Protein gels from the inside with neutron scattering

- Spin-echo small-angle neutron scattering (SESANS)

- Adding gelatine with whey aggregation
- Crosslinked casein micelles
- Acid to ovalbumin

Wim G. Bouwman, Carsten Ersch, Maaike Nieuwland

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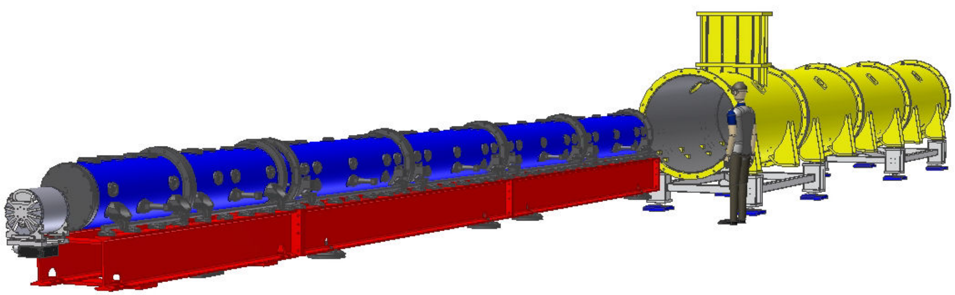
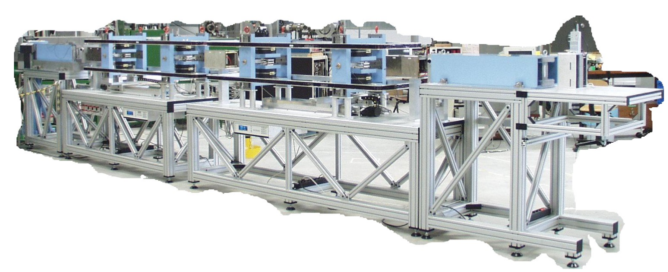
SANS vs SESANS

- Sensitivity:
  1 nm – 500 nm
- Length instrument:
  12 – 80 m
- Reciprocal space



- Sensitivity:
  30 nm – 20 μm
- Length instrument:
  5 m
- Real space



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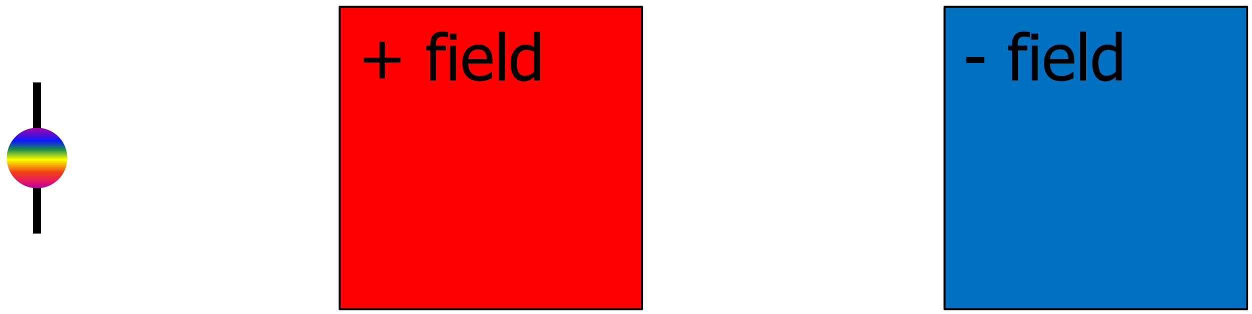
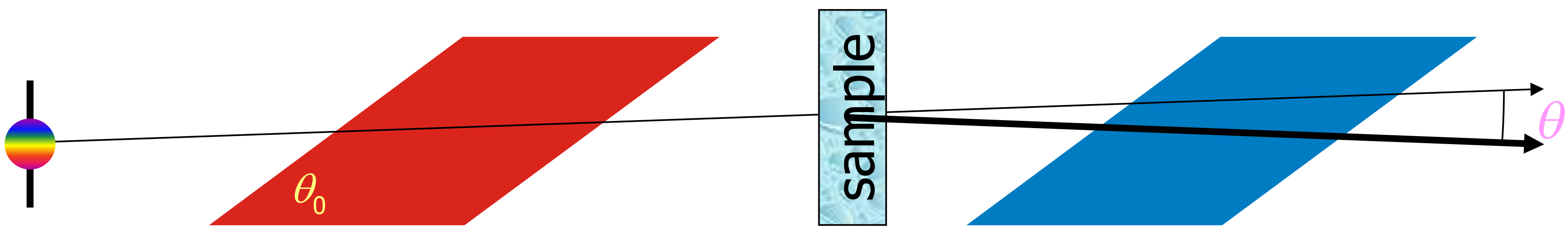
Larmor precession neutron spin magnetic field



Precession proportional to magnetic field line integral:

$$\phi \propto \int B dL$$

Larmor encoding of scattering angle spin-echo small angle neutron scattering



- Unscattered beam gives spin echo ϕ = 0 independent of height and angle
- Scattering by sample → no complete spin echo → net precession angle
- High resolution with divergent beam, sensitive to scattering over 3 μrad

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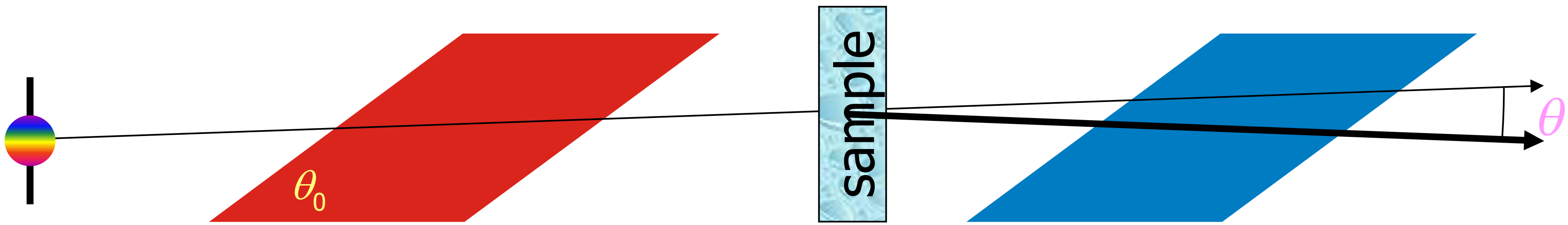
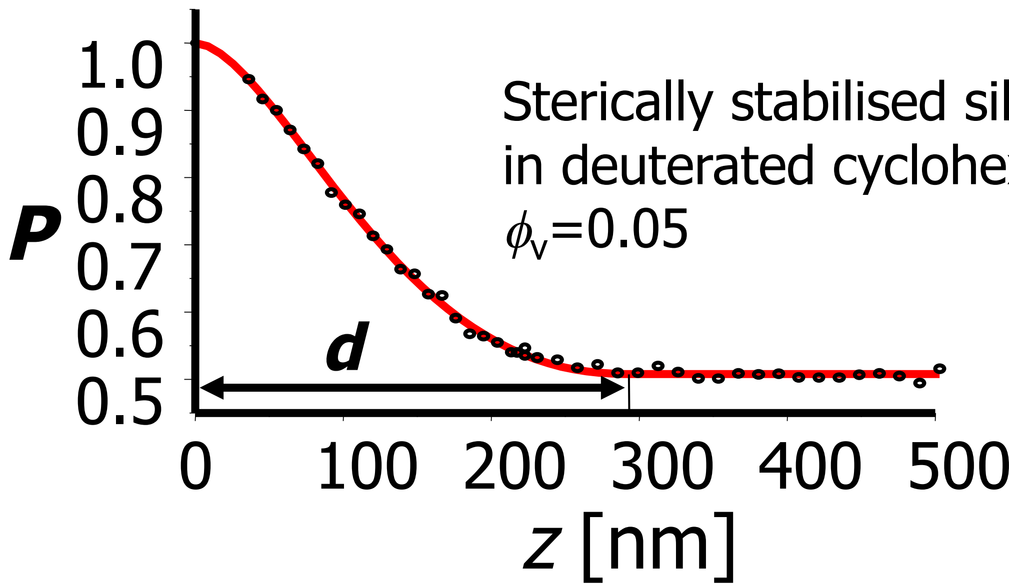
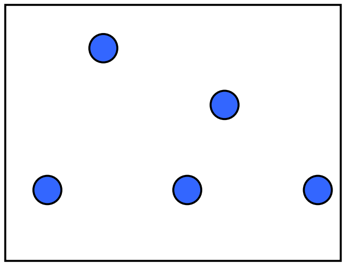
SESANS = Fourier transform scattering ⇒ projected density correlation function

