Applications of SANS II: Soft Matter & Life Sciences

Lecture 10

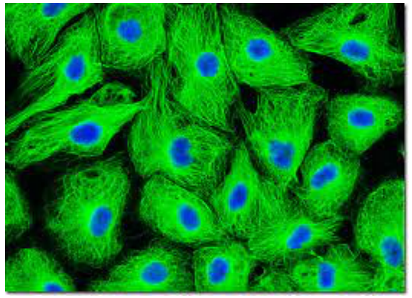
PRESENTED BY JUDITH HOUSTON

2021-06-01

Motivation

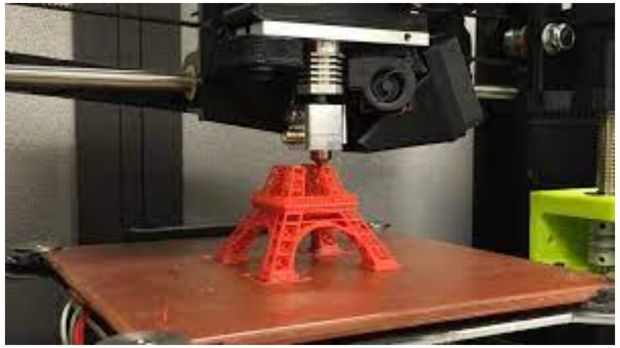
Soft Matter:
Materials with properties between **liquids** and **solids**

Biological materials



Foams

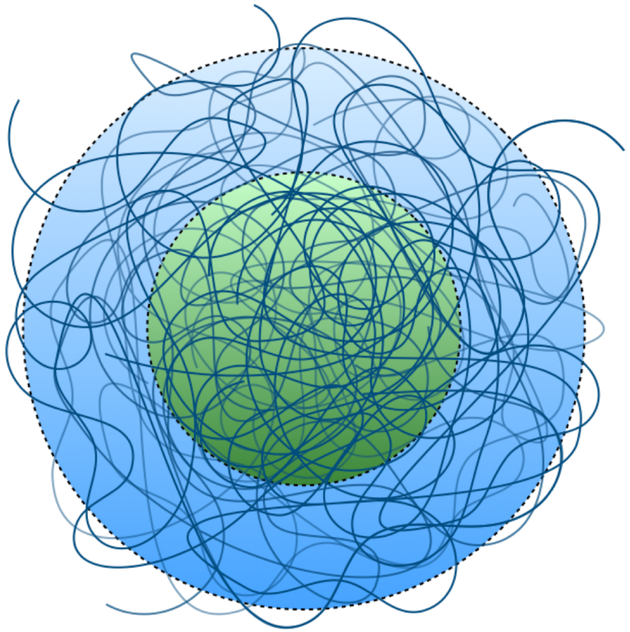
Polymers

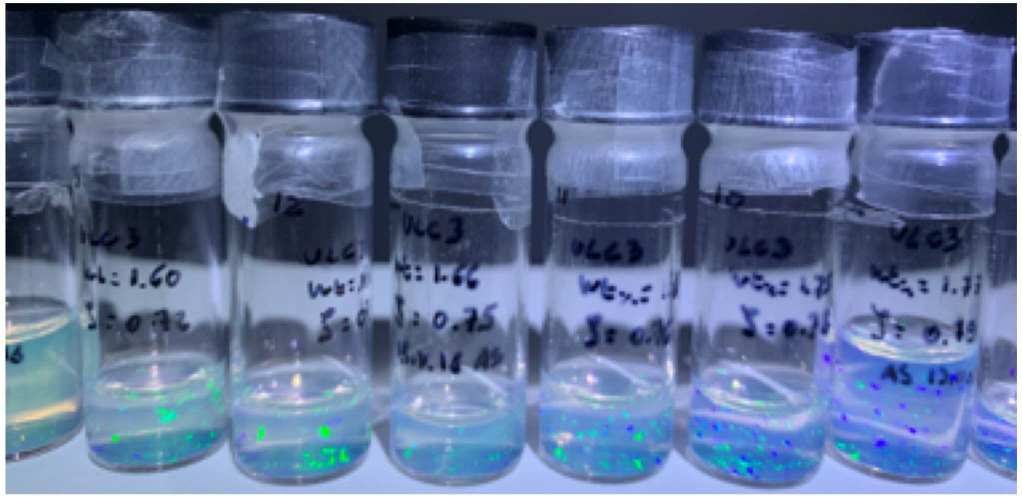


Colloidal suspensions

Liquid crystals

Example 1: Contrast matching & Microgels





Colloids, an excellent model system…

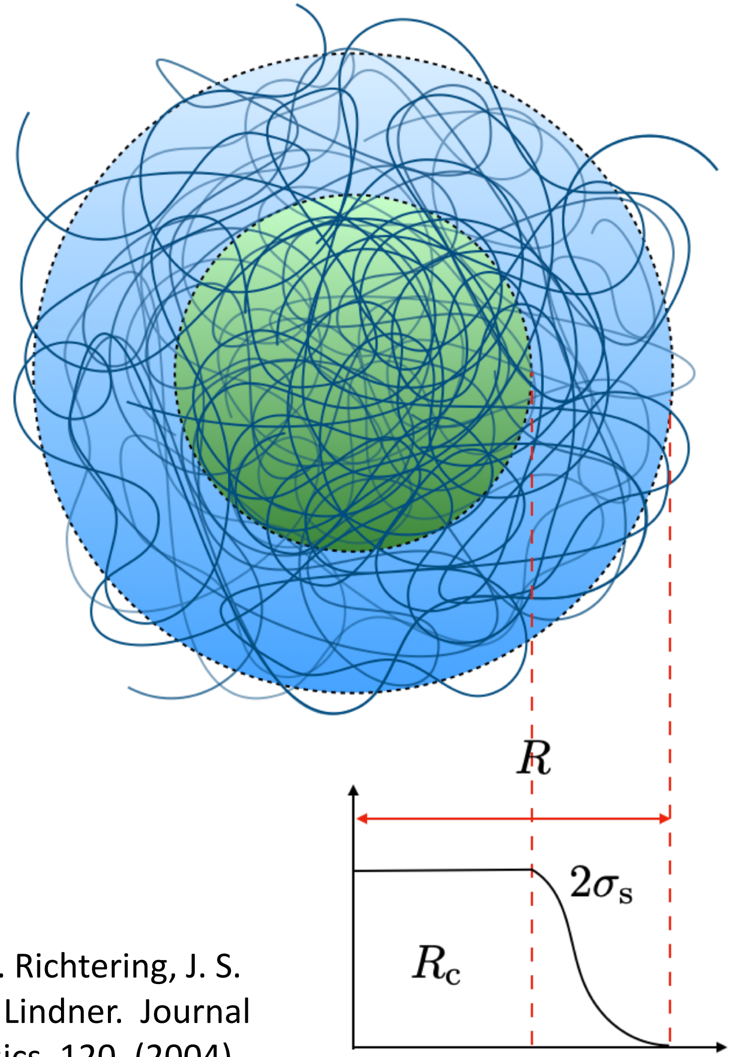
NATURE VOL. 320 27 MARCH 1986

Phase behaviour of concentrated suspensions of nearly hard colloidal spheres

P. N. Pusey & W. van Megen*

Length scale easily accessible in a lab (LS, microscopy)!

What are microgels?

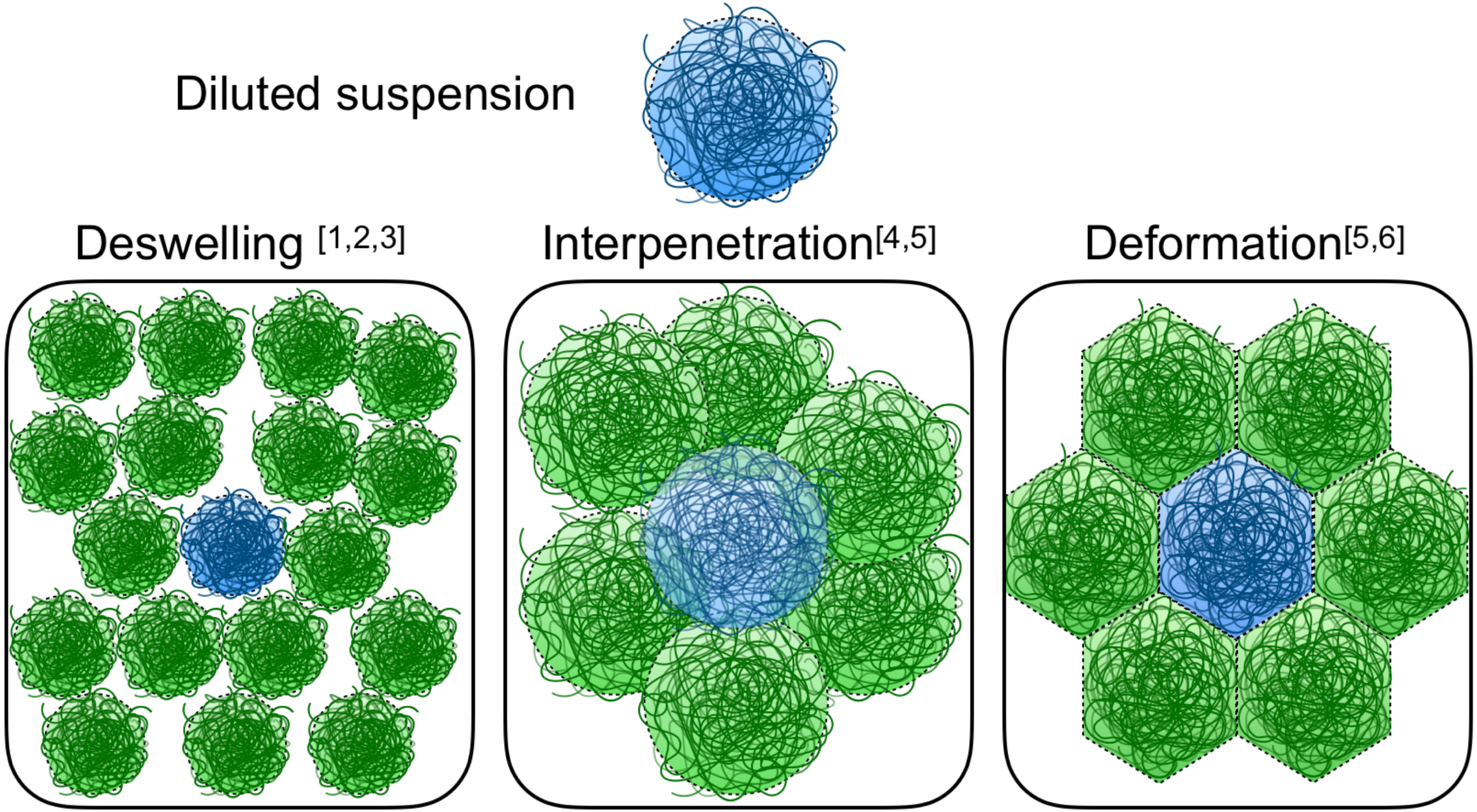


1. Polymeric network swollen in a solvent.
2. Changes in T, pH, P affect the solvent quality.
3. Core: approximated with a hard sphere [1].
4. Polymer density decays as a Gaussian [1].
5. Model system for soft-spheres.

How does softness affect the phase behaviour of colloids?

[1] M. Stieger, W. Richtering, J. S. Pedersen, and P. Lindner. Journal of Chemical Physics, 120, (2004).

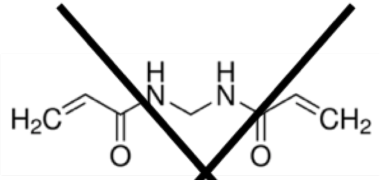
How does this model system behave?



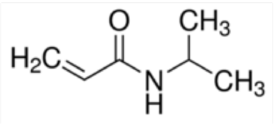
[1] A. S. J. Iyer and L. A. Lyon. Angew. Chem. Int. Ed. 48, 4562- 4566 (2009). [2] A. Scotti et al. Proc. Natl. Acad. Sci. USA 113, 5576-5581 (2016). [3] A. Scotti et al. Phys. Rev. E 96, 032609 (2017).
[4] P. S. Mohanty et al. Scientific Reports 7, 1487 (2017). [5] G. M. Conley et al. Science Advances 3, e1700969 (2017). [6] I. Bouhid de Aguiar et al. Scientific Reports 7, 10223 (2017).

Ultra-low crosslinked microgels

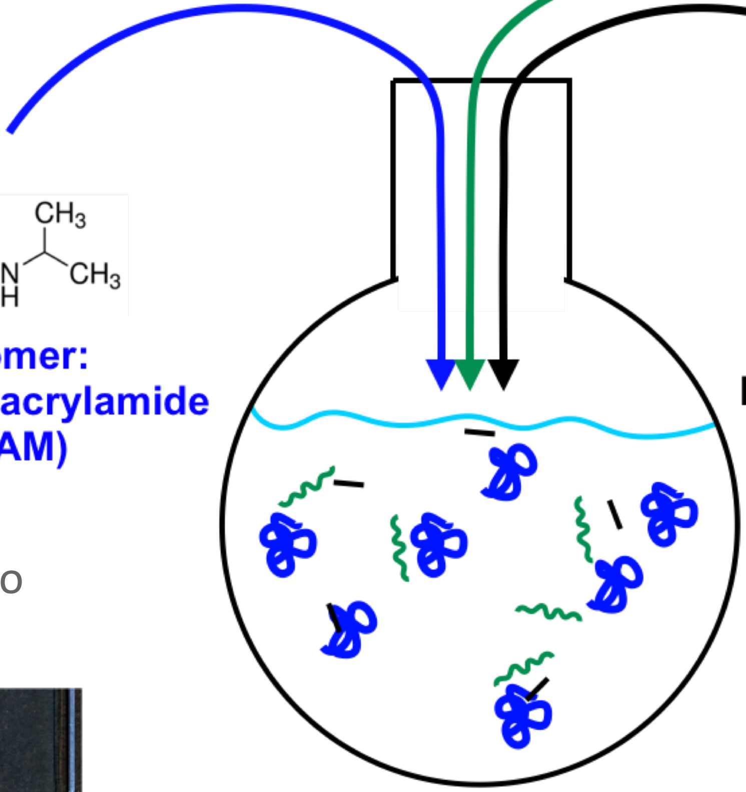
…aka *Super Soft* microgels

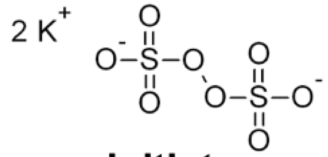


~~**Crosslinker: *N,N'*-Methylenebis(acrylamide) (BIS)**~~

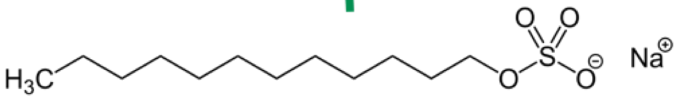


Monomer: *N*-isopropylacrylamide (NIPAM)



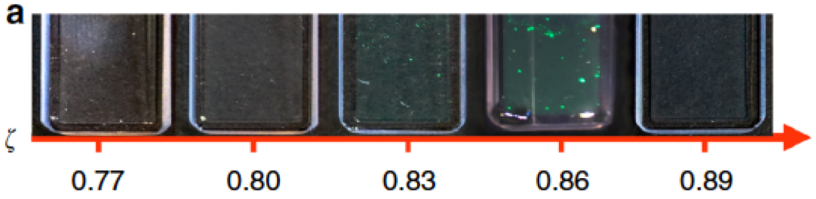


Initiator: Potassium persulfate (KPS)



Surfactant: Sodium dodecyl sulfate (SDS)

ULC microgels shown previously to crystallise [1]

