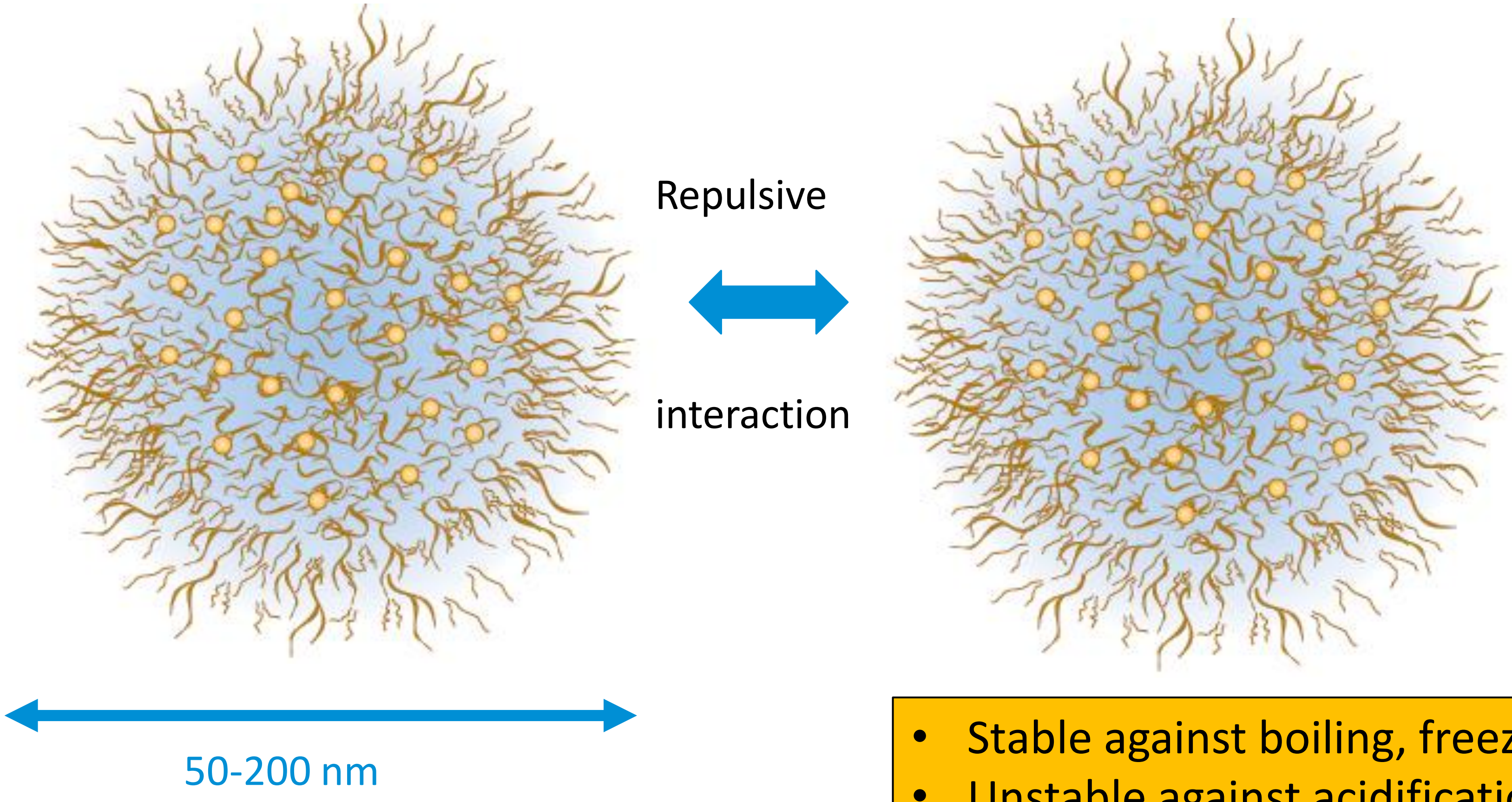


Hydrogen bond network:

- Structure of glassy state temperature dependent
- Liquid state less structured than in glassy state

Small angle neutron scattering

Casein micelles



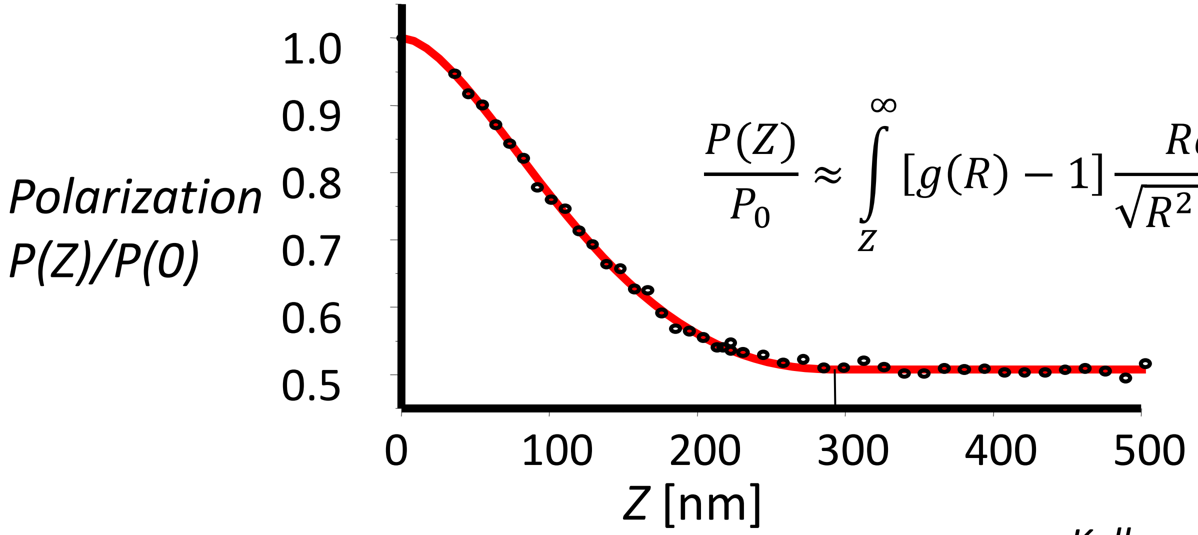
Casein micelles and their internal structure
C.G.de Kruif, Thom Huppertz, Volker S. Urban, Andrei V. Petukhov

- Stable against boiling, freezing, salinity
- Unstable against acidification and 'shaving'
- Unstable at high pressure