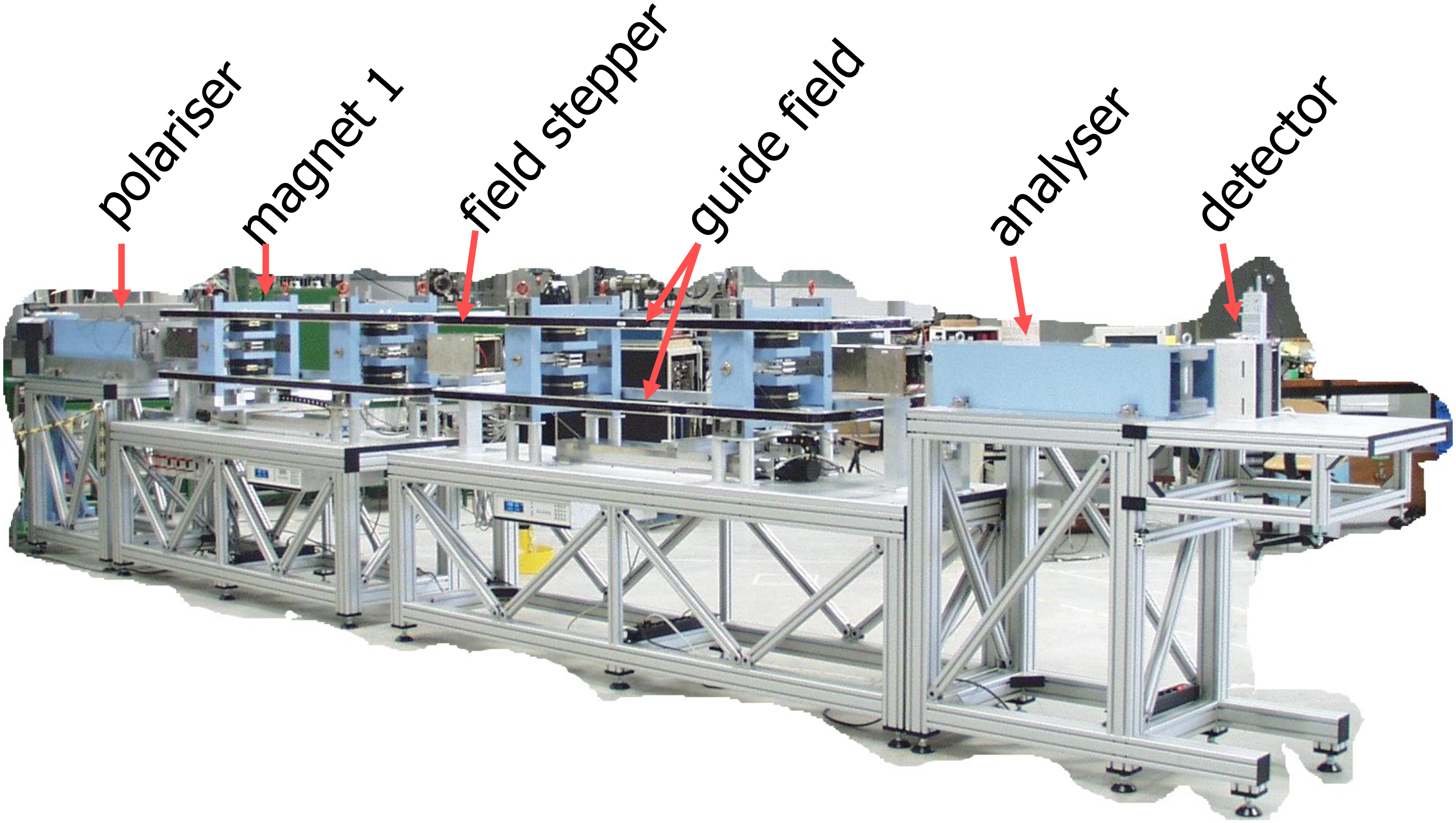




Sterically stabilised silica particles d=298 nm
in deuterated cyclohexane
ϕ_V=0.05



SESANS
spin-echo small-angle neutron scattering



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Food Hydrocolloids 55 (2016) 34–46

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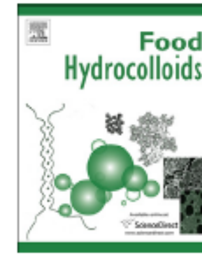

Present affiliation: Arla foods, Aarhus

Microstructure and rheology of globular protein gels in the presence of gelatin

Carsten Ersch [a, e], Marcel B.J. Meinders [a, d], Wim G. Bouwman [b], Maaike Nieuwland [a, c], Erik van der Linden [a, e], Paul Venema [e], Anneke H. Martin [a, c, *]

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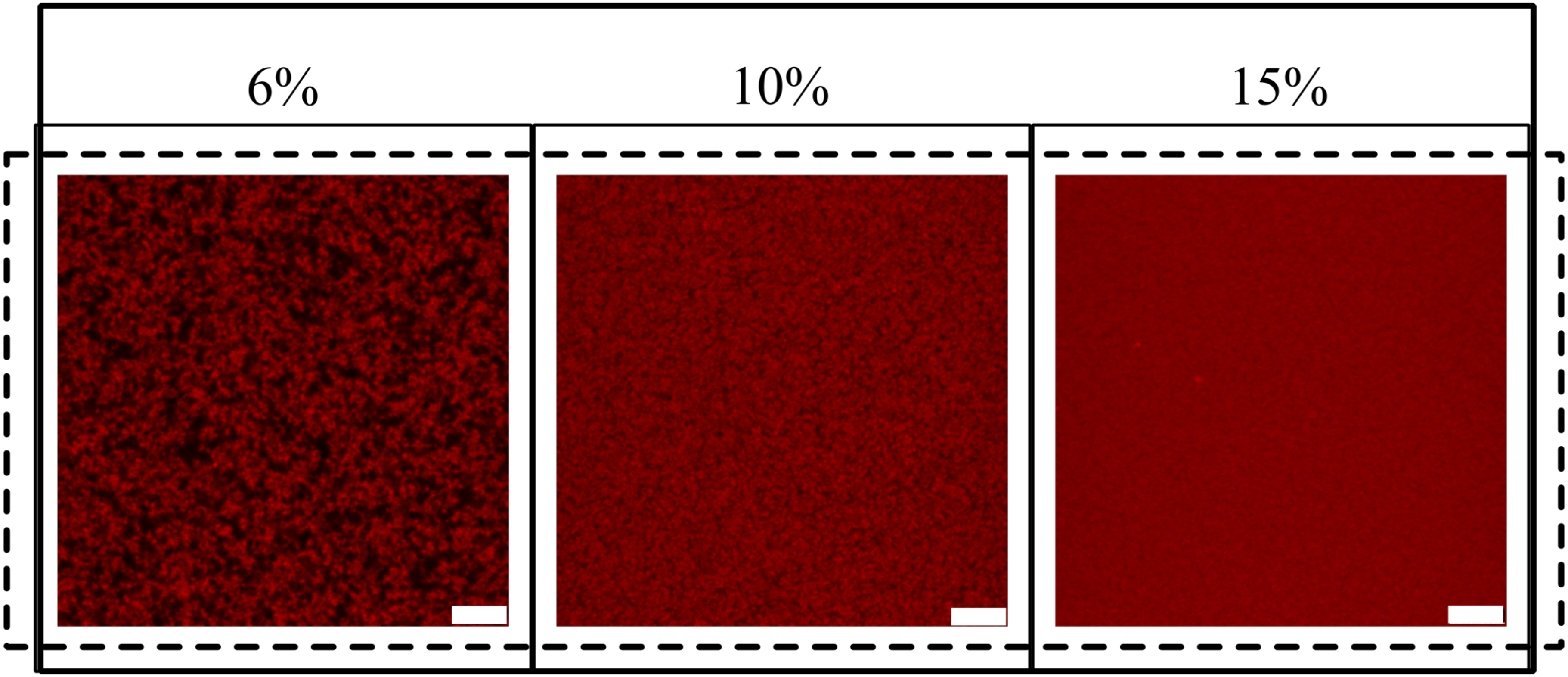
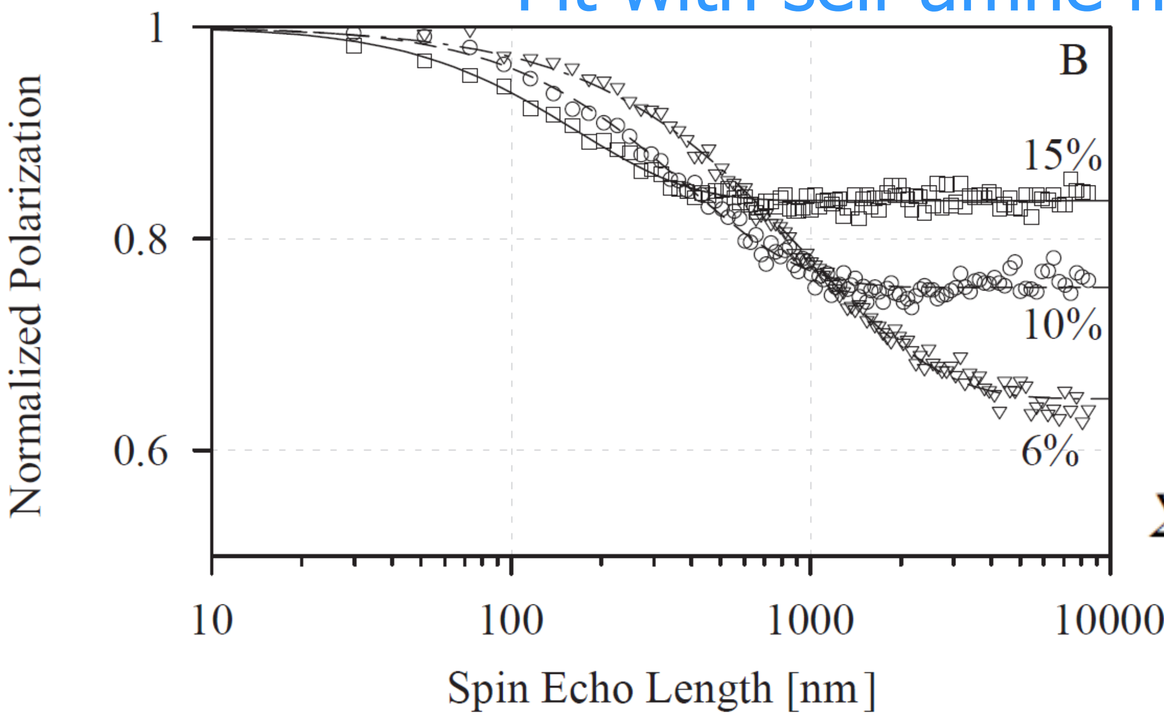
- Gelation, crucial in many food products
- How does 2nd gelating biopolymer effect structure?