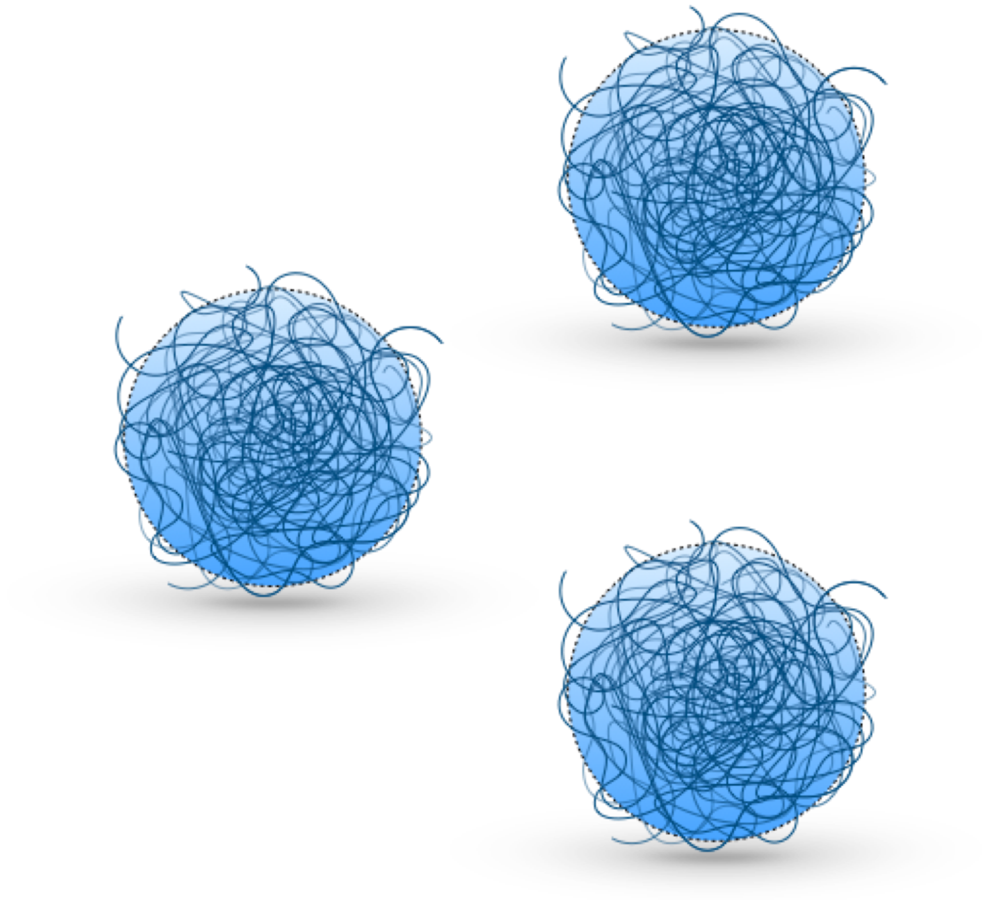


AIM: how do these *supersoft* microgels respond to crowding?

[1] A. Scotti, S. Bochenek, M. Brugnoni, M.-A. Fernandez-Rodriguez, M. F. Schulte, J. E. Houston, A. P. H. Gelissen, I. Potemkin, L. Isa and W. Richtering, *Nature Commun.*, 2019, **10**, 1418.

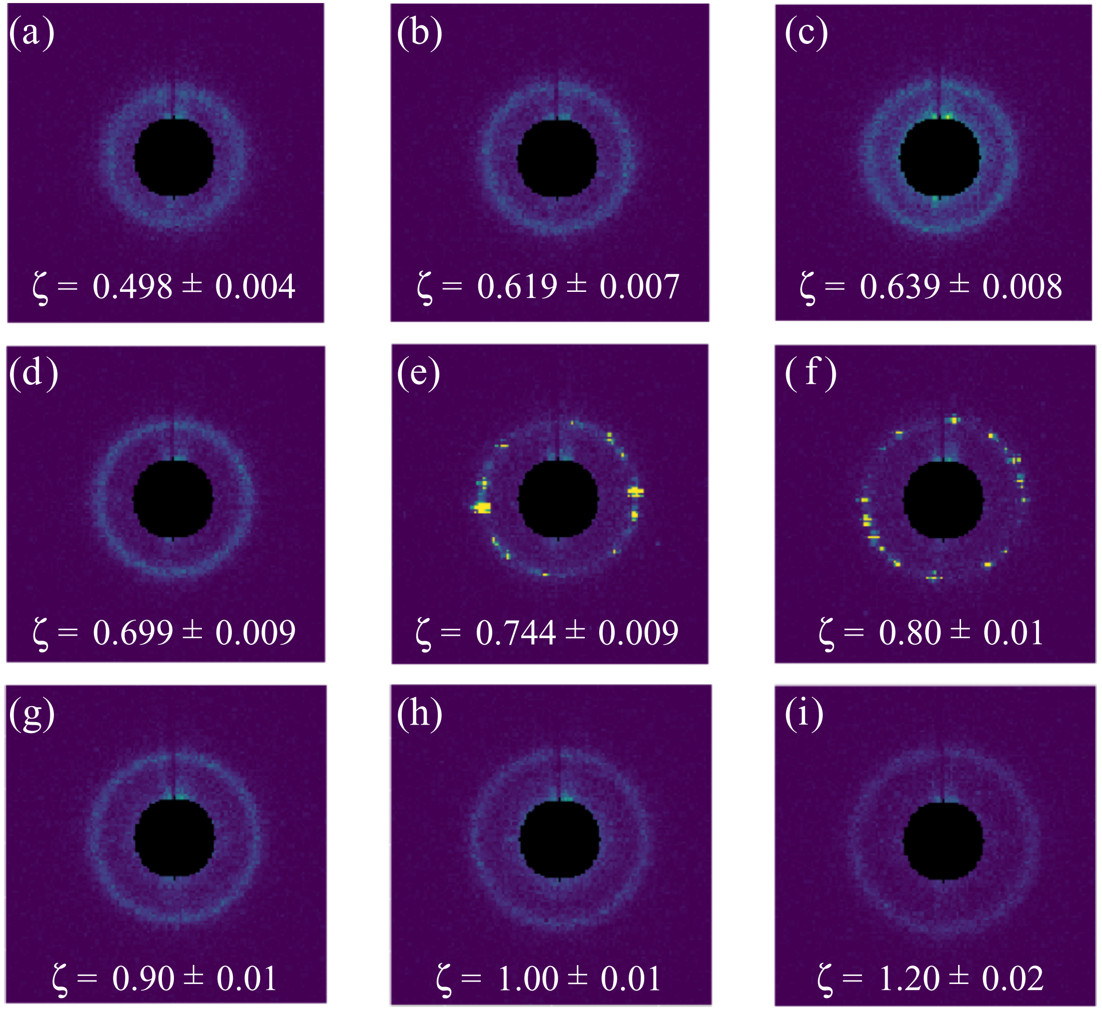
Generalized volume fraction, ζ

$$\zeta = \frac{NV_{swollen}}{V_{tot}}$$



Small-angle x-ray scattering (microgel-to-microgel arrangement)

2D detector images



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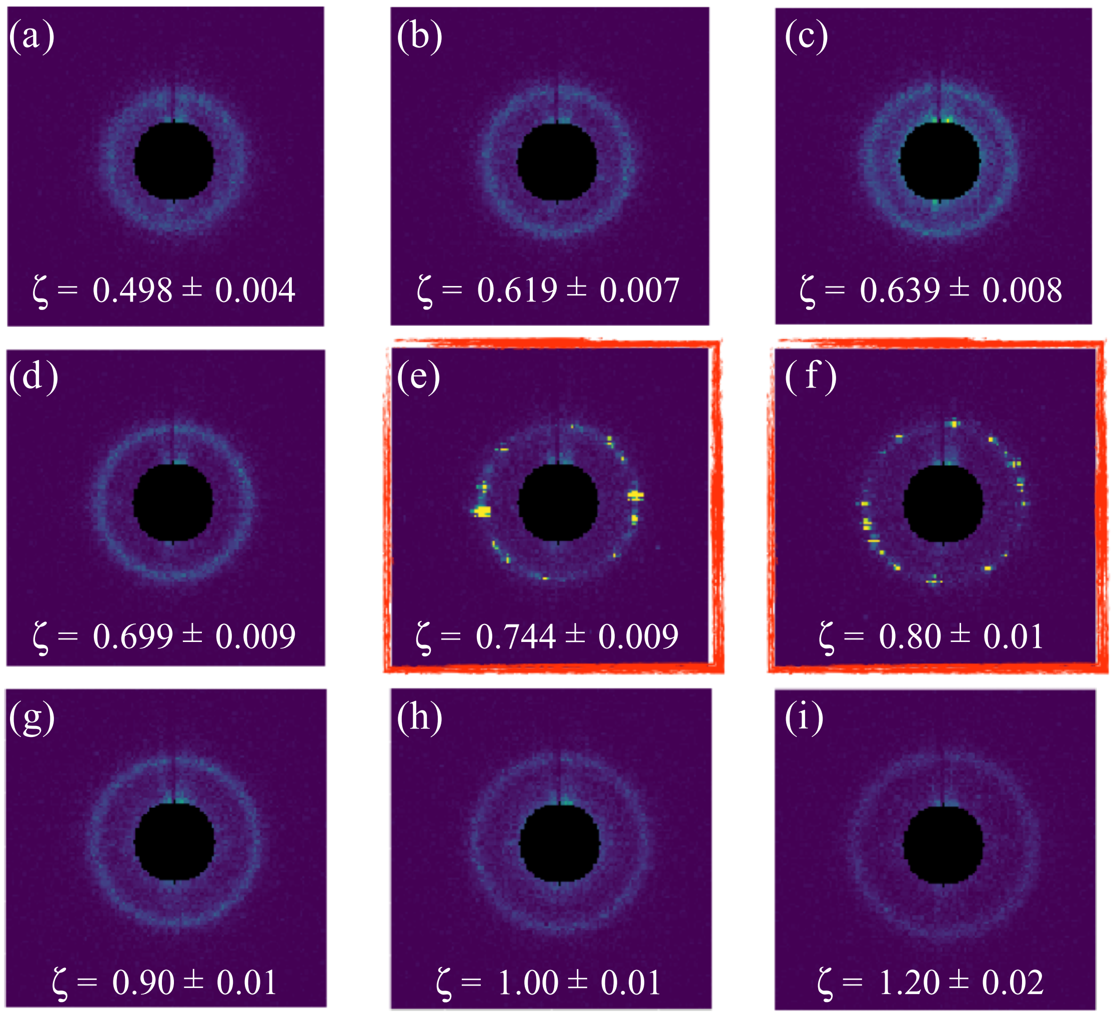
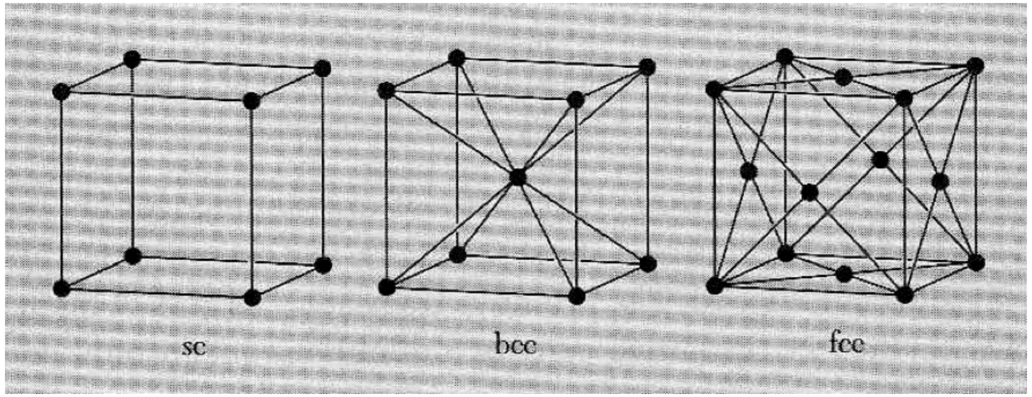
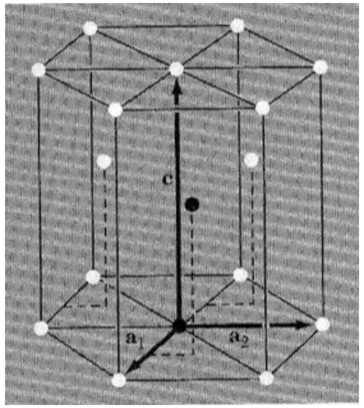


Crystals, but which lattice?





hcp

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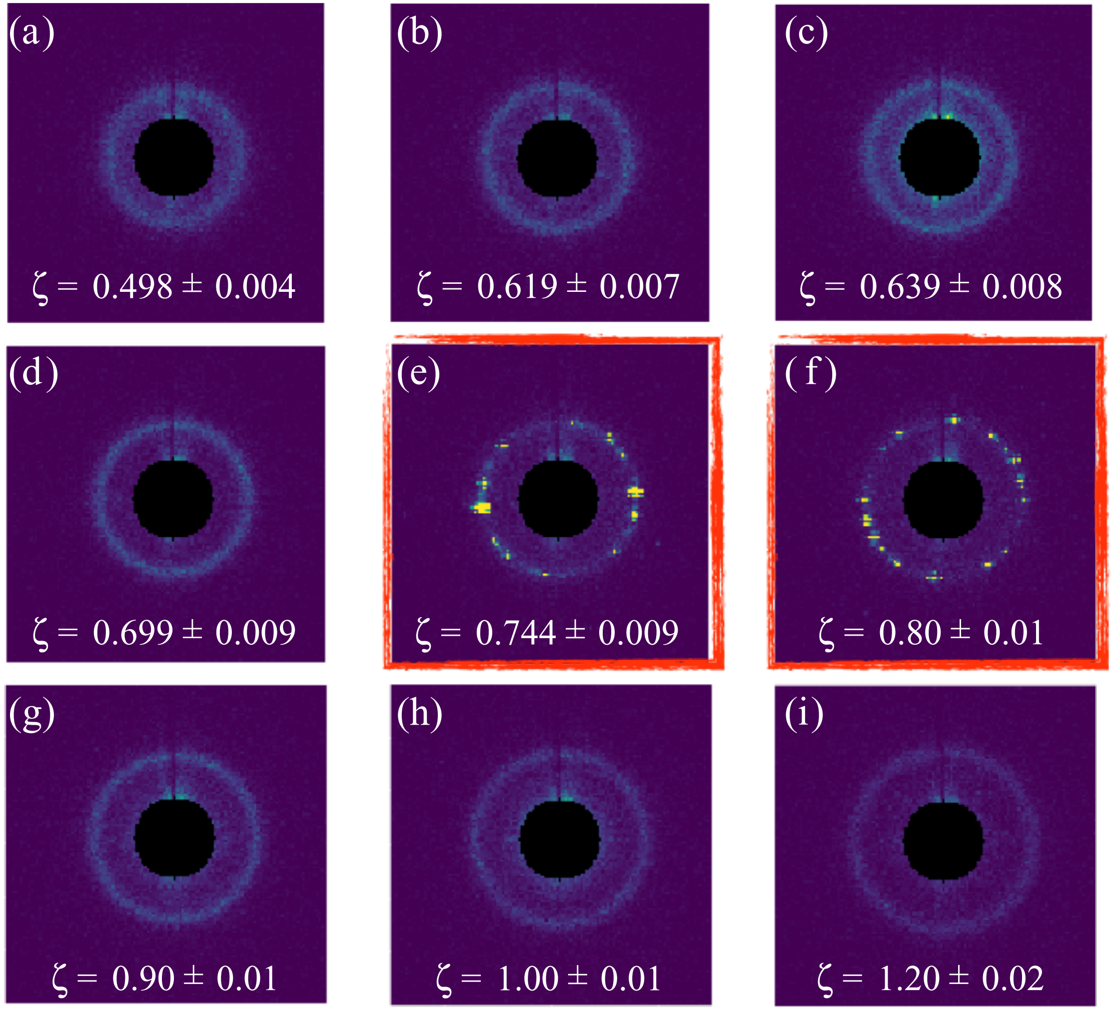