In situ observation of renneting/curdling (SESANS)
SESANS set up

Delft University of Technology

Silica spheres 200 nm
Delft University of Technology

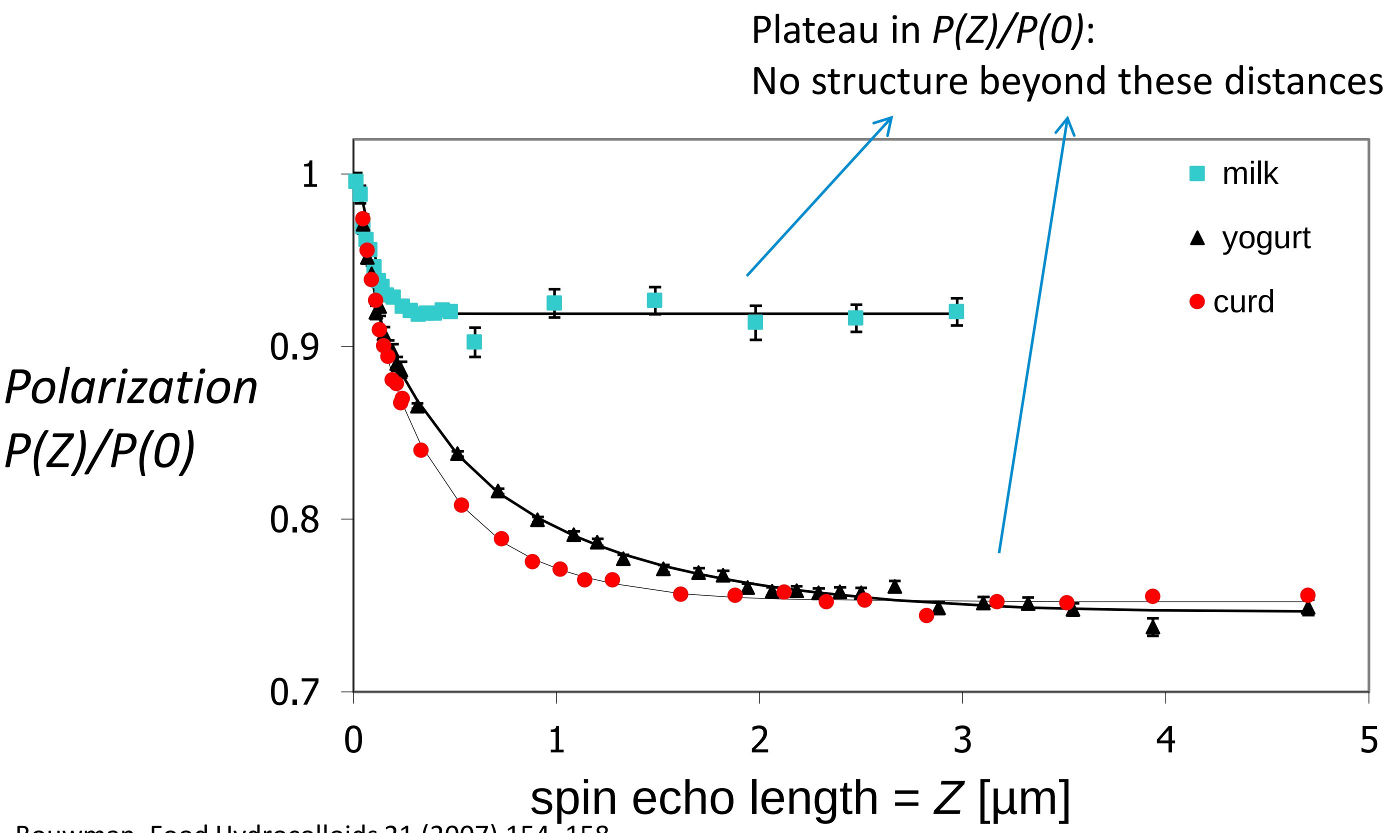


$$\frac{P(Z)}{P_0} \approx \int_Z^\infty [g(R) - 1] \frac{RdR}{\sqrt{R^2 - Z^2}}$$

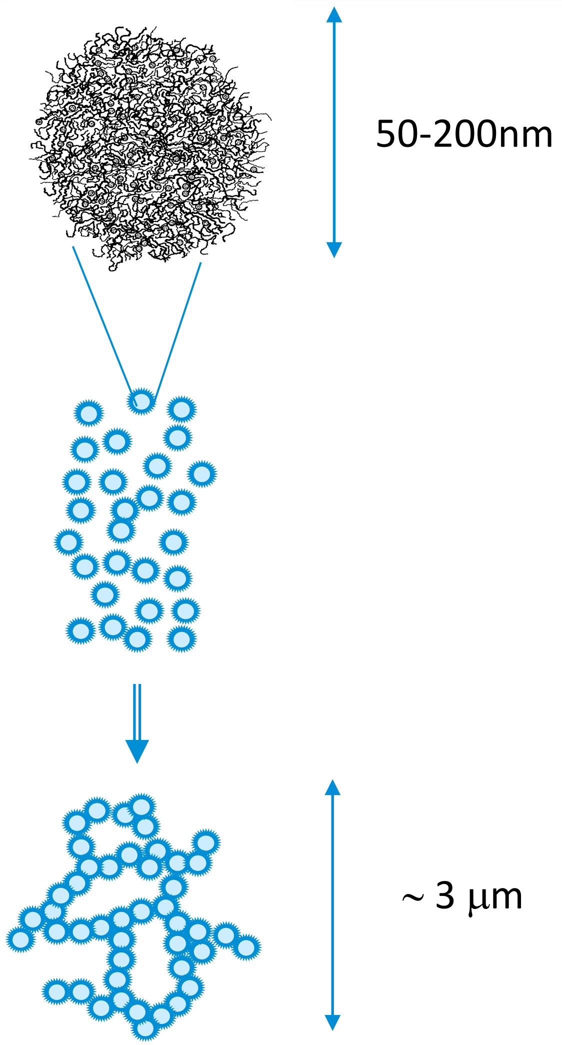
- Decay of polarization with spin-echo length *Z* shows presence of structure
- Point of levelling-off shows maximum size of structure