Pure system:
confocal laser scanning microscopy



scalebar 7.5 μm

Pure system, effect concentration
Fit with self affine model



With concentration:

- Initial slope increases
- Size decreases

$$P(z) = e^{\Sigma_t[G(z)-1]}$$

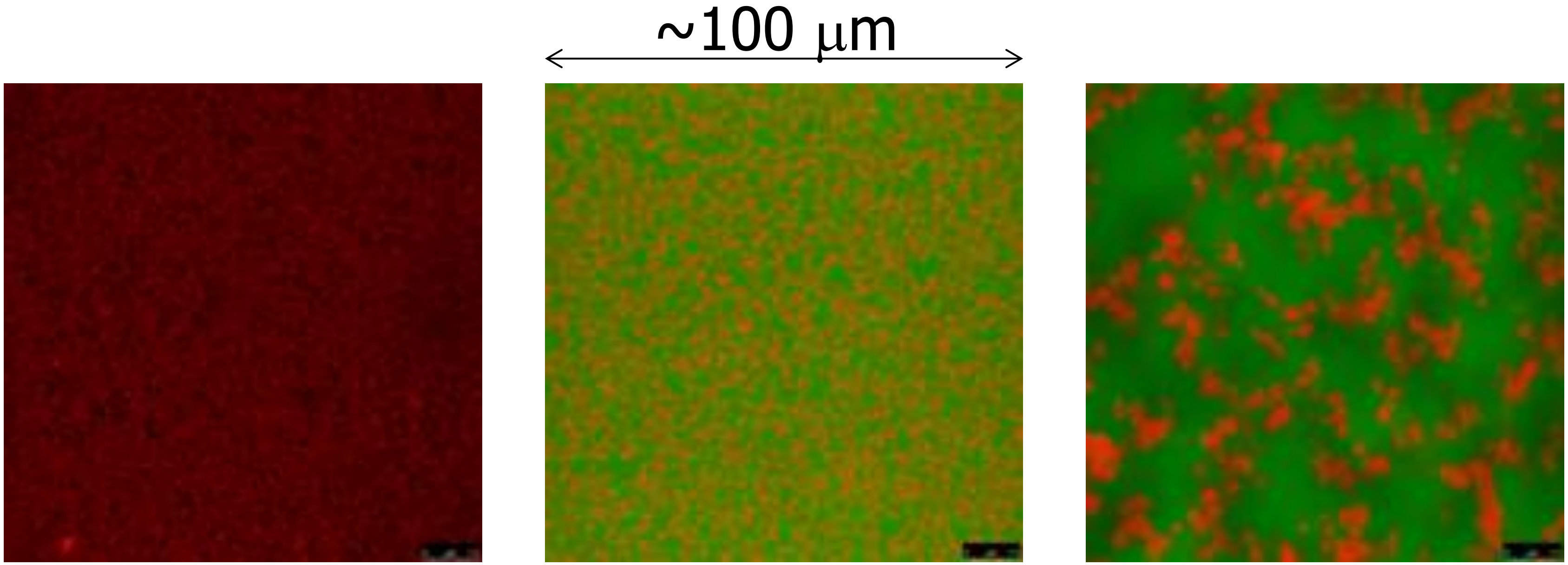
$$\Sigma_t = \lambda^2 t(\Delta\rho)^2 \xi \Phi(1-\Phi)$$

$$G(z) = \frac{2}{\Gamma\left(H+\frac{1}{2}\right)}\left(\frac{z}{2a}\right)^{\left(H+\frac{1}{2}\right)} K_{H+\frac{1}{2}}\left(\frac{2}{a}\right)$$

	6%	10%	15%
Σ_t	0.43	0.28	0.18
H	0.07	0.29	0.45
ξ [nm]	420	380	220

$$\xi = 2\pi^{1/2} a \frac{\Gamma(H+1/2)}{\Gamma(\mathrm{H})}$$

Effect of gelatine on aggregation whey protein



0% gelatine | 2% gelatine | 6% gelatine

Red is globular whey protein

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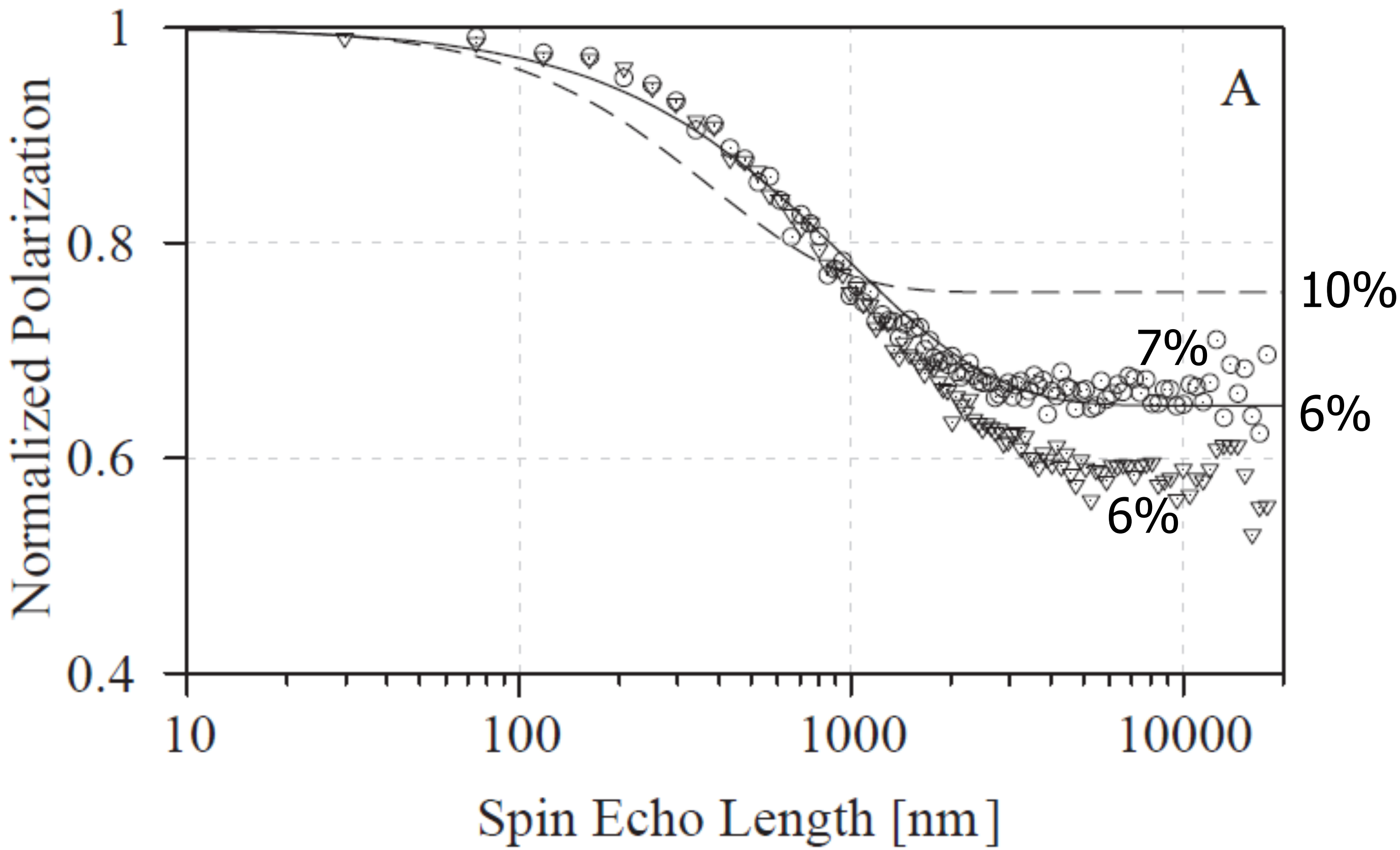
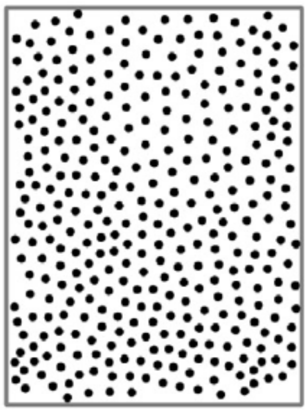
Mixed gel: larger structures
(Lines comparison without gelatin)