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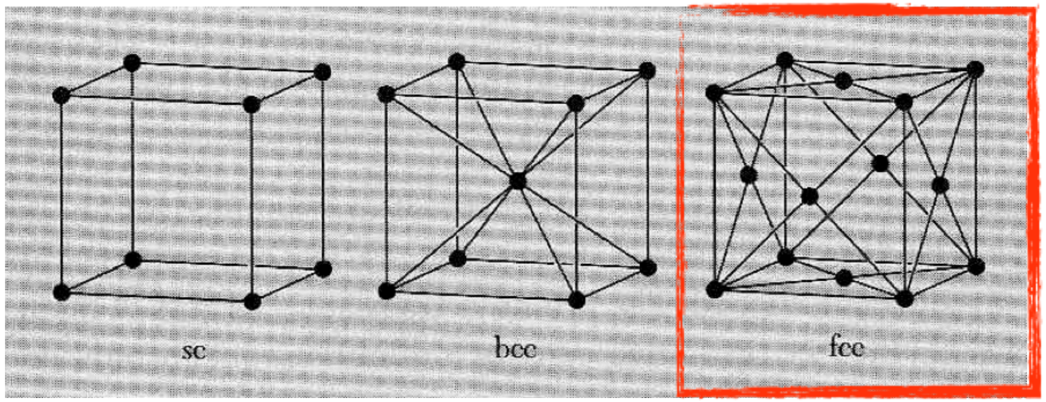

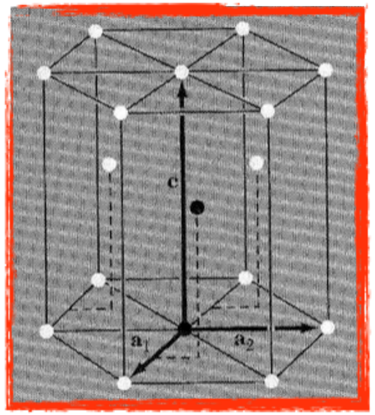

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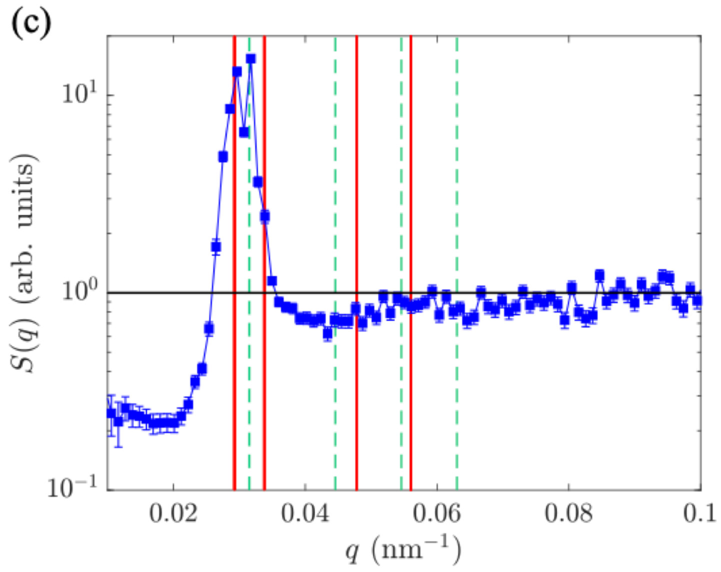
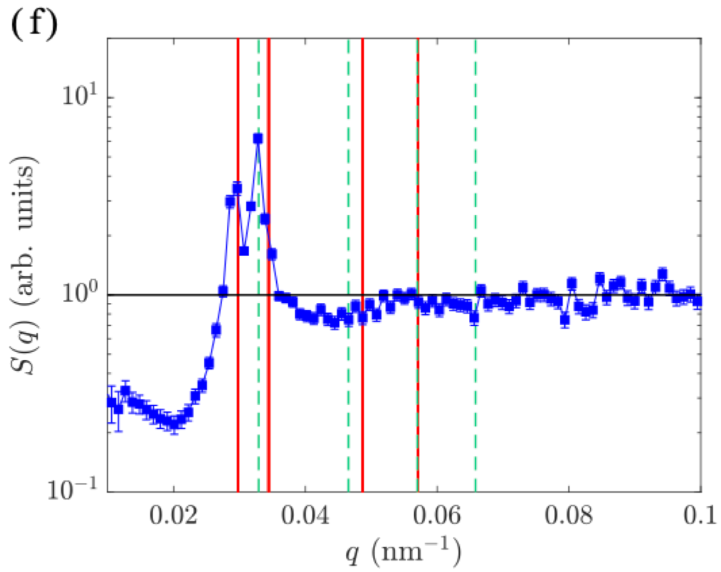
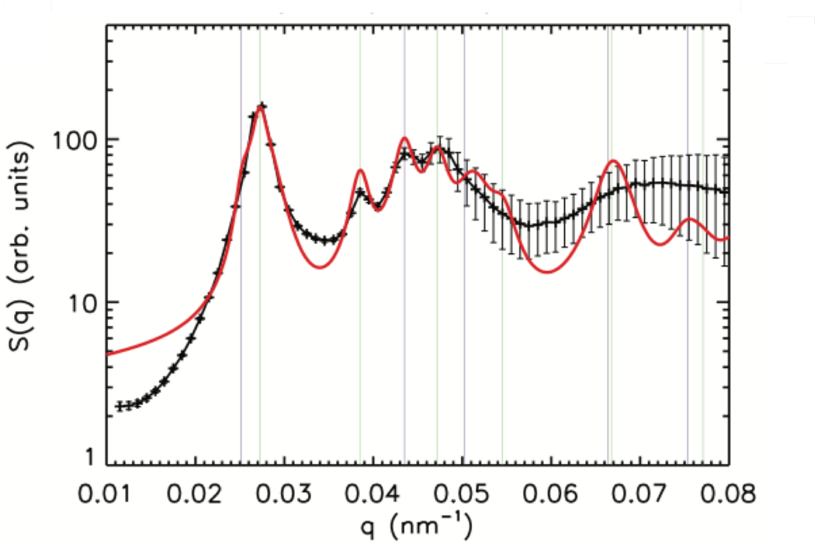
For hard spheres and crosslinked microgels

Small-angle x-ray scattering (microgel-to-microgel arrangement)



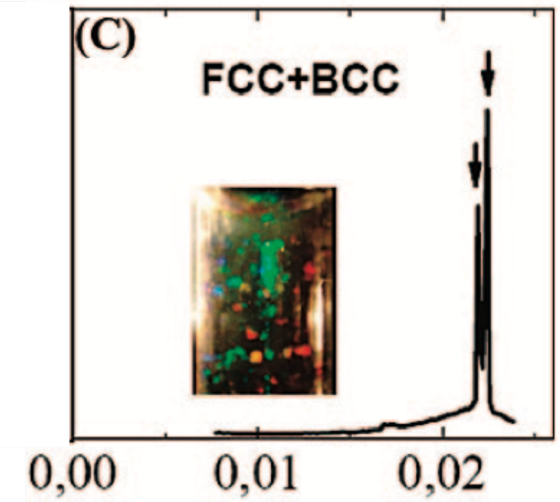


Coexistence of face-centred cubic and body-centred cubic

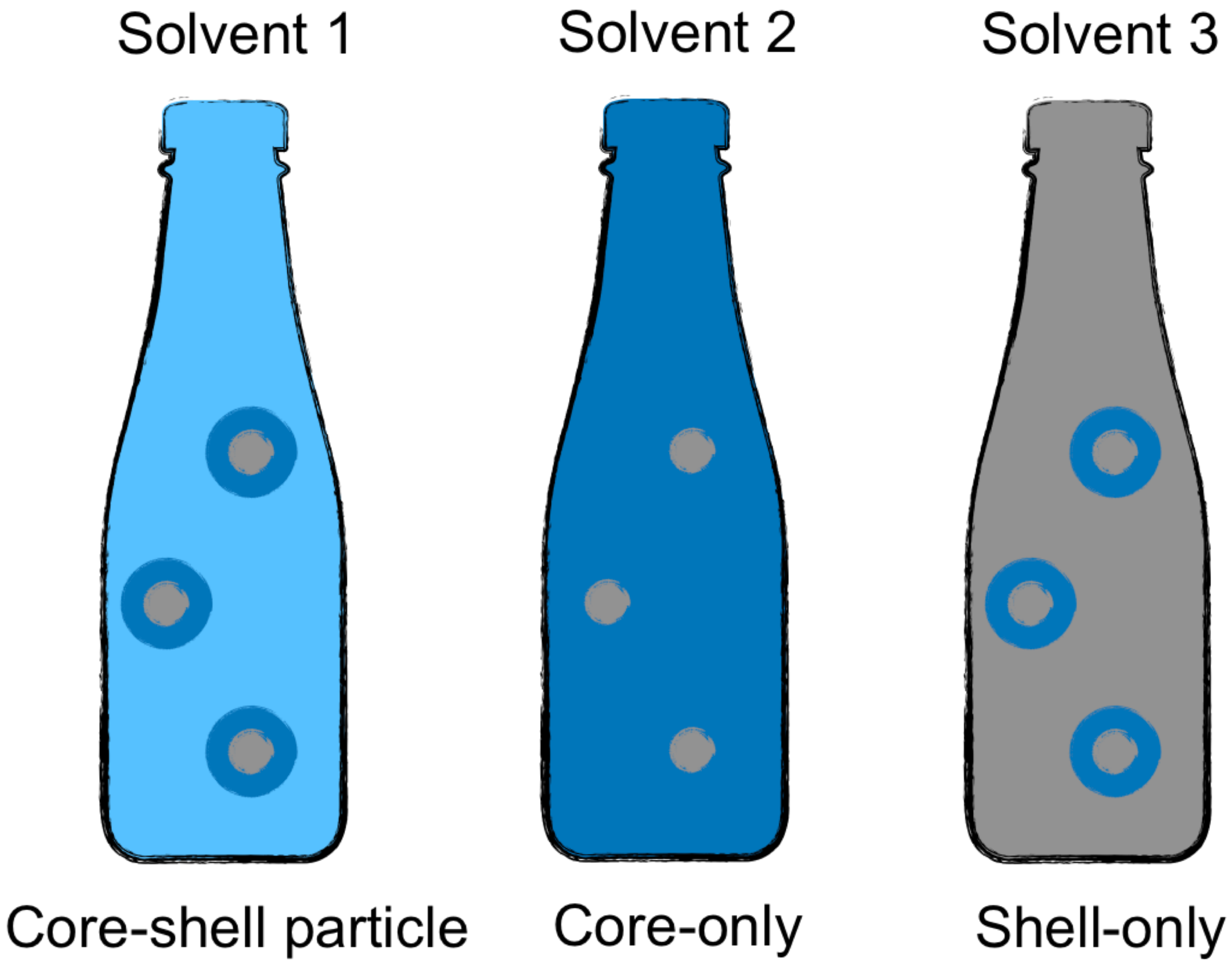


Found in the literature but *metastable:*

- Gasser *et al.*, *Phys. Rev. E*, 2013, **88**, 052308
- Mohanty & Richtering, *J. Phys. Chem. B*, 2008, **112**, 14692



Neutrons and contrast matching

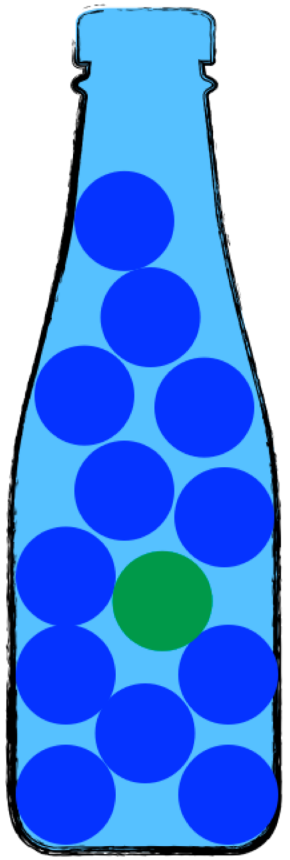


$$I_{exp}(q) = n\Delta\rho^2 V^2 P(q) S(q)$$

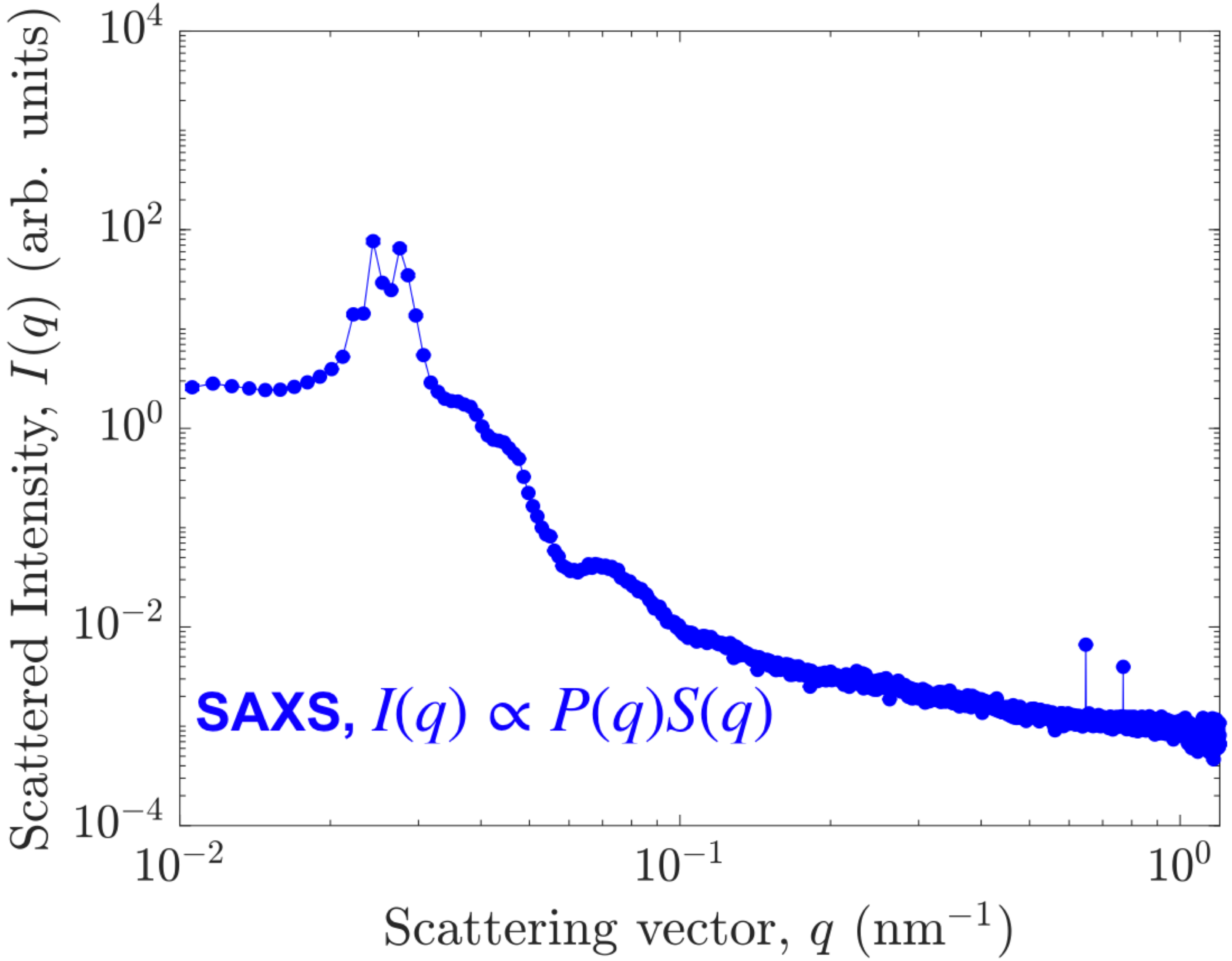
Selective deuteration in combination with neutrons lets us investigate selected parts of complex assemblies.