Keller et al. Neutron News 6, 16 (1995)
Rekveldt, NIMB 114, 366 (1996)

From milk to yoghurt or curd



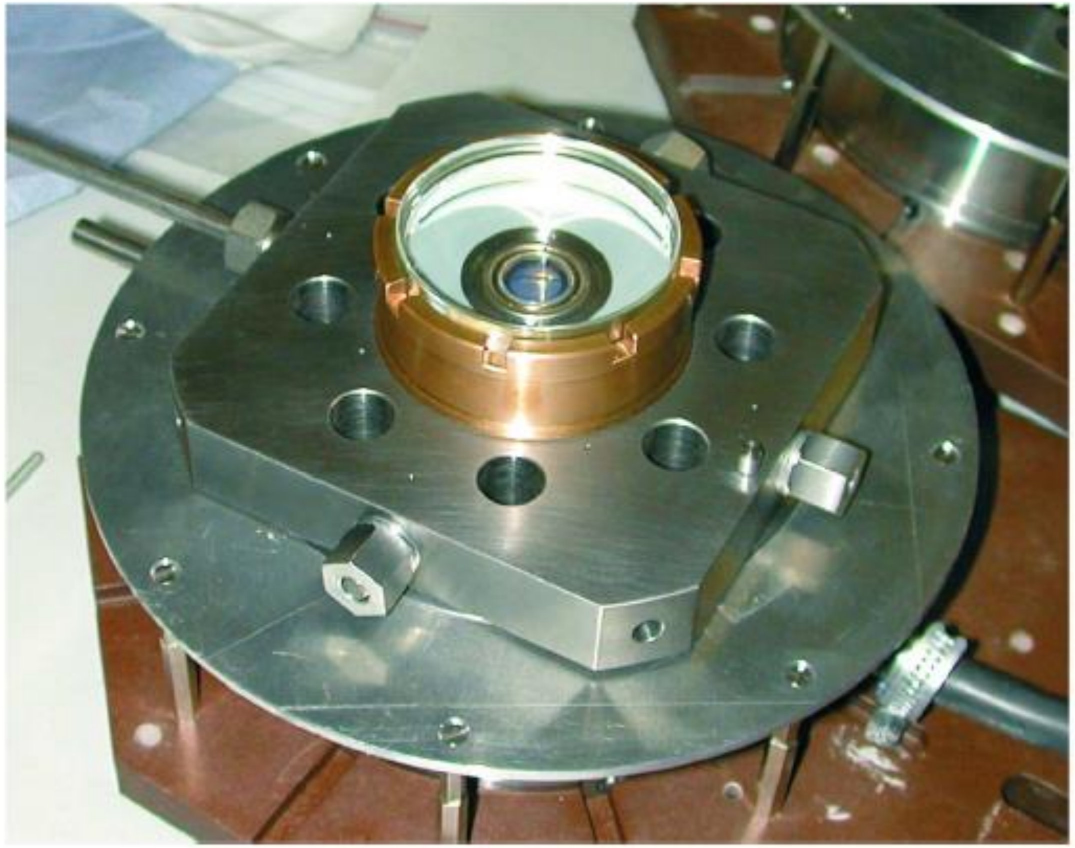
Tromp, Bouwman, Food Hydrocolloids 21 (2007) 154–158