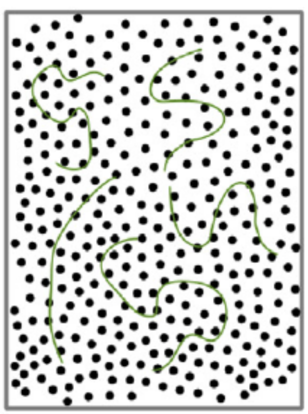
Conclusion:
Gelatine enhances early phase separation

Initial aggregation	Phase separation	Bicontinous gel

Pure



With gelatine



Food Biophysics (2015) 10:416–427
DOI 10.1007/s11483-015-9399-y

ORIGINAL ARTICLE

Characterizing Length Scales that Determine the Mechanical Behavior of gels from Crosslinked Casein Micelles

Maaike Nieuwland[1,2] · Wim G. Bouwman[3] · Martin L. Bennink[4] · Erika Silletti[1,5] · Harmen H. J. de Jongh[1,6]

- Mechanical behaviour of gels important for sensory properties
- Crosslinking is way to tune it
- How does it work?

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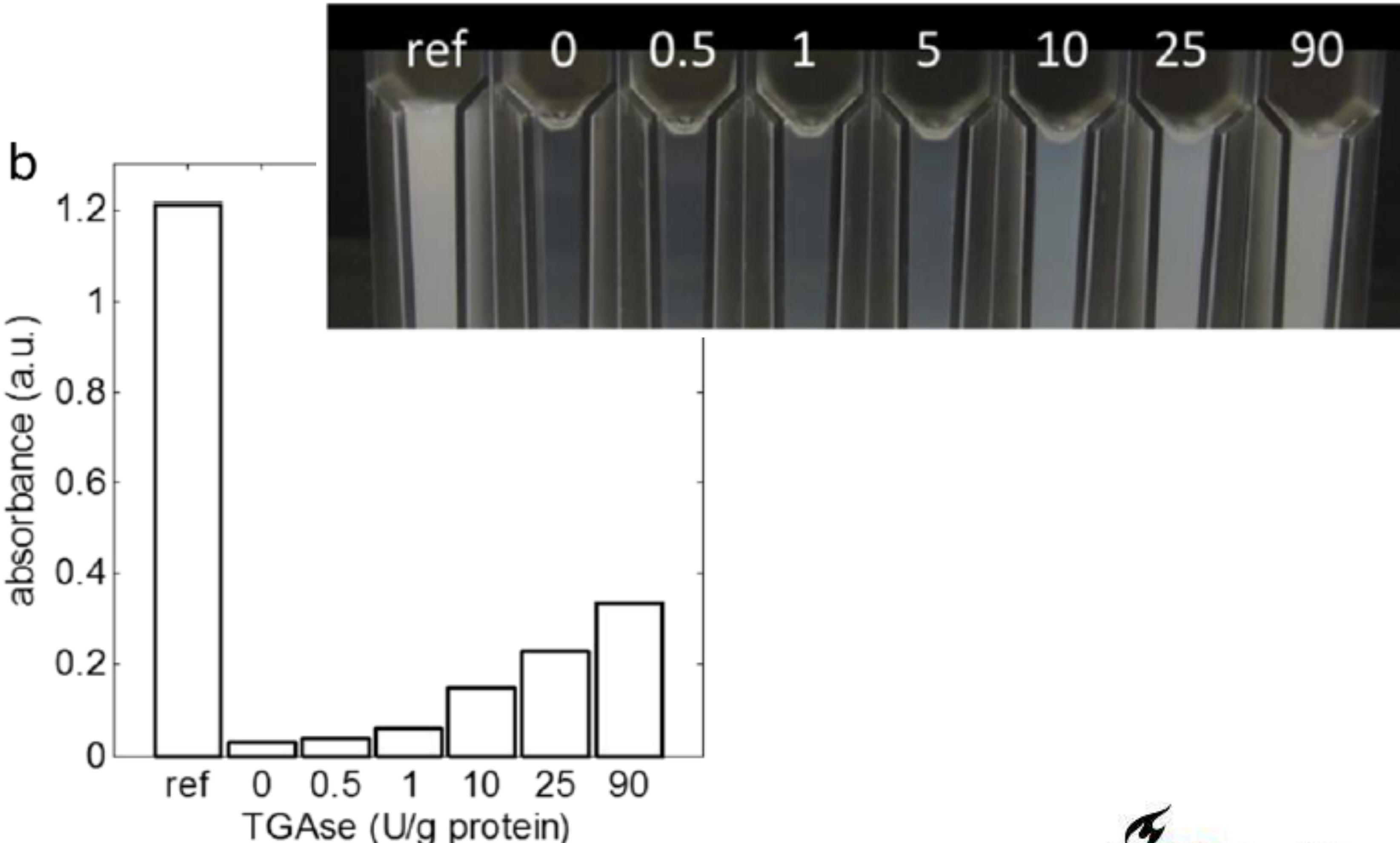
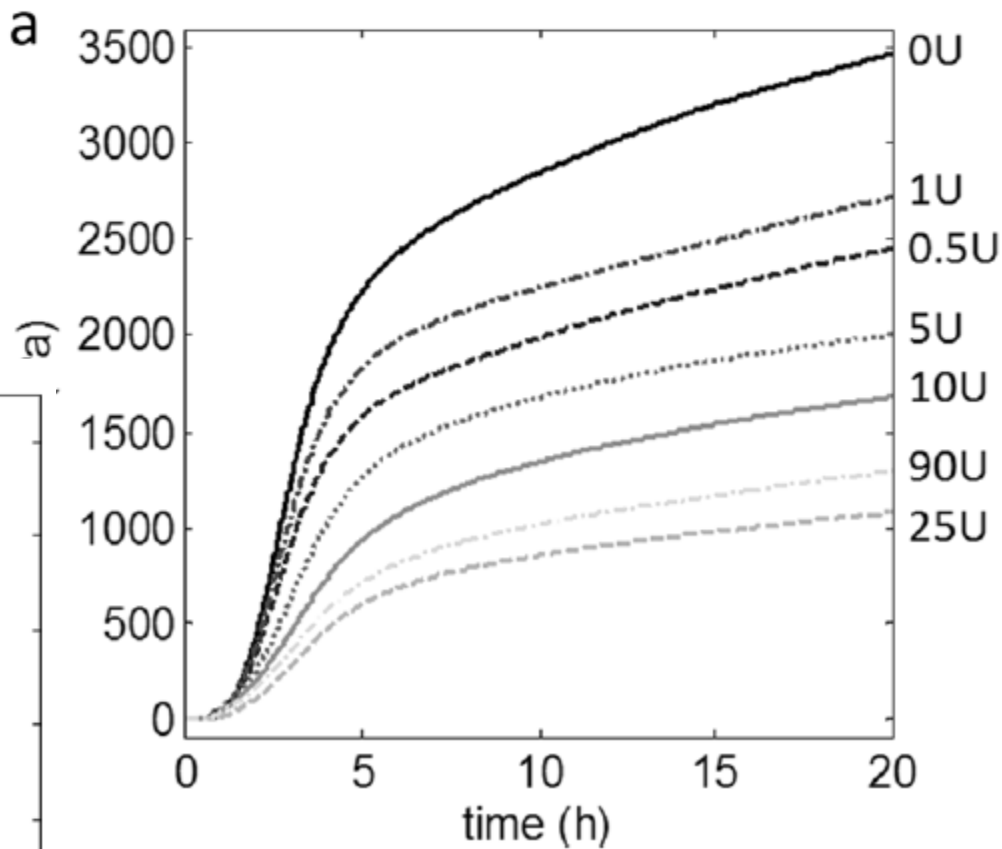
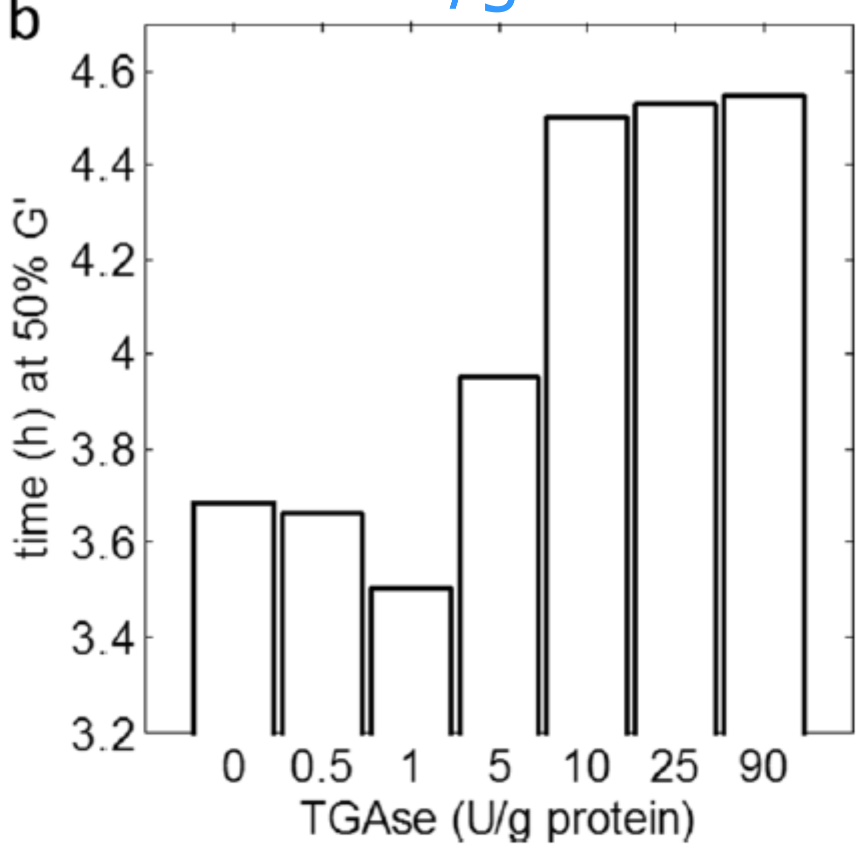
Effect of concentration crosslinker on: Stability against citric acid increases