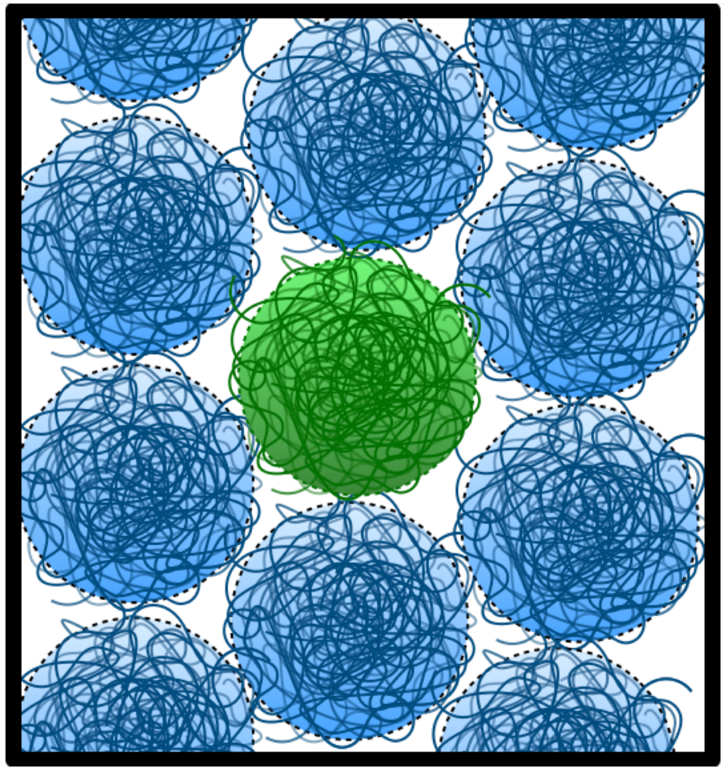
Combining X-Ray and Neutron measurements provides more information

Let’s consider microgels in crowded environment



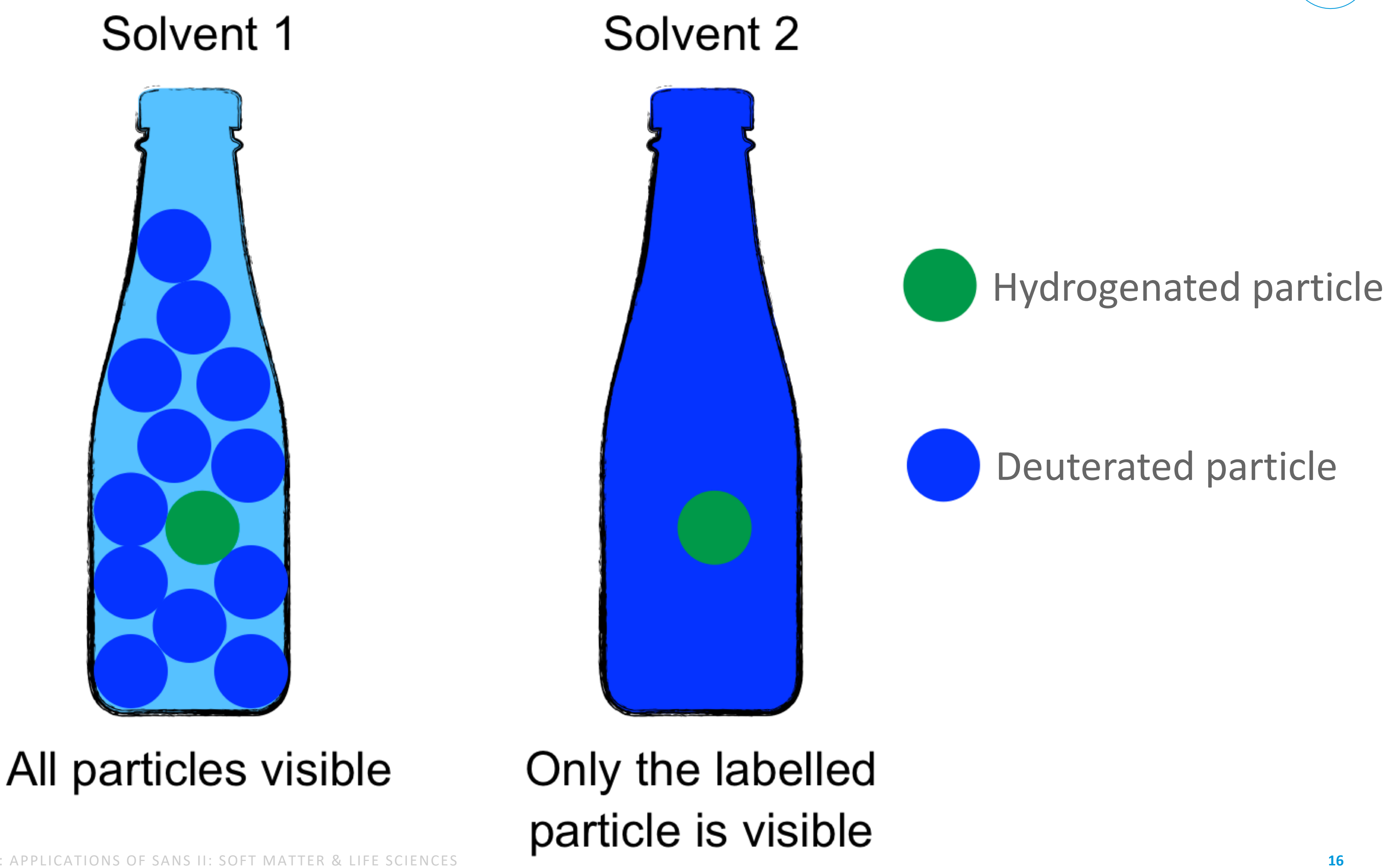
Microgels in crowded environment



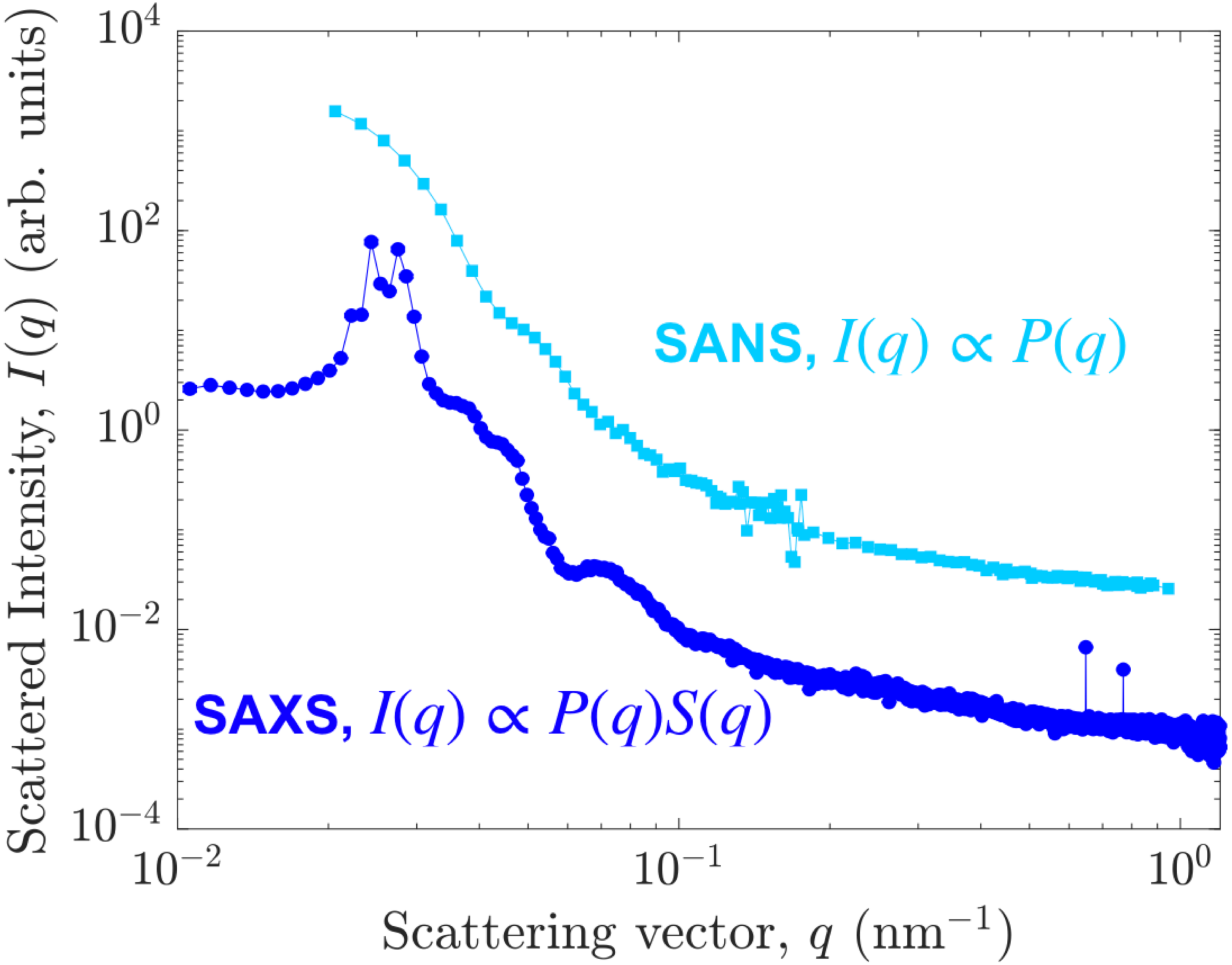


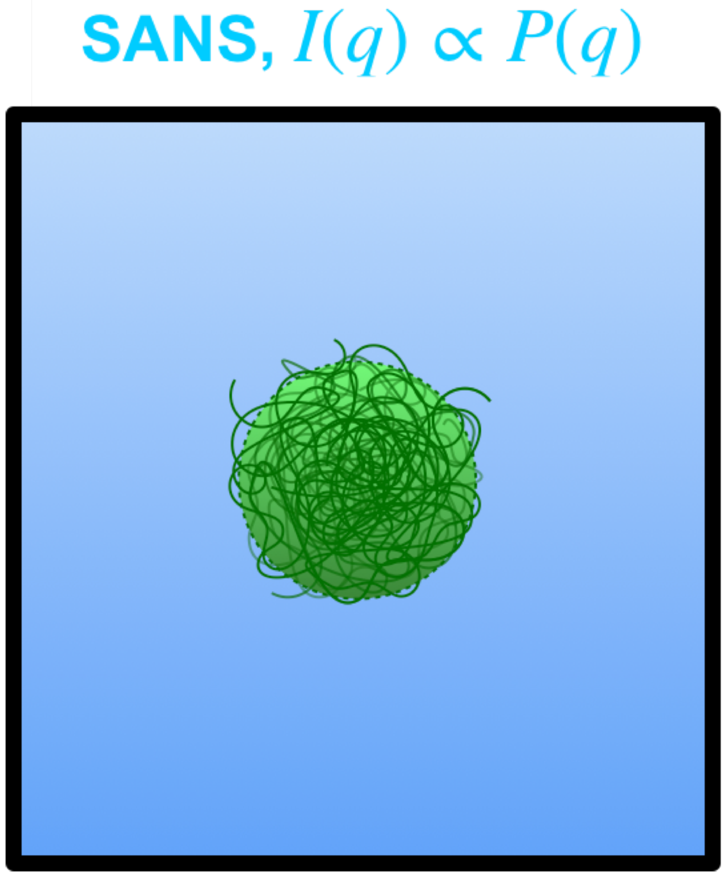
Courtesy of Andrea Scotti (RWTH)

Microgels in crowded environment



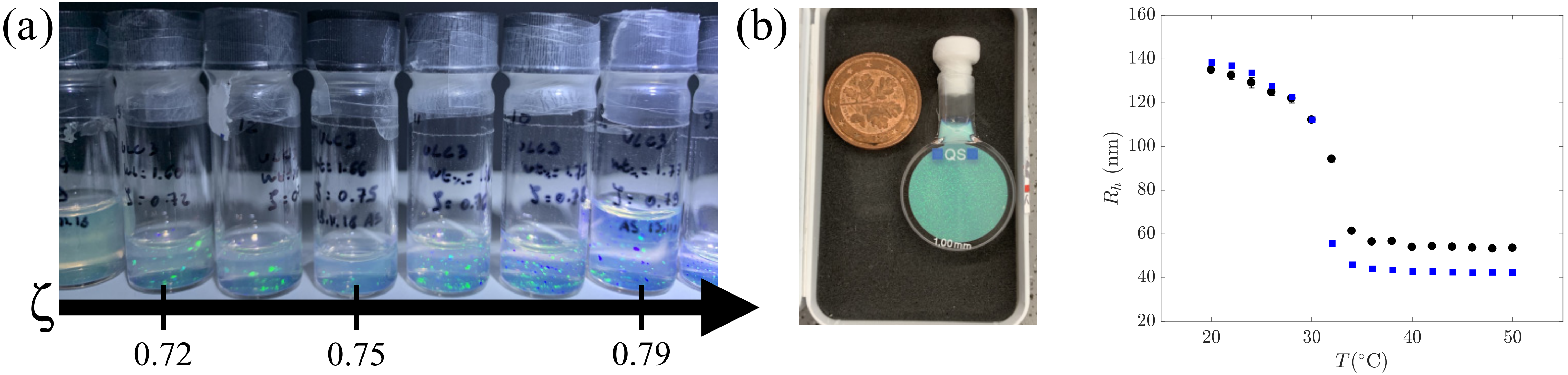
Microgels in crowded environment





Courtesy of Andrea Scotti (RWTH)

Phase behaviour (of protonated & deuterated)