- In milk no structure at $Z > 300$ nm → diameter of largest micelles
- Acid and enzymatic aggregation after several hours give rise to similar structures

SANS under high pressure
The sample and sample cell

High pressure sample cell; up to 500 bar



Sample:

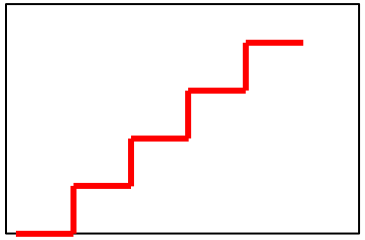
- A fat-free and serum protein-free suspension in D_2O of casein micelles containing 7.2% total solids and 1.8% micellar casein (i.e. solvent is milk serum)

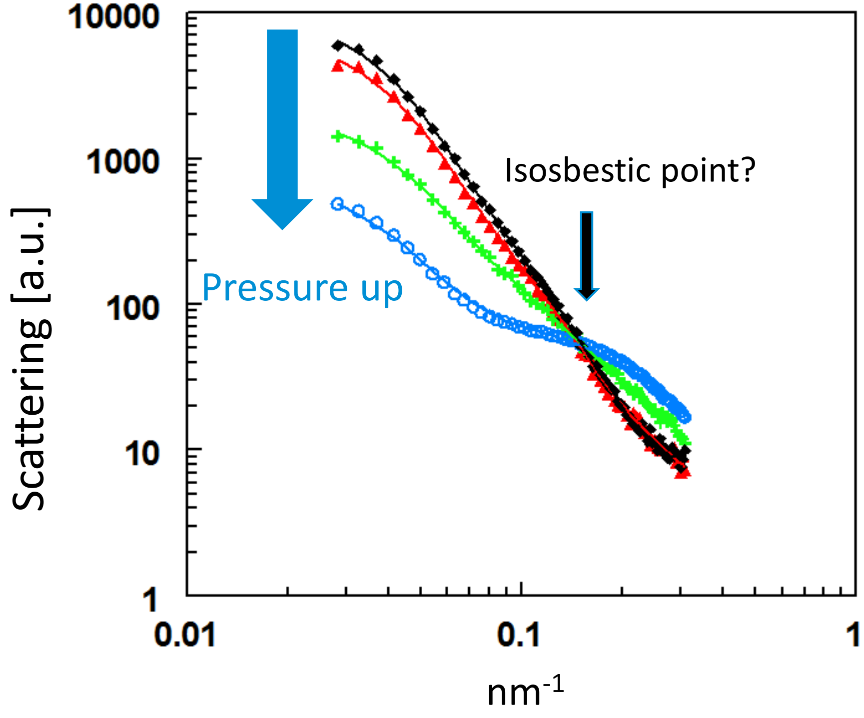
- Reference: (for background subtraction) a solution in D_2O of 5.4% dry freeze-dried 10 kDa permeate of milk

From: Kohlbrecher et al, Rev.Sci.Instr. ***78****, 125101 2007*

Increasing pressure (time step 45 min)