Crosslinking results in softer gel



Fastest at 1 U/g TGAse



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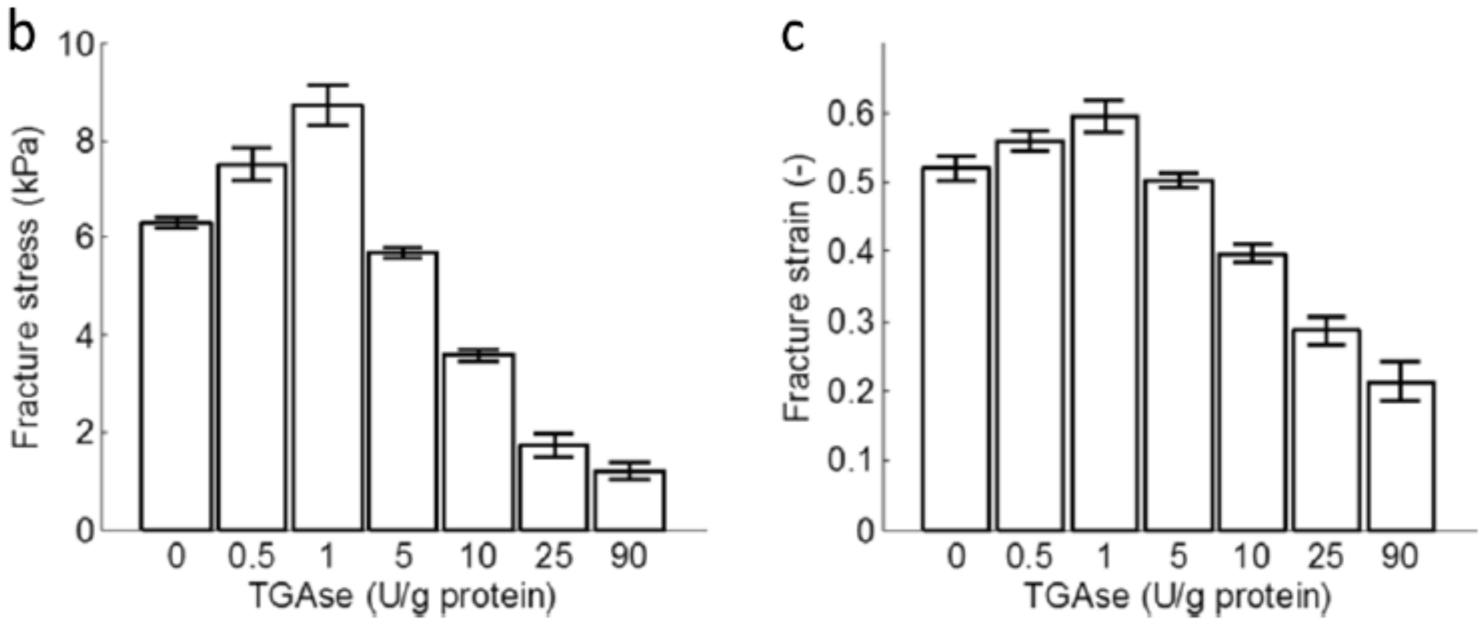
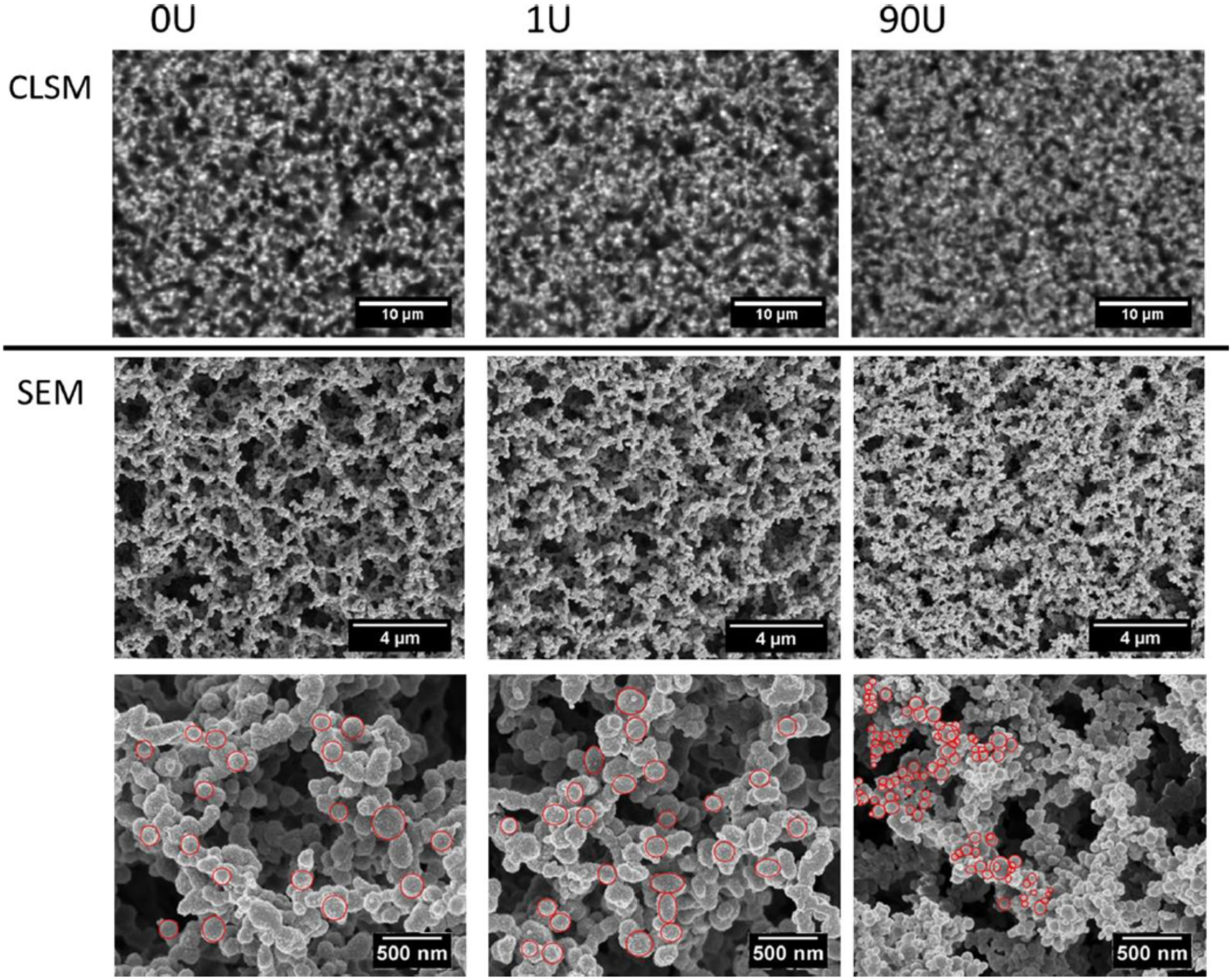
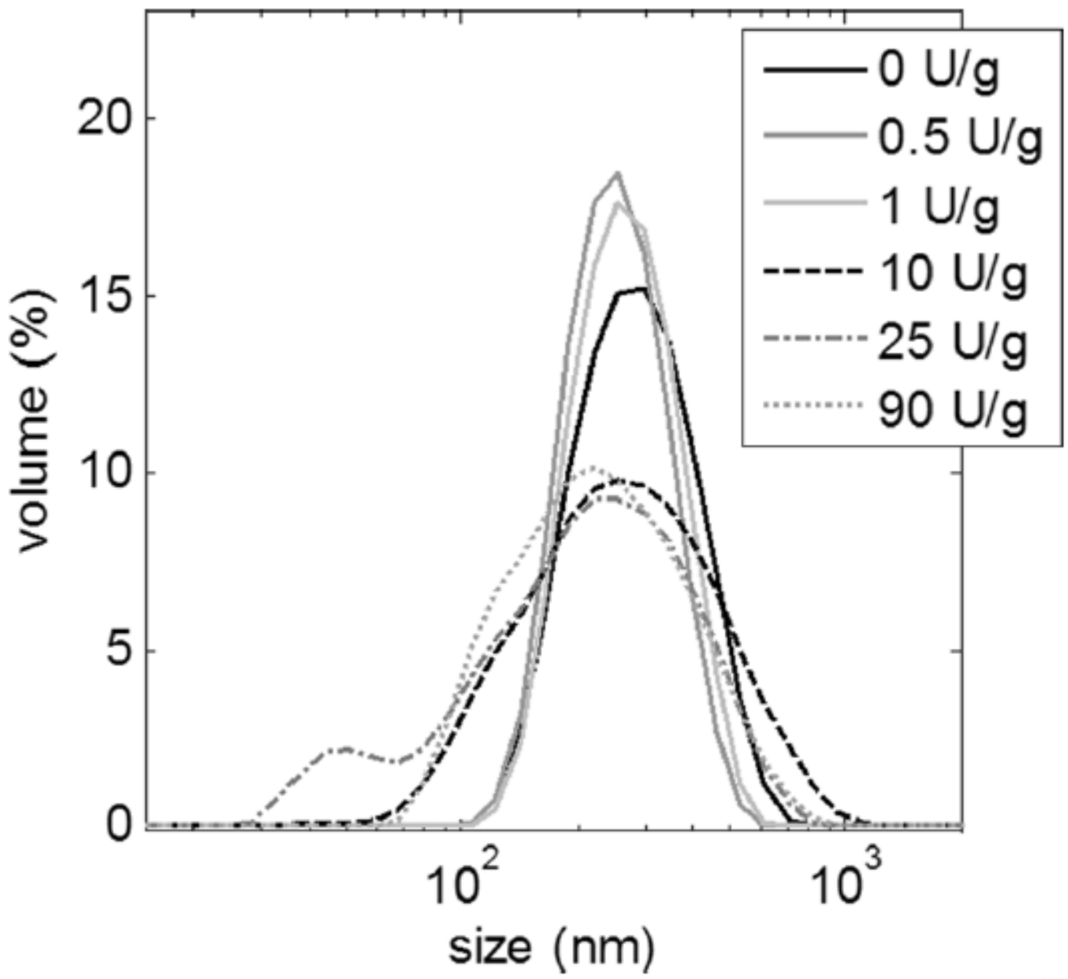
Strongest at 1 U/g TGAse