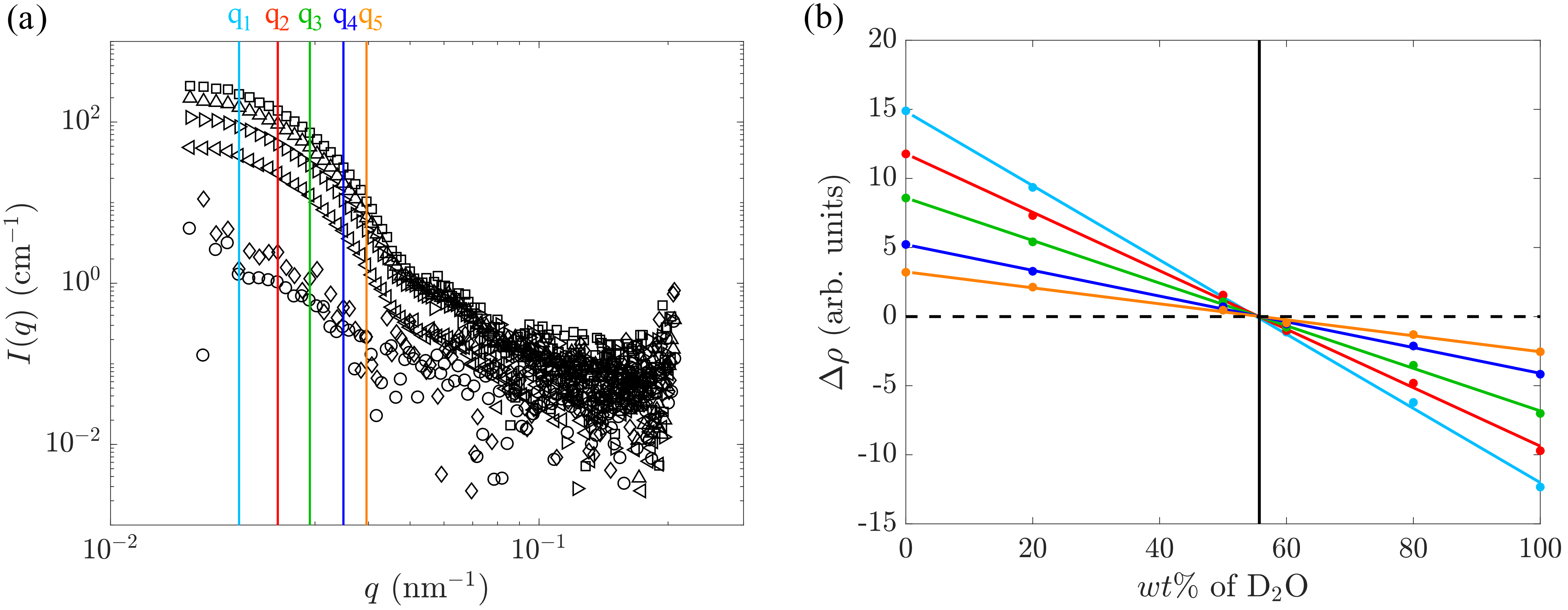
Identical phase behaviour (phase transitions at same)

and

very similar swelling ratio (softness)

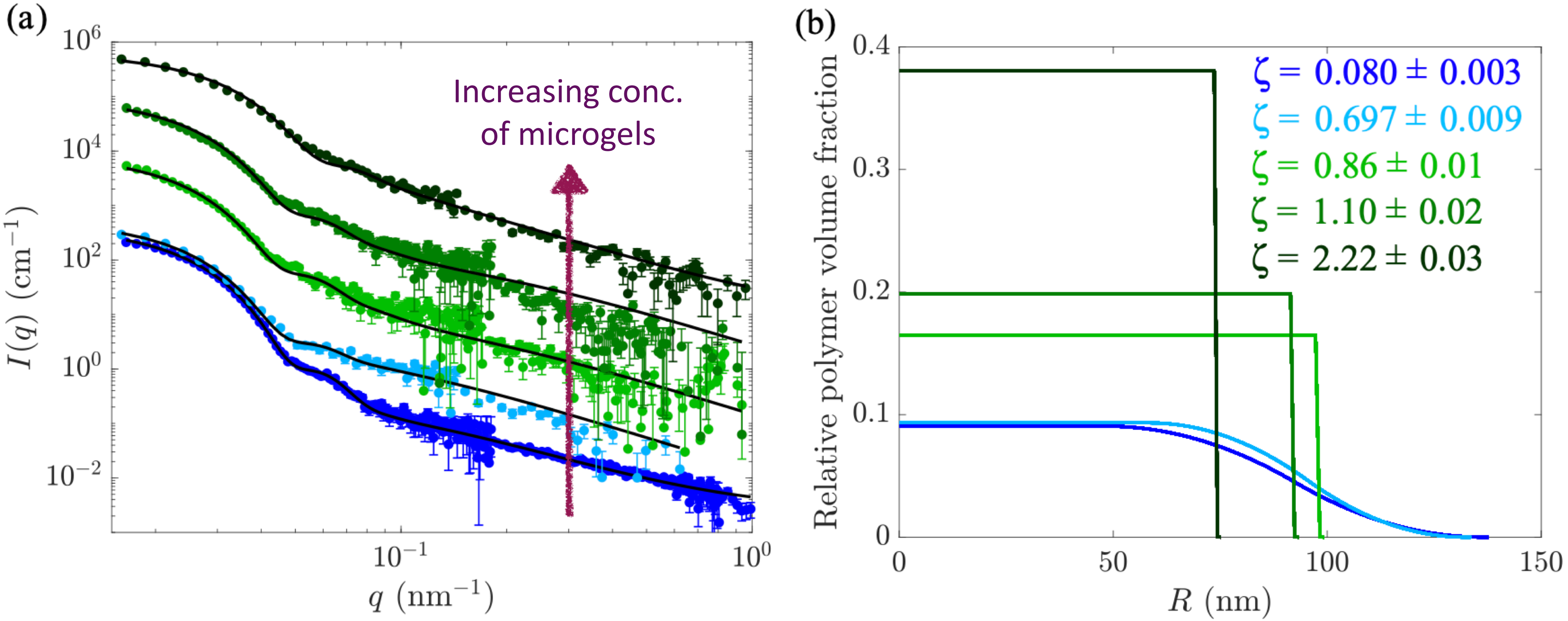
Small-angle neutron scattering with contrast variation

Deuterated ULC made from $(C_6D_3H_8NO)_n$



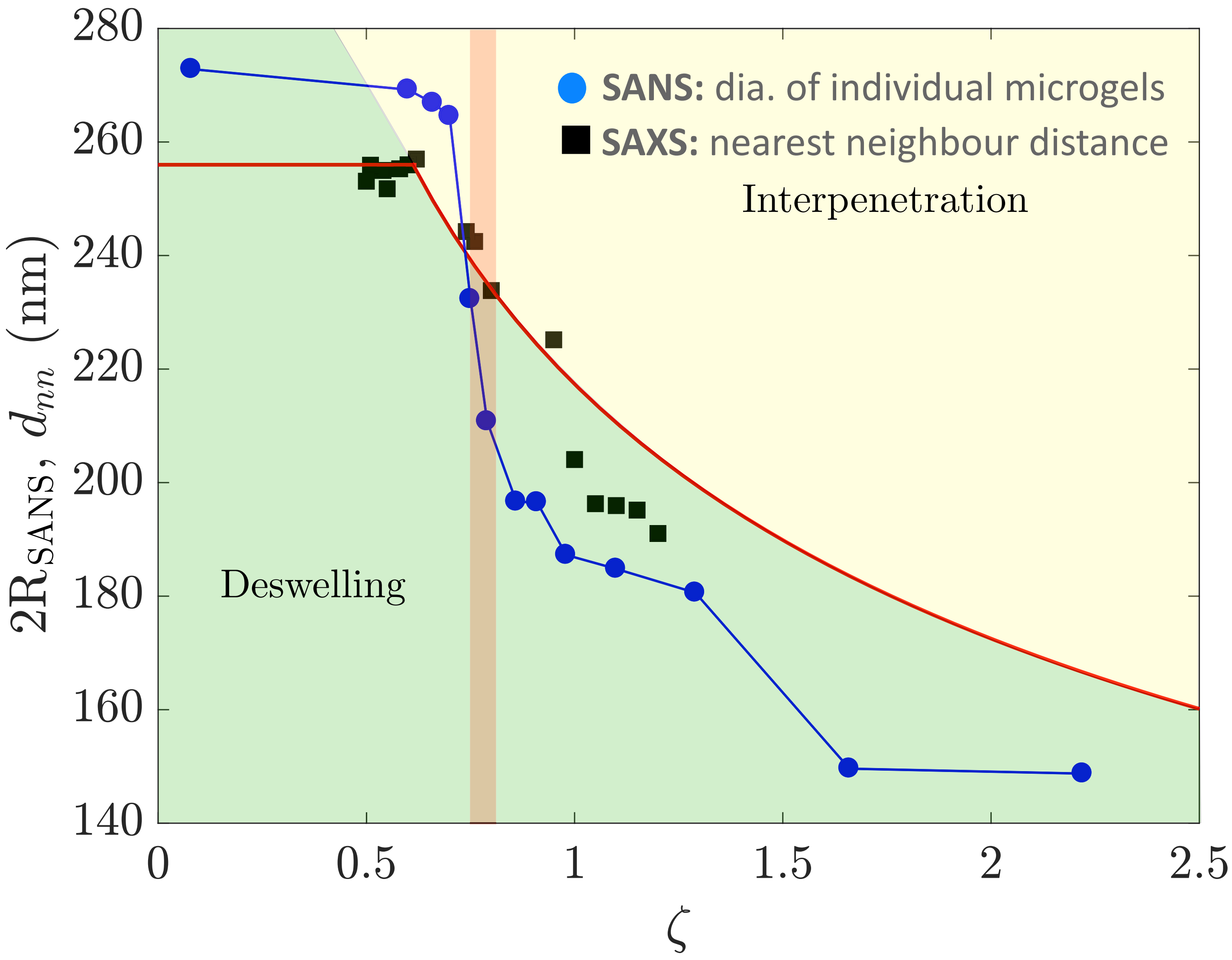
Small-angle neutron scattering with contrast matching

Fitting with core-fuzzy shell model…



- Increasing conc. of microgels (mostly deuterated, a few hydrogenated)
- Solvent of 55 wt% D_2O to match-out the majority of deuterated microgels

Comparison between SANS and SAXS



Low conc: partially swollen ULC microgels, still with fuzziness

Higher conc: collapsed harder spheres

In the red area there is transition between deswelling and interpenetration

→ mixed **BCC** and **FCC** crystals

A. Scotti, J. E. Houston, M. Brugnoni, M. M. Schmidt, M. F. Schulte, S. Bochenek, R. Schweins, A. Feoktystov, A. Radulescu, and W. Richtering, *Phys. Rev. E*, 2020, 102, 052602

Example 2:
RheoSANS

What is rheology?

"The study of flow"

Essential Elements

What controls a material's rheological properties?

1. Inner Structure:
   - how is it built?
   - what is it molecular make-up?

2. Morphology:
   - what is the shape and size of the components?
   - e.g. small needle-like structure, or bulky cotton-like structure

3. External Forces:
   - What are the forces causing the system to flow or deform?

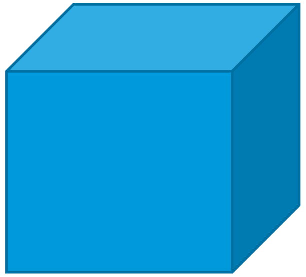
4. Ambient Conditions:
   - what environment is the stressed materials in?
   - e.g. temperature

Rheology and materials

Liquids

Viscoelastic

Solids



Viscous Liquids

Viscoelastic Liquids

Viscoelastic Solids

Elastic Solids

Viscosity

- A measure of a fluid's resistance to flow by an applied deformation force
- Internal friction of a moving fluid

e.g. Honey

→ **large viscosity**

→ restricted motion due to its molecular make-up and morphology which cause internal friction

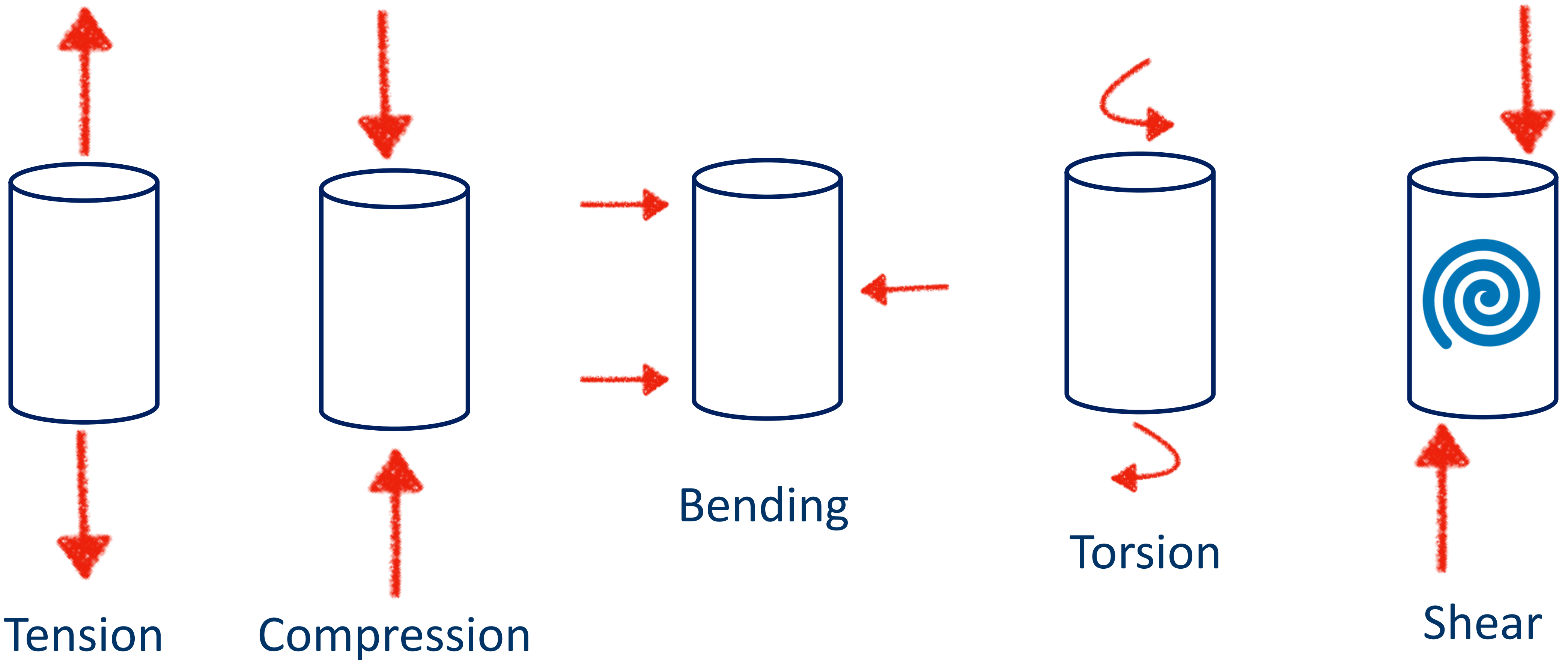
e.g. Water

→ **low viscosity**

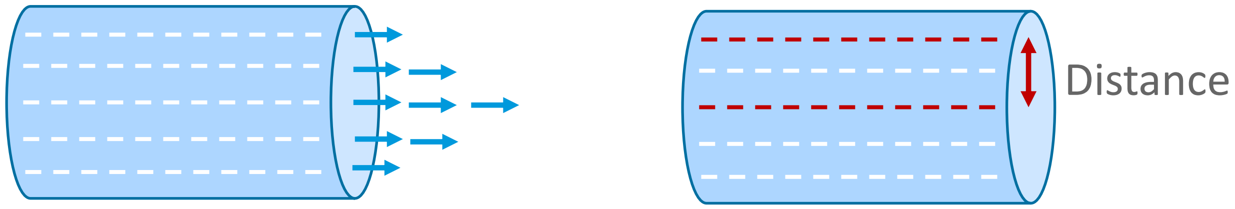
→ flows easily, very little internal friction

Deformation forces

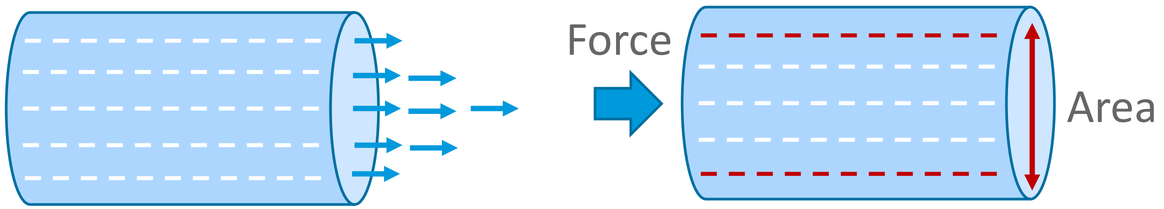
What are the type of deformation forces we can apply?