Pressure in time





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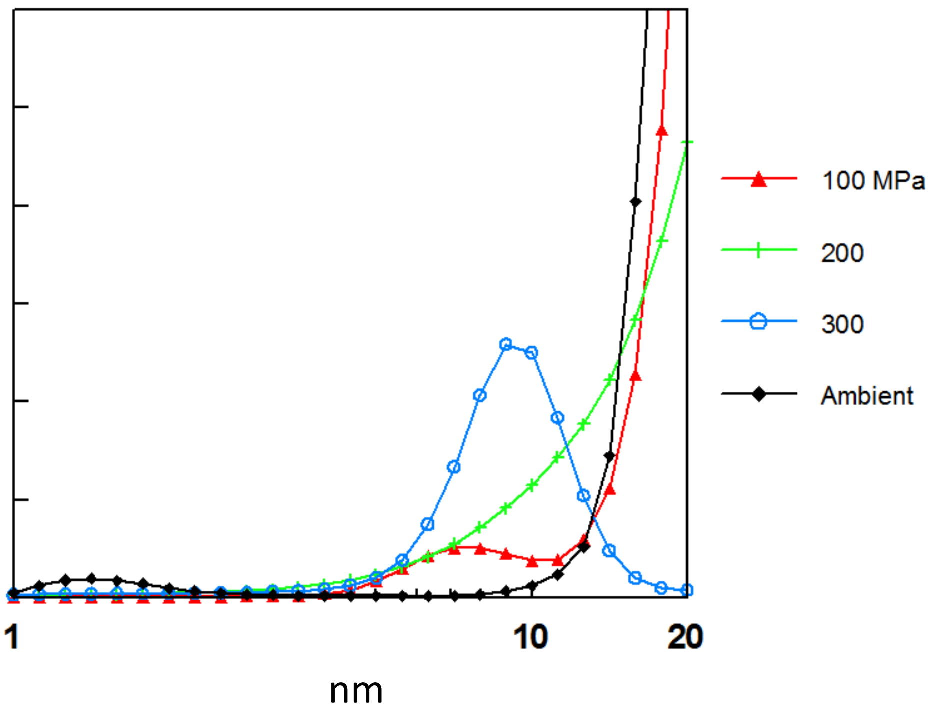
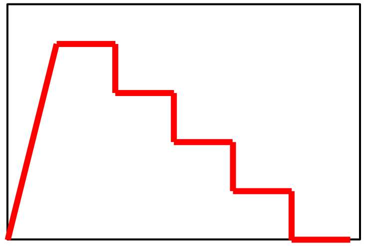


See also: Andrew J. Jackson at al. Chem. Commun., 2011, 47, 487–489

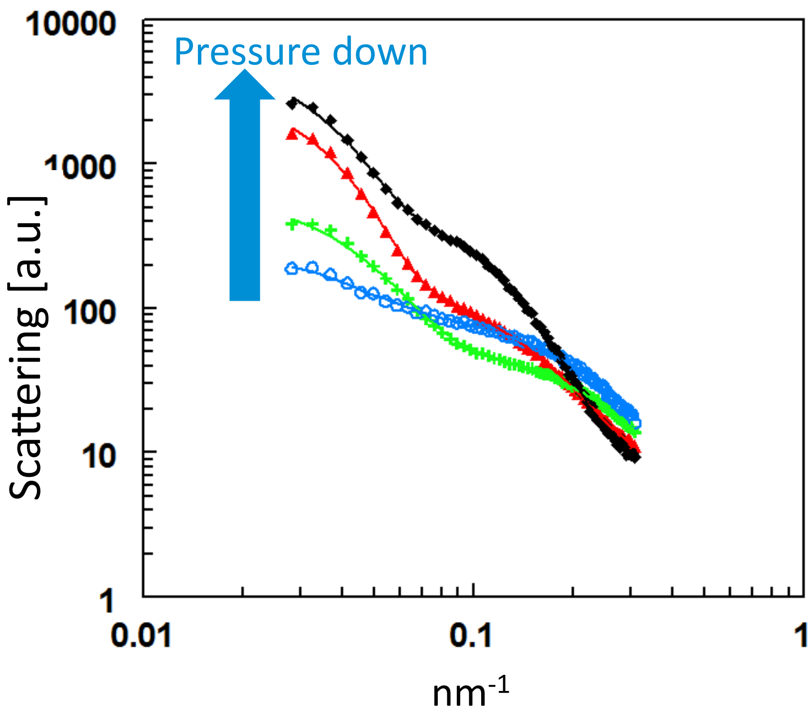
- *Smooth scattering function → polydispersity in structure*
- *Shoulder in scattering intensity → preferential size*

Pressure decreasing (time step 45 min)