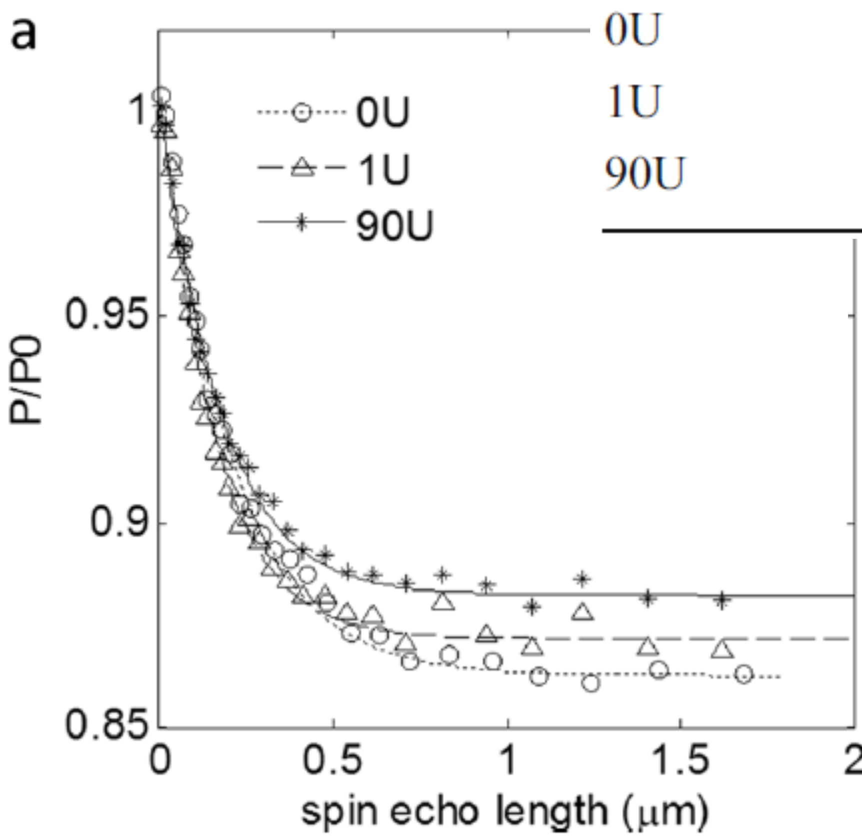
0U
1U
90U
CLSM
SEM
10 µm
10 µm
10 µm
4 µm
4 µm
4 µm
500 nm
500 nm
500 nm

High crosslinking gives some smaller micelles DLS



Finally: neutrons!
1 U yields most scattering per length

Sample (TGAse/g protein)	a (μm)	Σ_t	Σ_t/a (μm^{-1})
0U	0.20±0.01	0.148±0.003	0.74±0.03
1U	0.15±0.01	0.137±0.003	0.91±0.05
90U	0.16±0.02	0.125*	0.78±0.08



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Scattering power related to water holding

$$\Sigma_t = \lambda^2 t (\Delta\rho)^2 \xi \phi (1 - \phi)$$

protein-water contrast

fitted size

volume fraction protein

- Disagreement composition sample
- Swollen protein with water?
- Volume protein swollen with volume *c*

$$\phi = \phi_0 (1 + c) \qquad \Delta\rho = \frac{\Delta\rho_0}{1 + c}$$

Measurement yields attached water *c*

$$\Sigma_t / a \propto \Delta\rho'^2 \varphi' \propto 1 / (1+c)$$

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Finally: neutrons!
1 U ~20% less water