Viscosity: Shear Stress & Shear Rate



Shear Rate = $\frac{\text{Difference in velocity}}{\text{Distance}}$



Shear Stress = $\frac{\text{Force}}{\text{Area}}$

Shear rate ~ shear stress

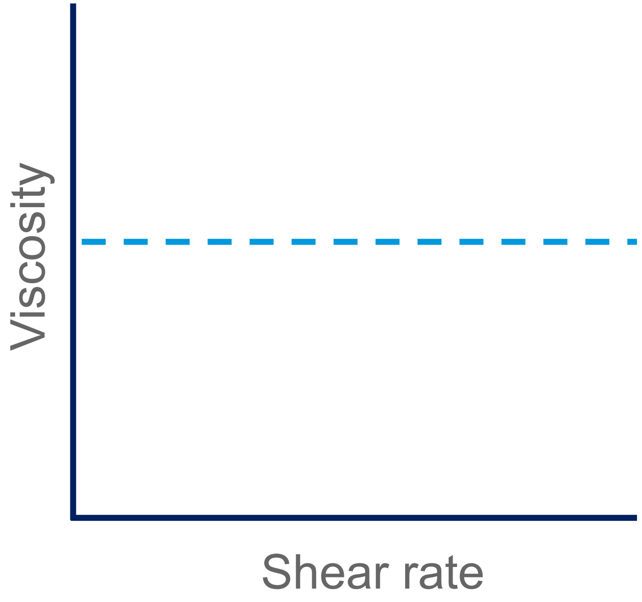
- High shear stress we can expect a higher shear rate
- Higher the viscosity higher the shear stress required to flow at the same rate of less viscous liquids

$$\text{Viscosity (V)} = \frac{\text{Shear Stress (SS)}}{\text{Shear Rate (SR)}}$$

Flow Profiles

Let's consider the different types of flow…

1. **Newtonian**
   - viscosity doesn't change with shear rate
   - e.g. water



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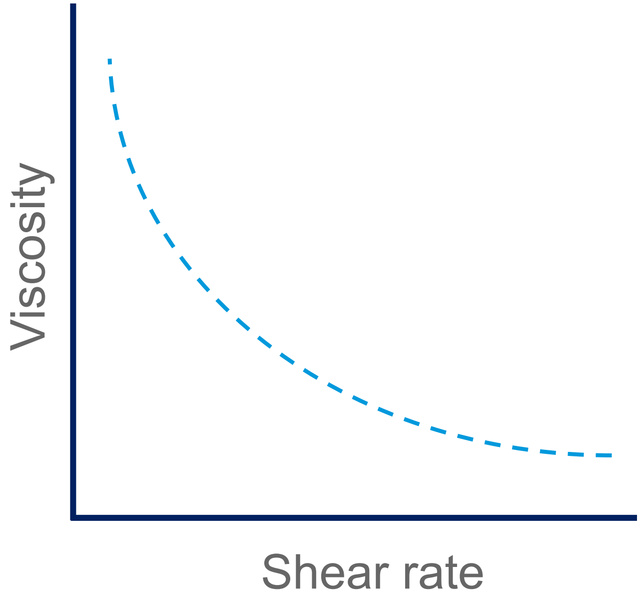
2. Non-Newtonian

i. Pseudo plastic (shear-thinning)
- Viscosity decreases with increasing shear rate
- e.g. mayonnaise



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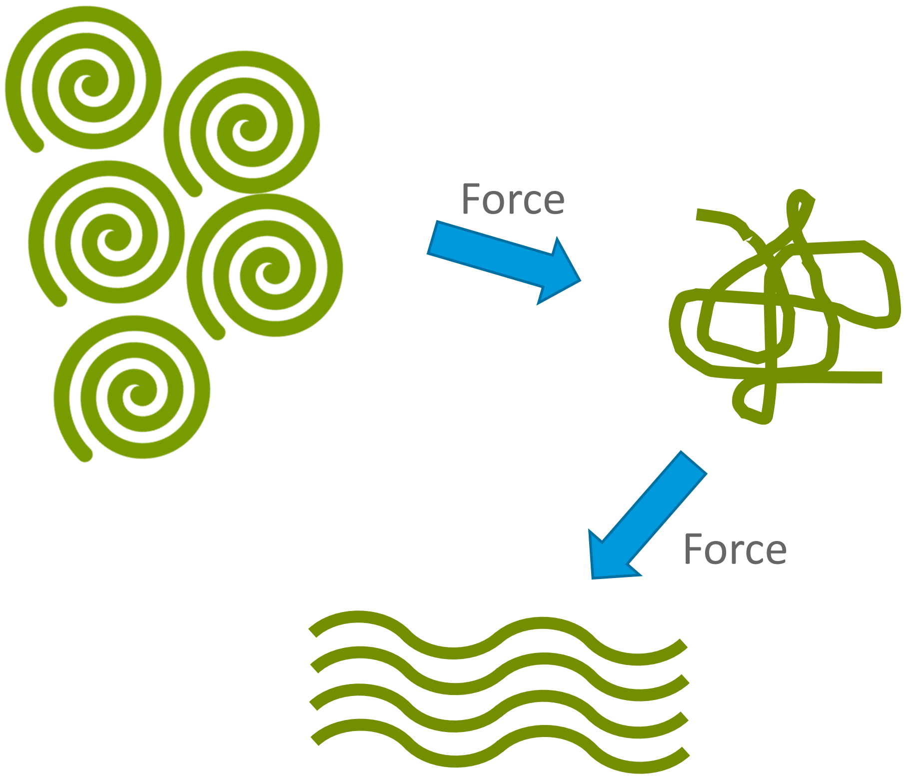

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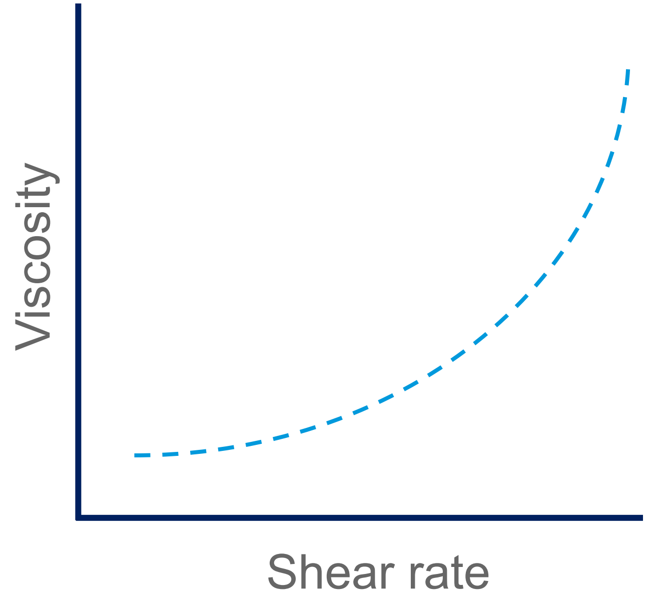
   - e.g. quick sand or cornstarch



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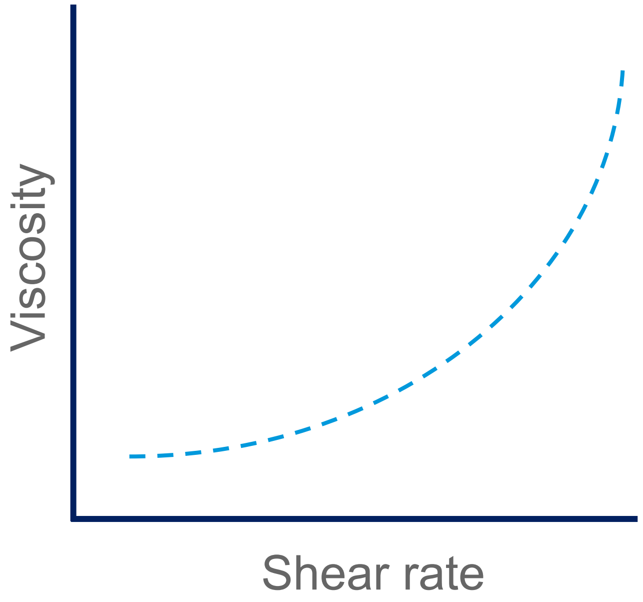

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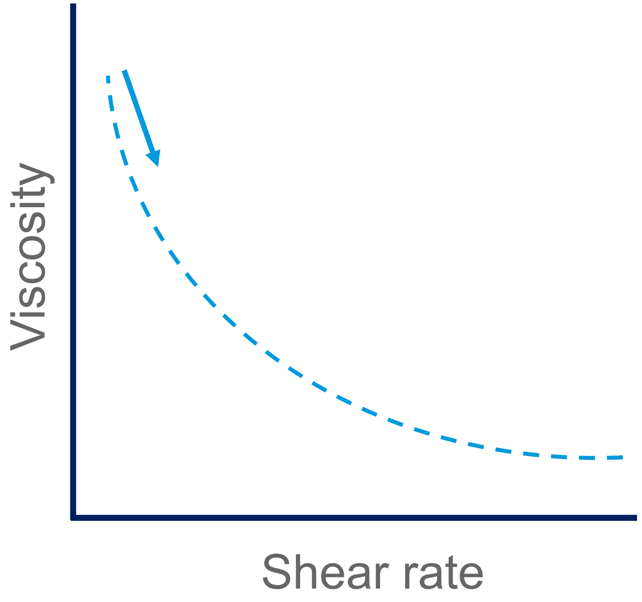
iii. Thixotropic
- shear-thinning but **time dependant**
- e.g. ketchup, coatings, paints, inks



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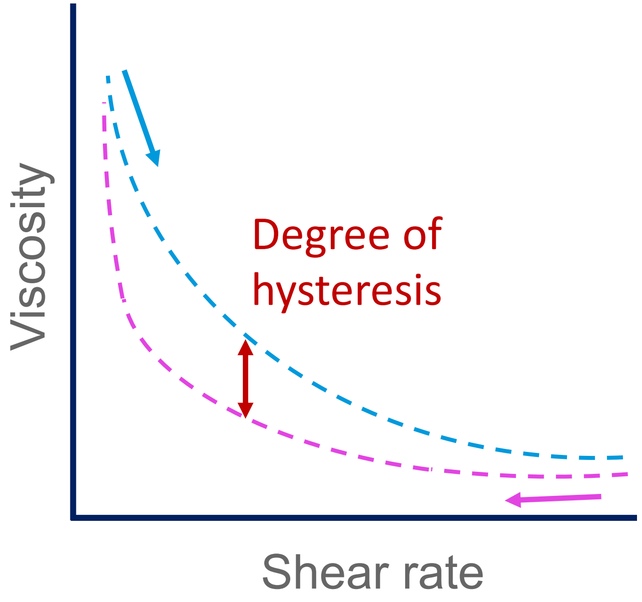

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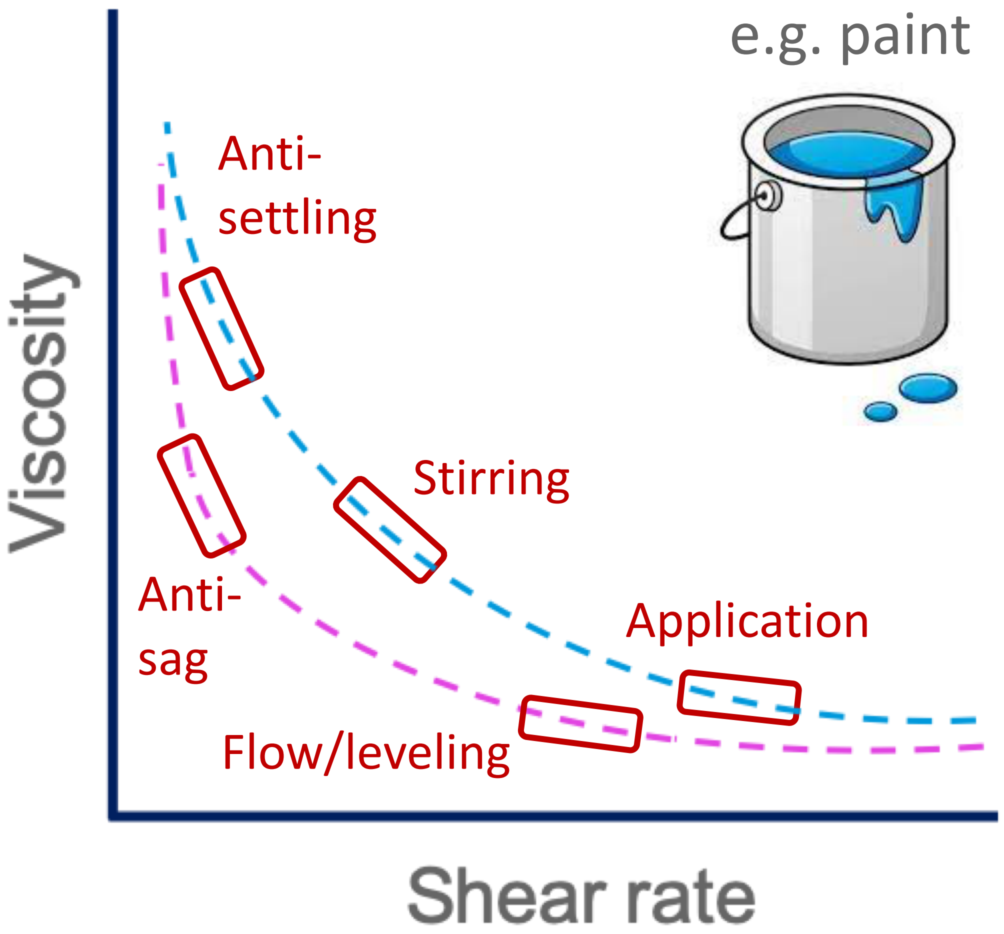
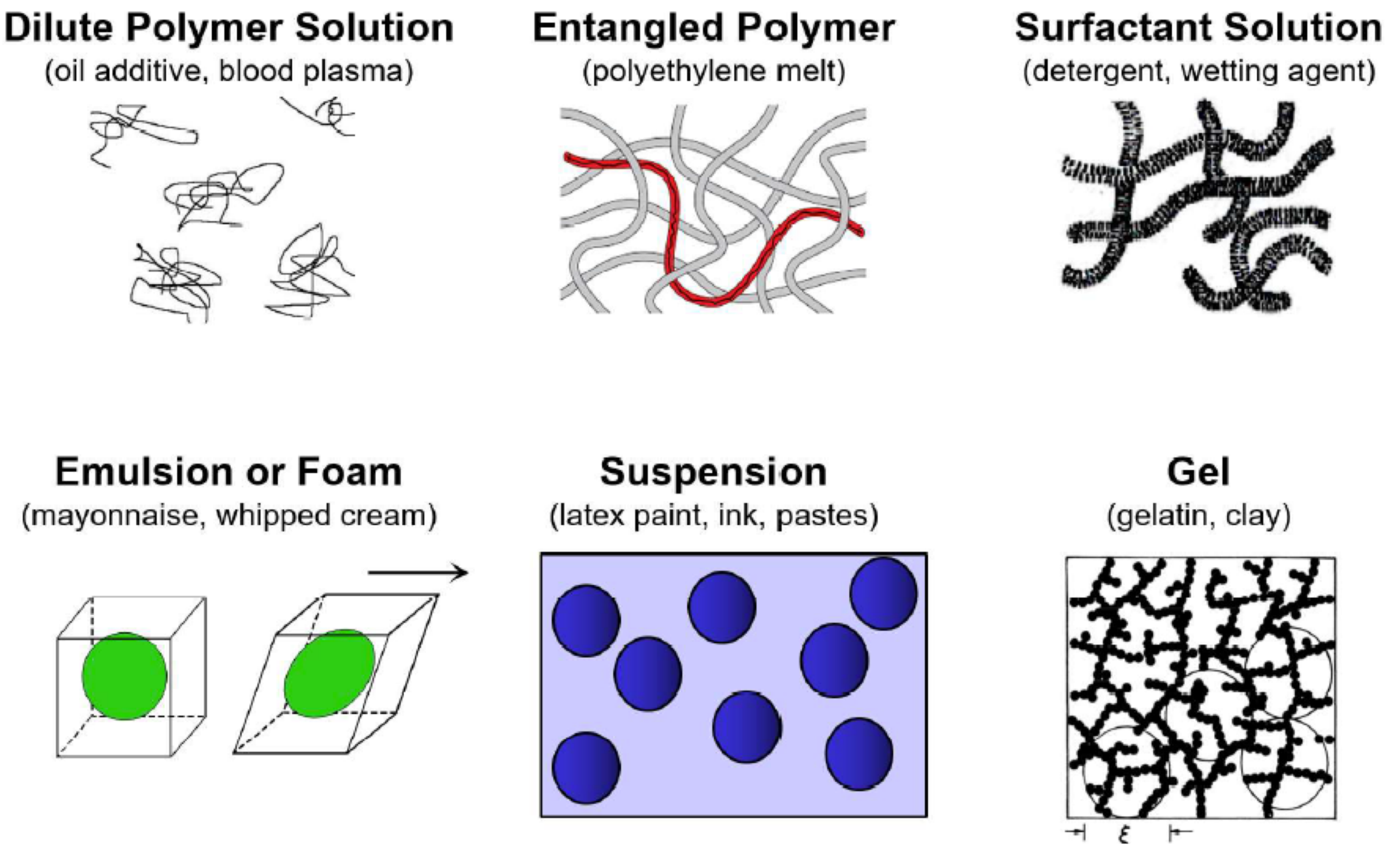