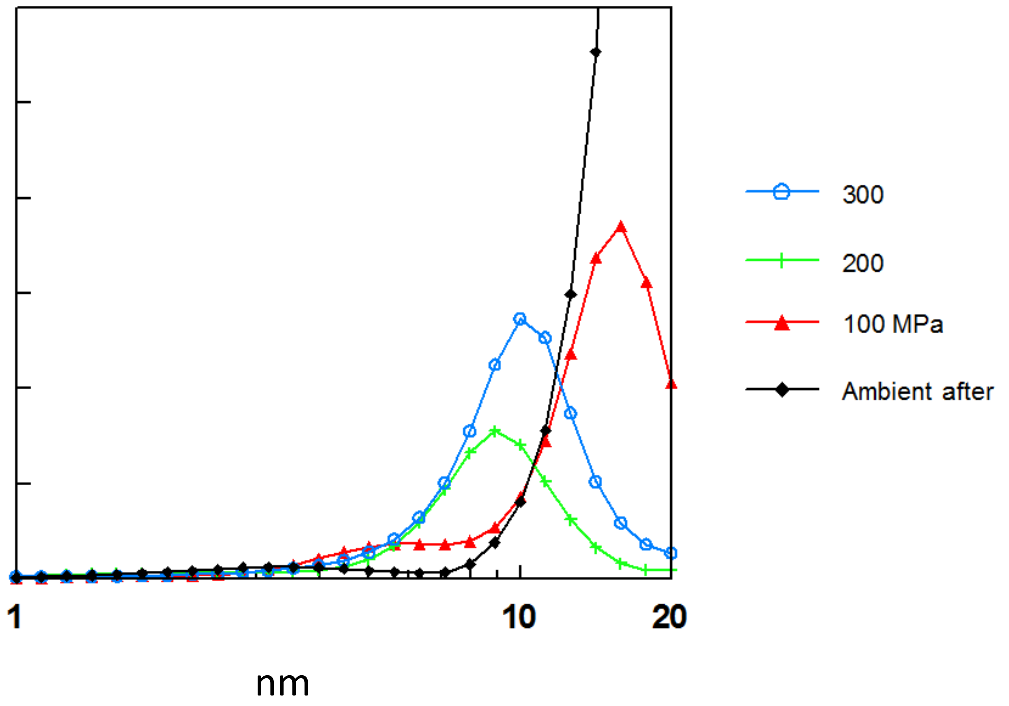
Pressure in time



Scattering intensity



Calculated size distribution



- Micelles reassemble after release of pressure
- Final size smaller than native micelles

Casein micelle suspension before and after pressure

Casein micelles:

- Fall apart above 100-200 MPa
- Partial reassemble on return to ambient pressure

Before pressure

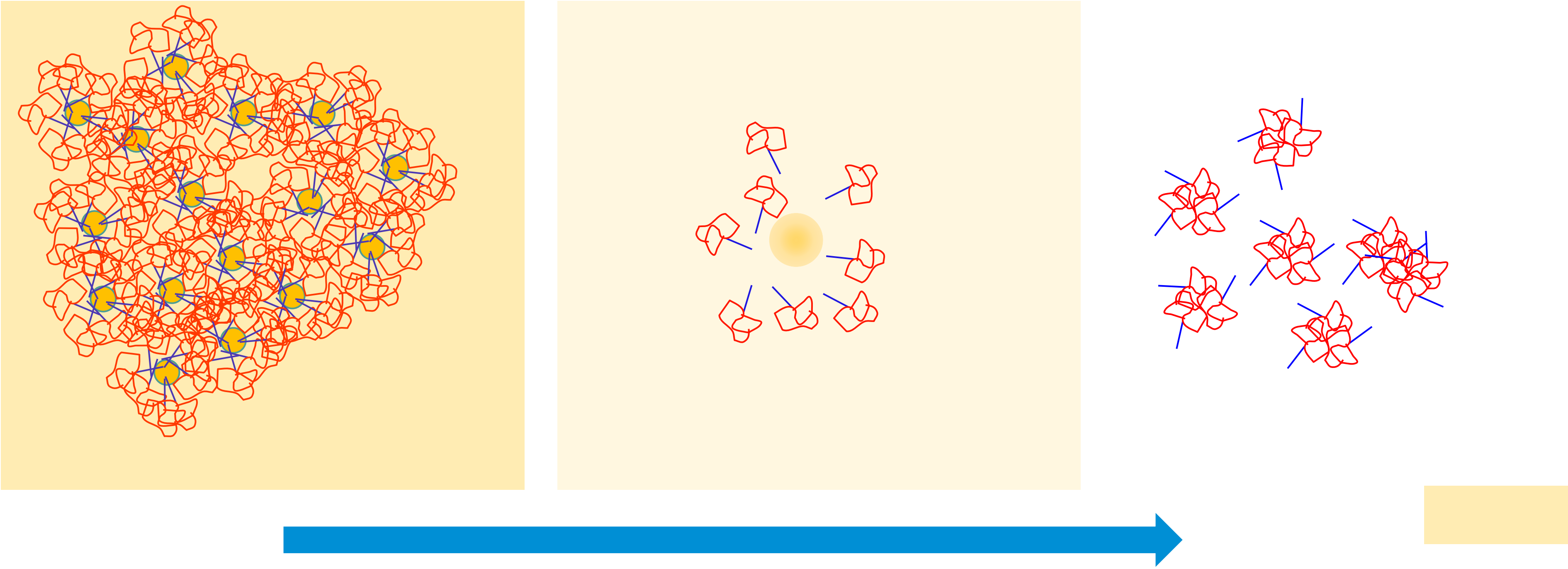
After pressure (300 MPa)