Sample (TGAse/g protein)	a (μm)	Σ_t	Σ_t/a (μm^{-1})
0U	0.20±0.01	0.148±0.003	0.74±0.03
1U	0.15±0.01	0.137±0.003	0.91±0.05
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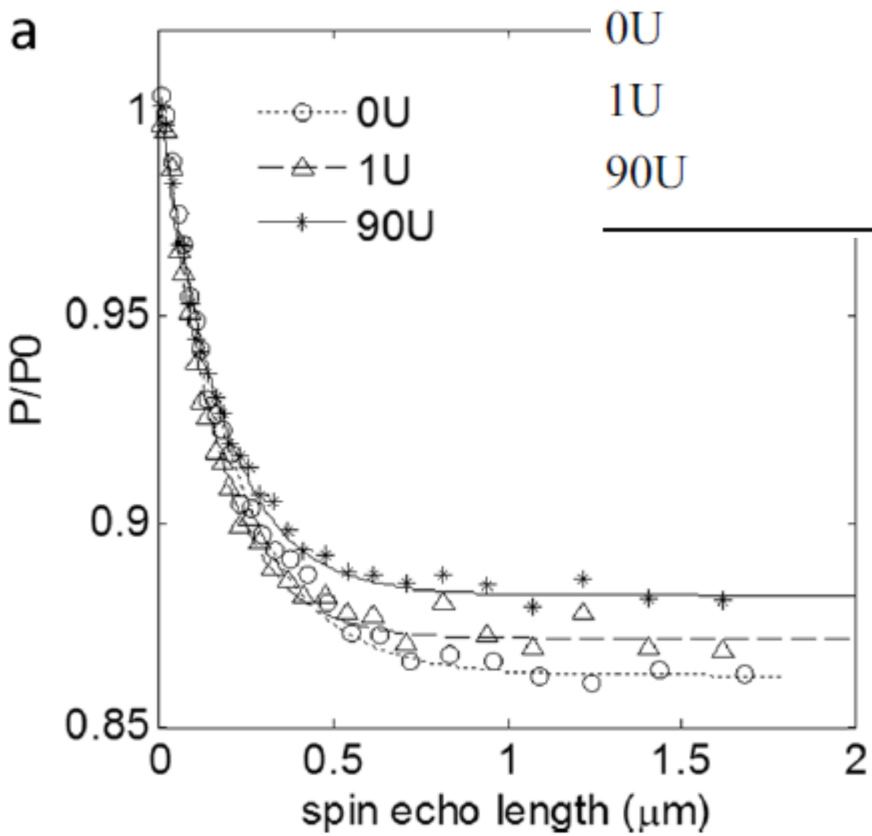

- Conclusion: Crosslinking tunes mechanical and water holding of protein gels
- SESANS 1 of 9 techniques in article

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Food Hydrocolloids 52 (2016) 87–94

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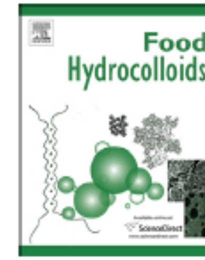

Relating water holding of ovalbumin gels to aggregate structure

CrossMark

Maaike Nieuwland [a, b, *], Wim G. Bouwman [c], Laurice Pouvreau [a, d], Anneke H. Martin [a, b], Harmen H.J. de Jongh [a, e]

[a] *TI Food and Nutrition, P.O. Box 557, 6700 AN, Wageningen, The Netherlands*
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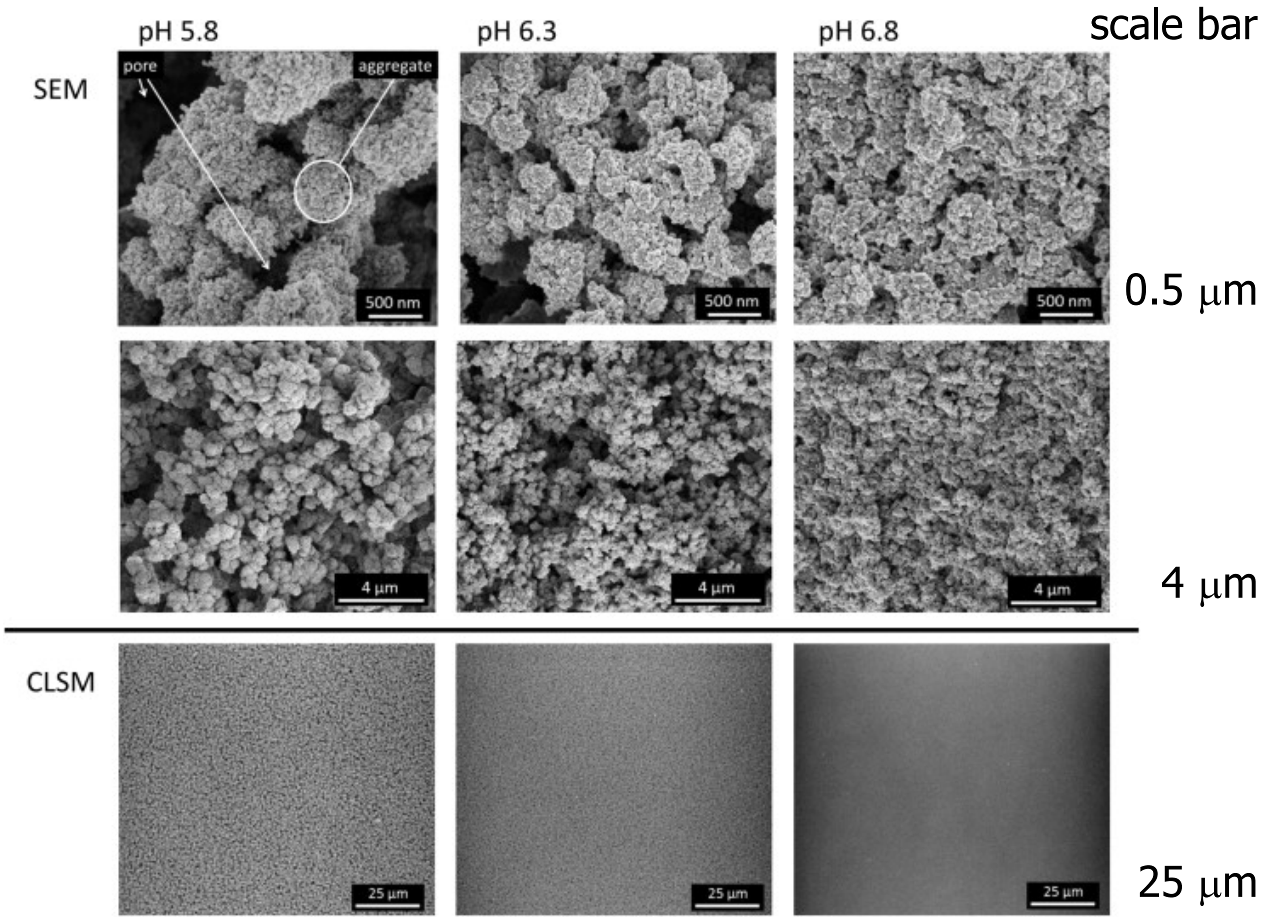
Water holding of ovalbumin gels
Juiciness, release tastants



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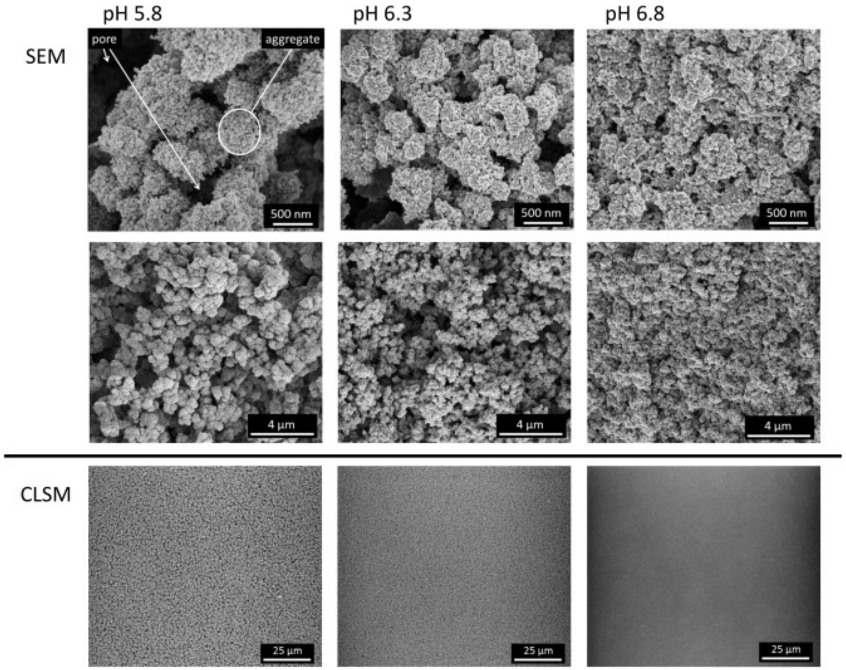
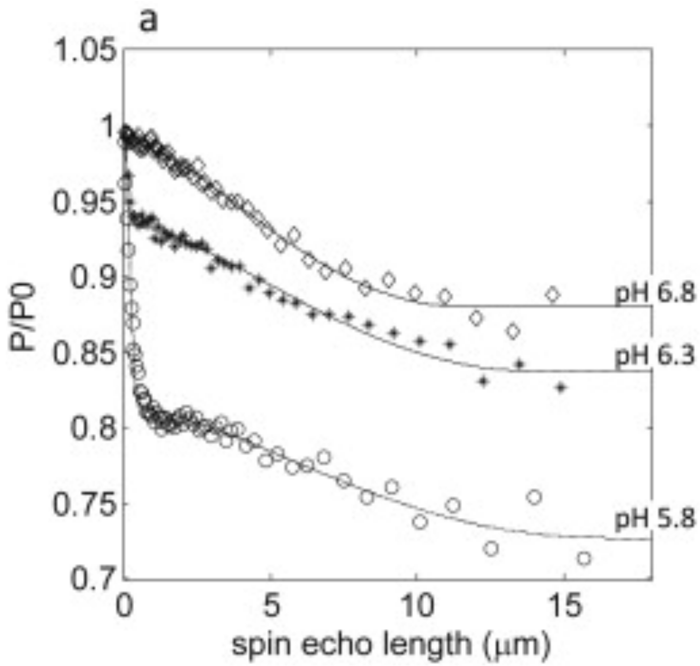
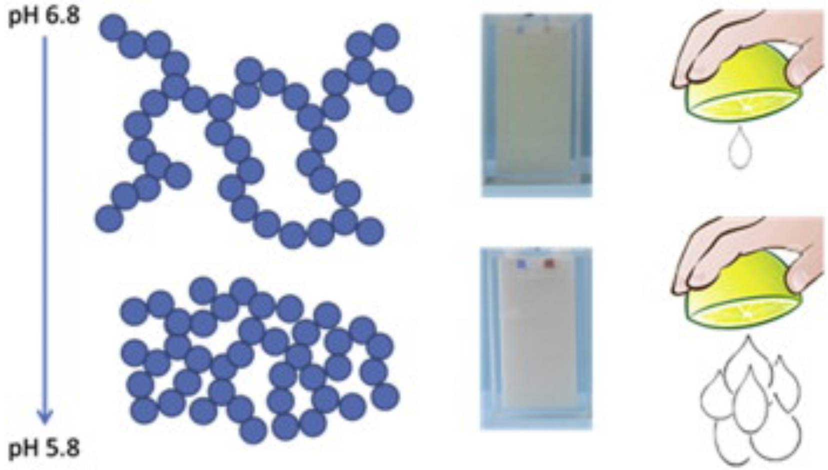
Acid yields more scattering

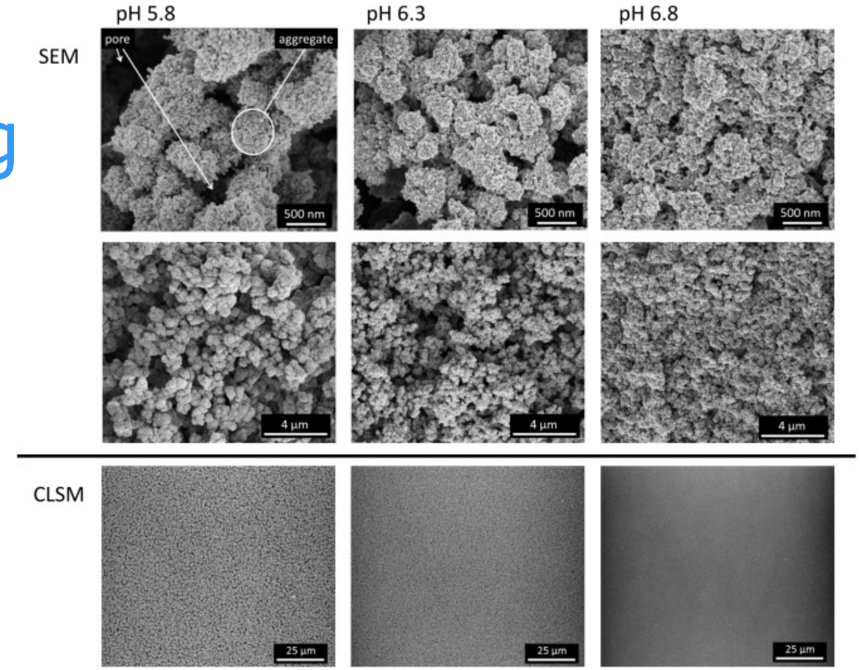
pH	Σ_{t1}	r_1 mm	Σ_{t2}	r_2 mm
5.8	0.21	0.29	0.11	9
6.3	0.06	0.19	0.11	7.4
6.8	0.01	0.15	0.11	6

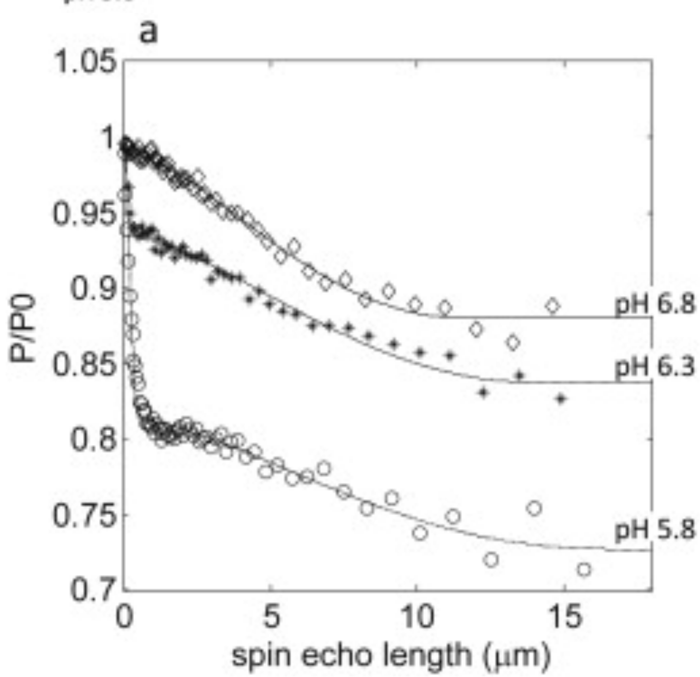


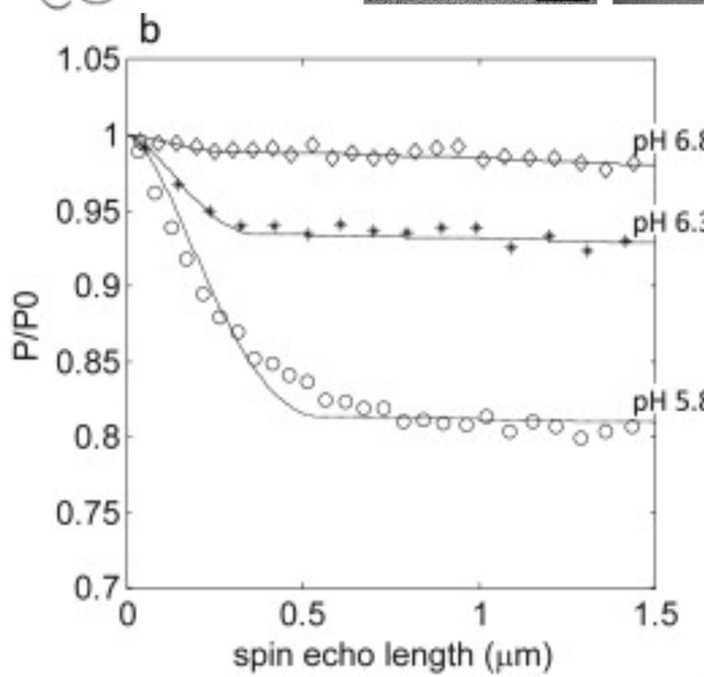


Acid reduces water holding









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Food and neutrons are a tasty combination

- Bulk
- Texture micrometre
- Quantitative

- Aggregation
- Water holding

Wim G. Bouwman, Carsten Ersch,
Maaike Nieuwland

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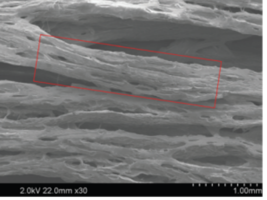

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Relating water holding of ovalbumin gels to aggregate structure, M. Nieuwland, W.G. Bouwman, L. Pouvreau, A.H. Martin, H.H.J. de Jongh, Food Hydrocolloids **52** 87-94 (2016)

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Food Biophysics **10** 416-427 (2015)

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