Model
Increasing pressure

Native, saturated in CaPP
- Intact micelles
- Metastable

p =100-200 MPa
- CaPP dissolves

p =300 MPa
- Clusters from protein-protein interactions

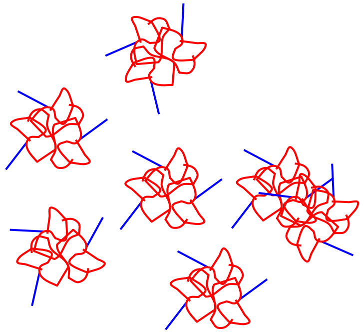


Increasing pressure

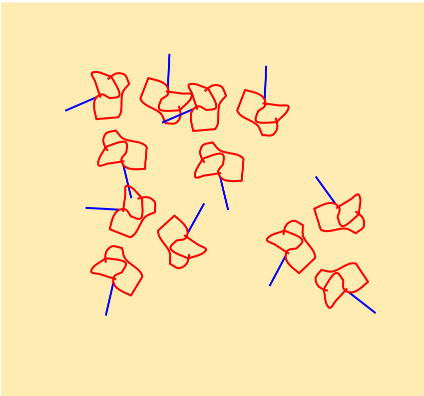
Saturated CaPP (= Ca phosphate) solution

Model
Release of pressure

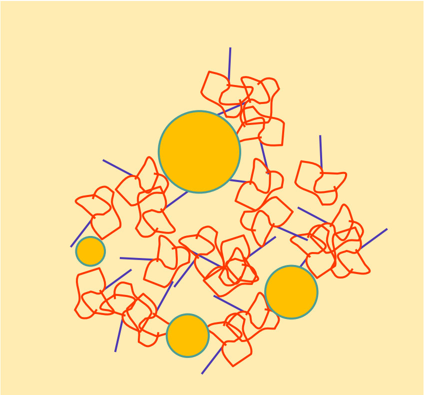
p = 300 MPa
- Clusters from protein-protein interactions



p =100-200 MPa
- Resaturation of CaPP



p ambient:
- Polydisperse CaPP crystallites?
- Irregular protein matrix?
  (Expected from heterogeneous nucleation)



Decreasing pressure

Saturated CaPP (= Ca phosphate) solution

Concluding remarks

Neutron scattering uniquely suitable to shed light specific issues in fundamental food science

Possible further work:

- Solubility of Ca-phosphate at high pressure (using isotopic substitution on Ca?)
- Unfolding of proteins at high pressure
- Interaction of proteins with steel at industrial conditions (high T, high P, high flow)

- Structure of glassy carbohydrates containing water
- Structure of glassy cryo-protectants

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