Structure-Property relationships

The rheology of a complex fluid is directly linked to the structure

We need to understand:

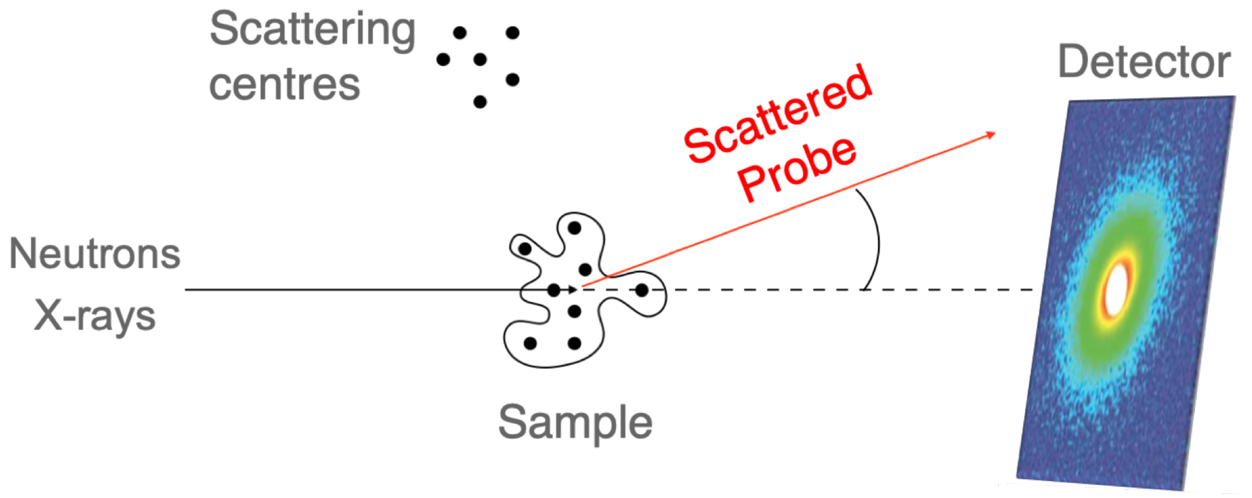
- structural reorganization due to flow
- the relationship between flow and stress which govern the bulk rheological properties of a system



Eberle & Porcar, *Curr. Op. Coll. Inter. Sci.*, 2012, **17**, 33

Small-angle scattering

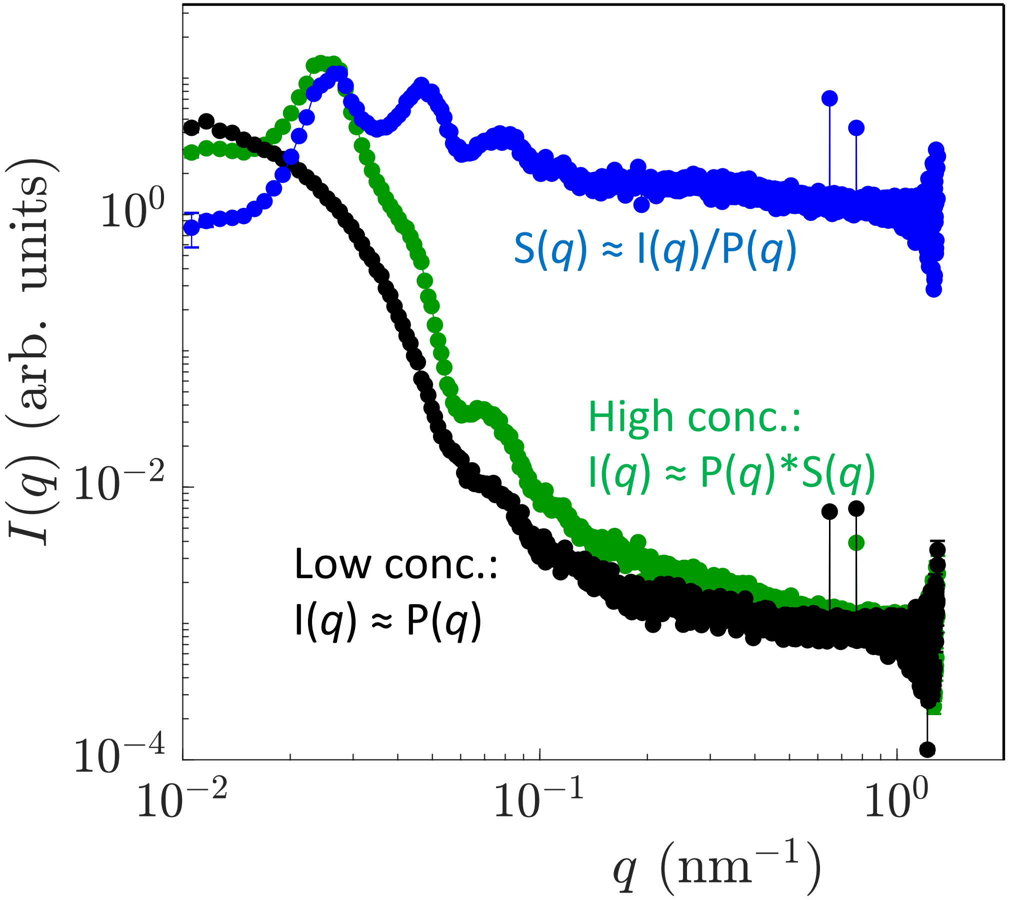
Experimental technique which uses **elastic scattering** at **small angles** to investigate the structure of substances at length scales of ~1–300 nm



$$I_{exp}(q) = n\Delta\rho^2 V^2 P(q) S(q)$$

Form factor: Shape, size

Structure factor: Arrangement



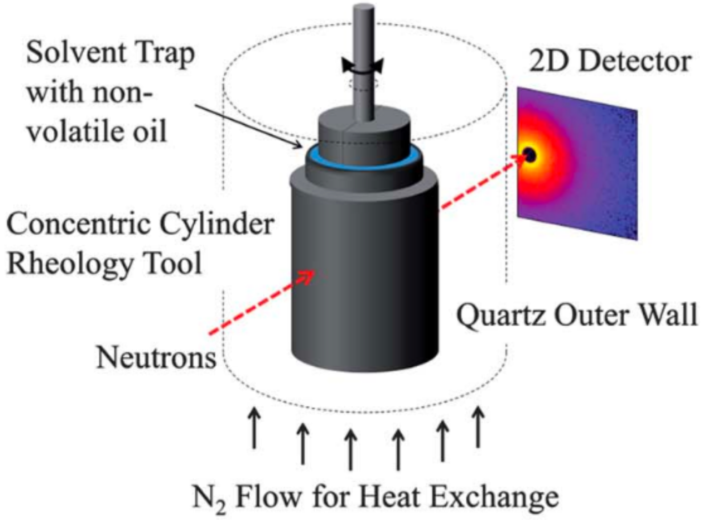
Rheology SANS

RheoSANS experiments help us understand:

i) structural reorganization of fluids as a result of flow;

ii) the relation between flow and stress governing the bulk rheological properties of a system.

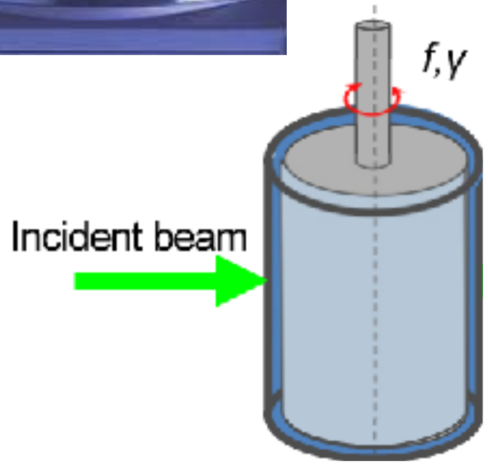
e.g. Couette cell

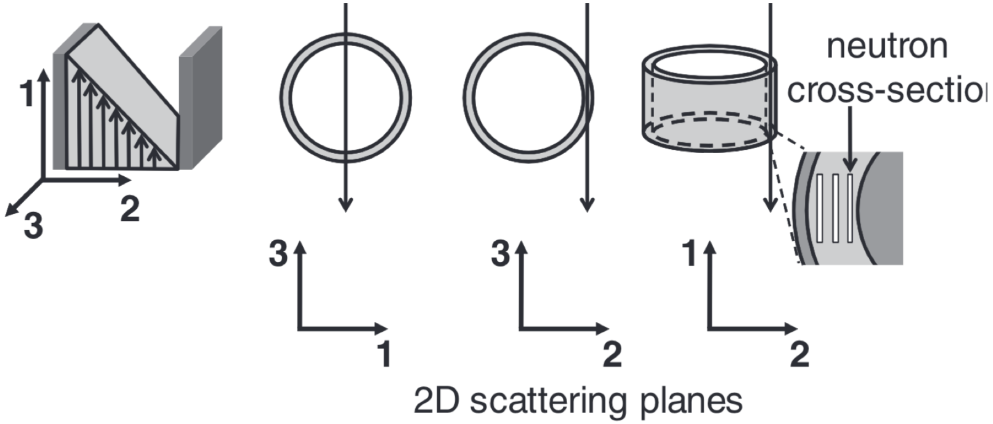


Newbloom *et al.*, *Soft Matter*, 2012, **8**, 8854

Planes of interest

What information can we get?





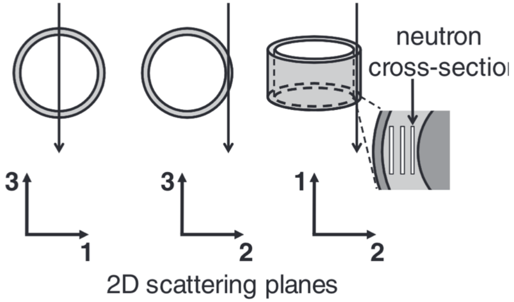
Each plane offers specific and unique information for describing the structure/property relationships

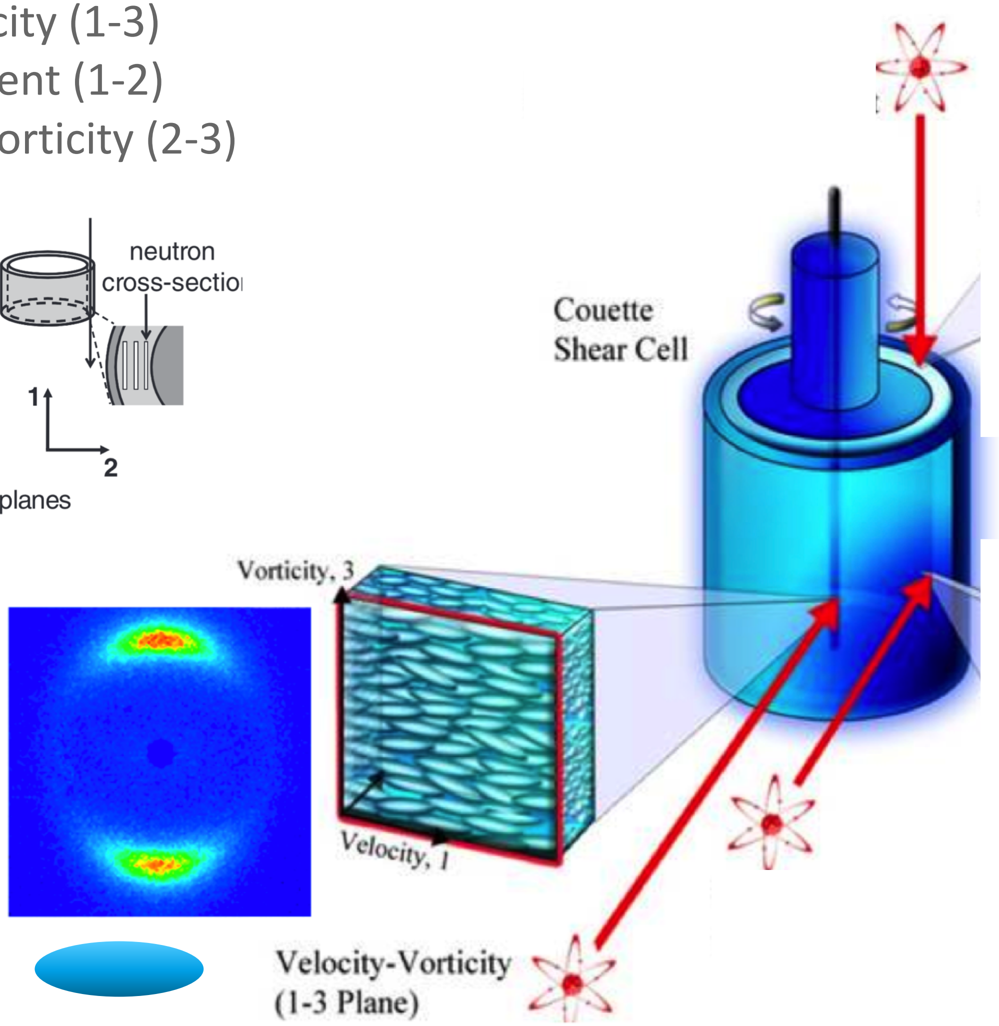
Eberle & Porcar, *Curr. Op. Coll. Inter. Sci.*, 2012, **17**, 33

Planes of interest

For simple shear flow:

- flow-vorticity (1-3)
- flow-gradient (1-2)
- gradient-vorticity (2-3)





M.A. Calabrese, N. Wagner *New insights from RheoSANS*, RSC pre-print

Planes of interest

For simple shear flow:

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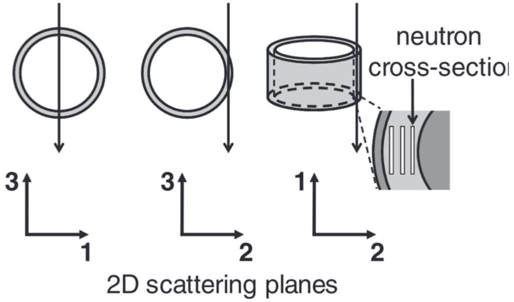

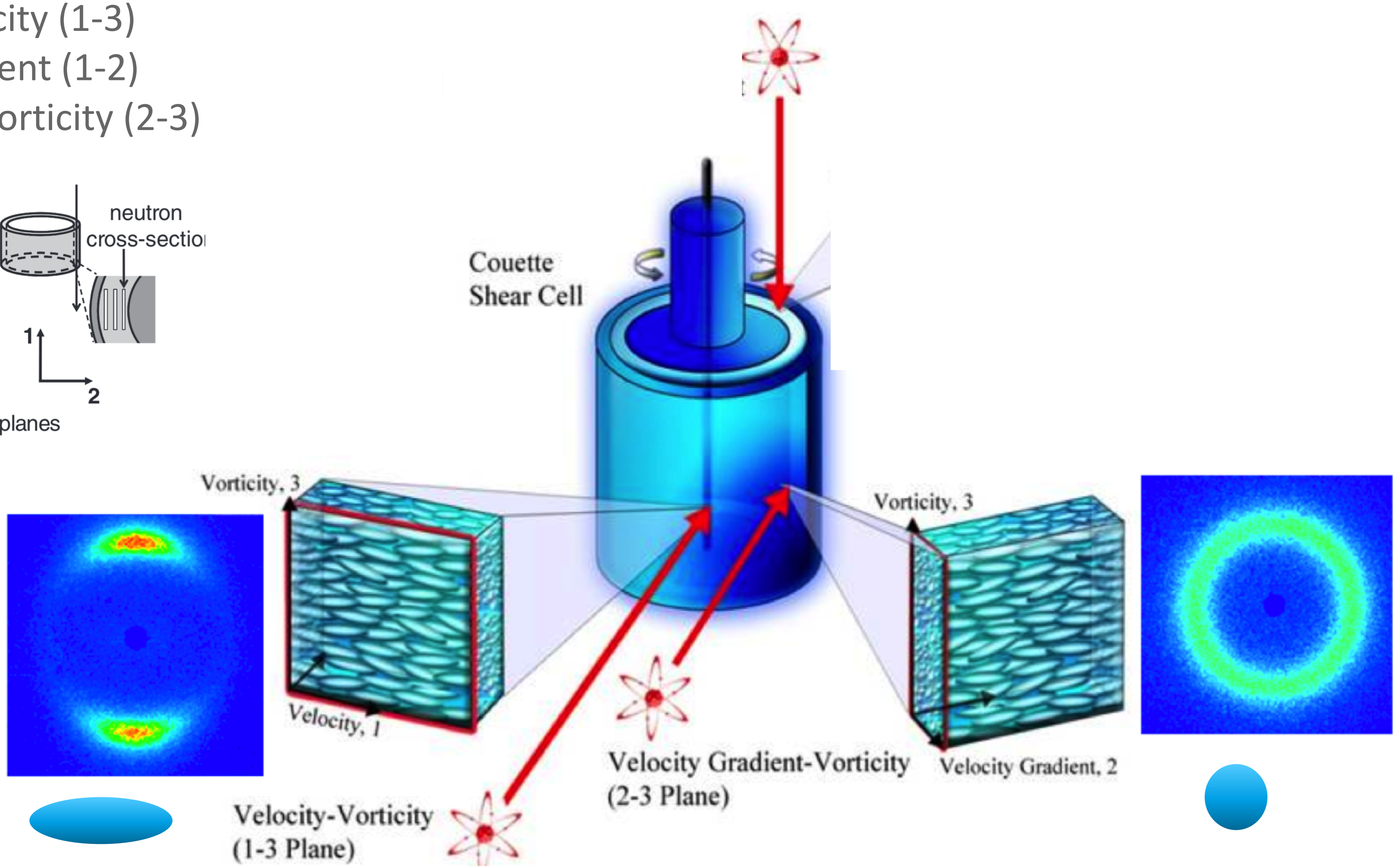

M.A. Calabrese, N. Wagner *New insights from RheoSANS*, RSC pre-print

Planes of interest

For simple shear flow:
- flow-vorticity (1-3)
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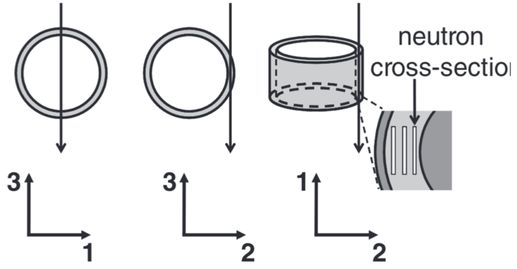
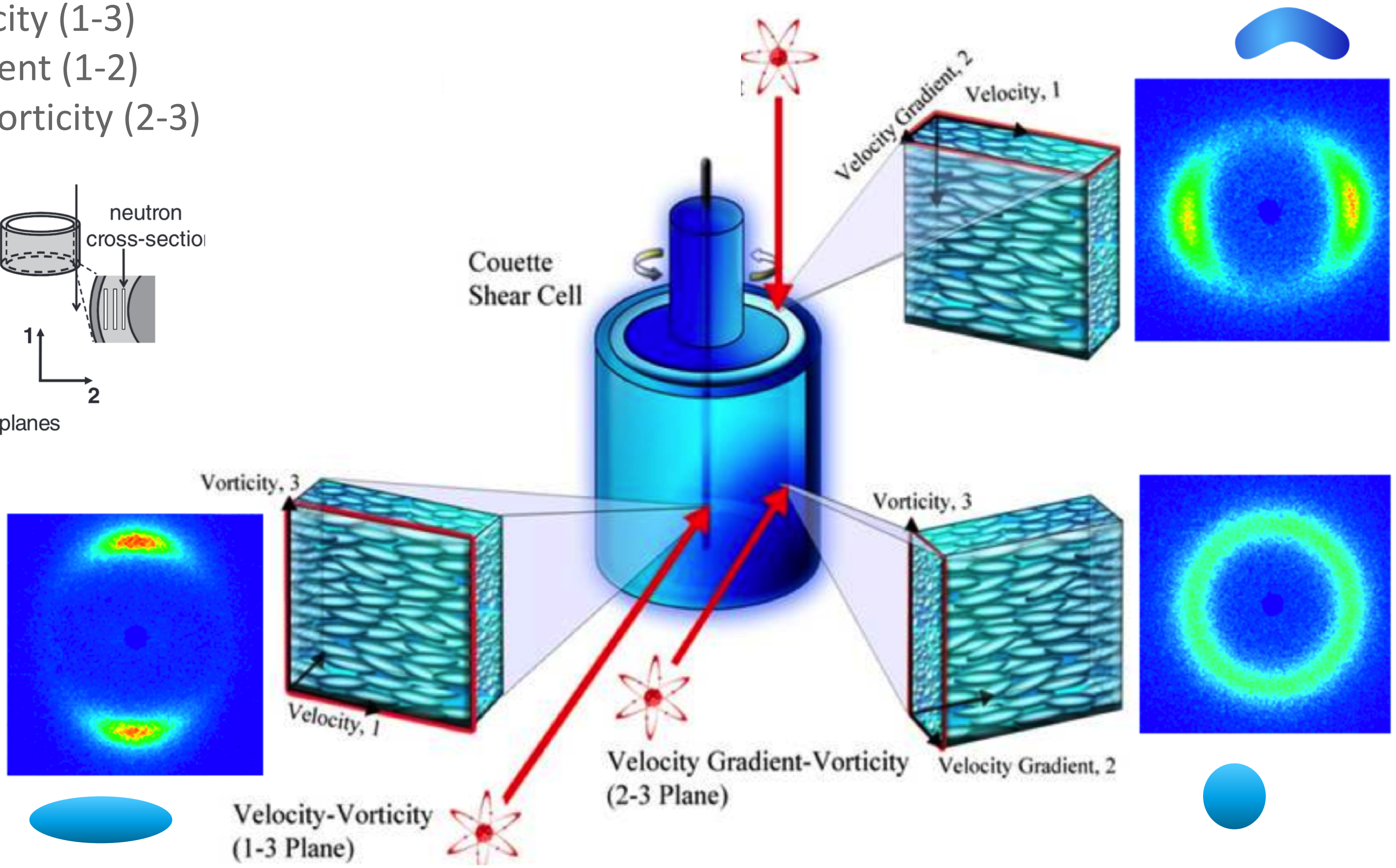
- gradient-vorticity (2-3)





 M.A. Calabrese, N. Wagner *New insights from RheoSANS*, RSC pre-print

Example: Body armor

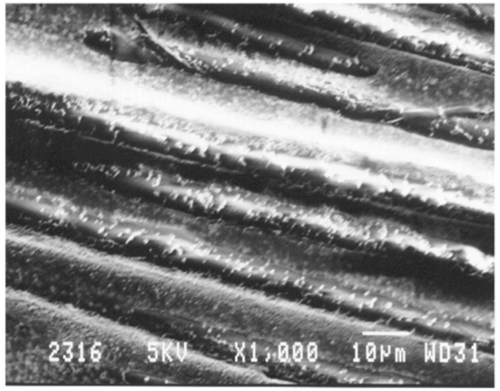
Published: July 2003

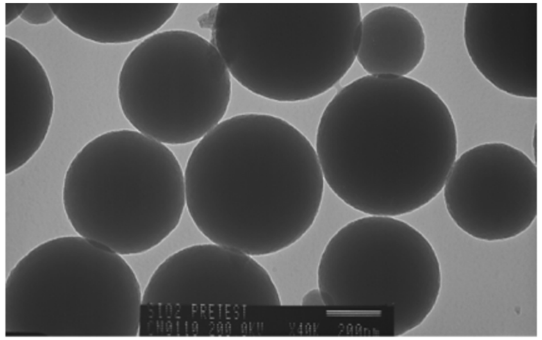
The ballistic impact characteristics of Kevlar® woven fabrics impregnated with a colloidal shear thickening fluid

Young S. Lee, E. D. Wetzel & N. J. Wagner

Journal of Materials Science **38**, 2825–2833(2003) | Cite this article

Flow-SANS show a shear-induced structure near the shear thickening transition - consistent with the hydrocluster mechanism of shear thickening colloidal dispersions





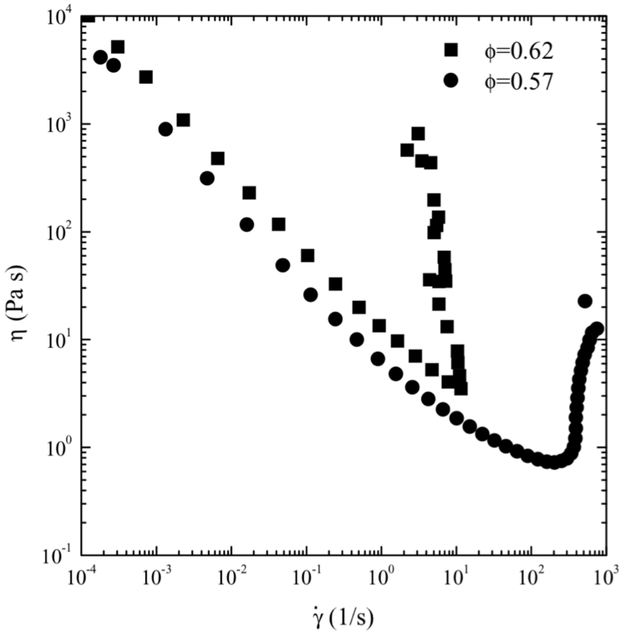
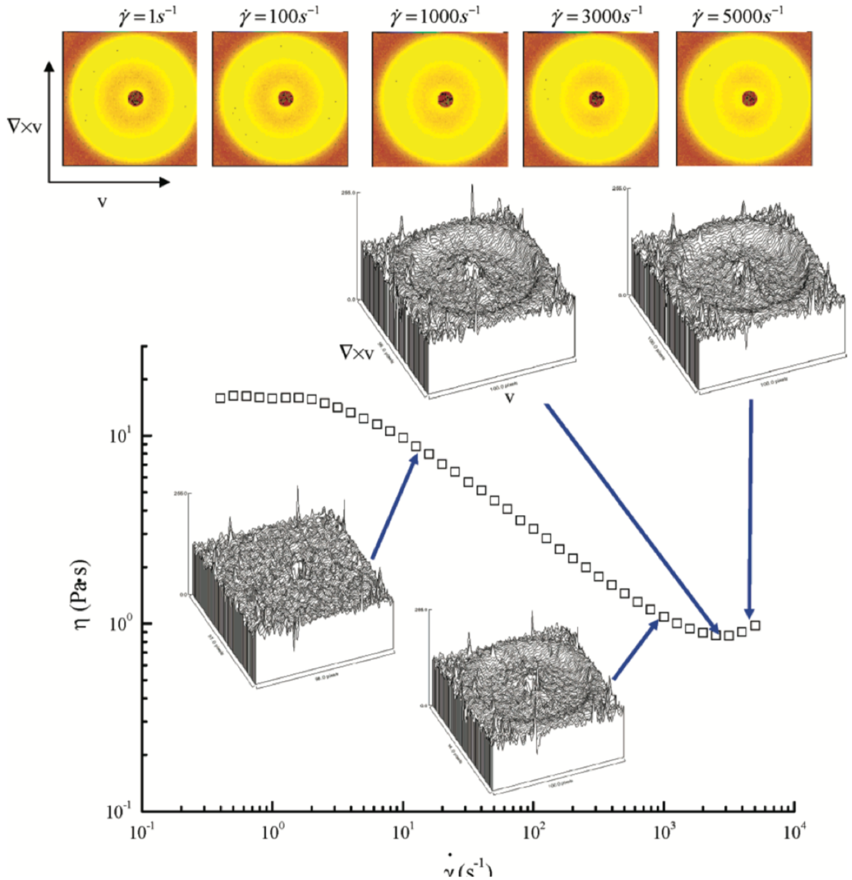
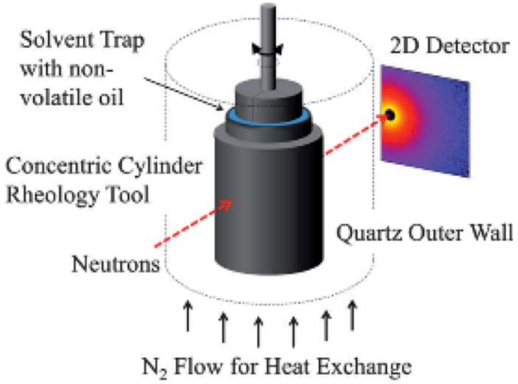


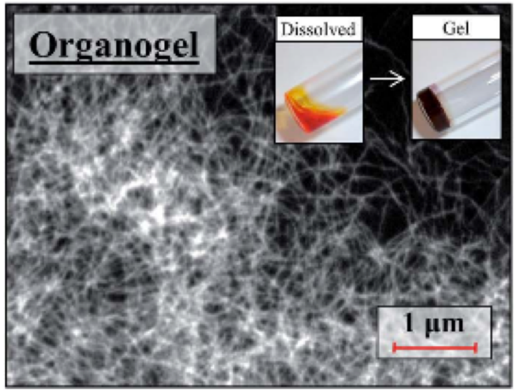
Figure 7 Shear thickening behavior of 57 and 62 volume % colloidal silica dispersed in ethylene glycol for steady shear flow.



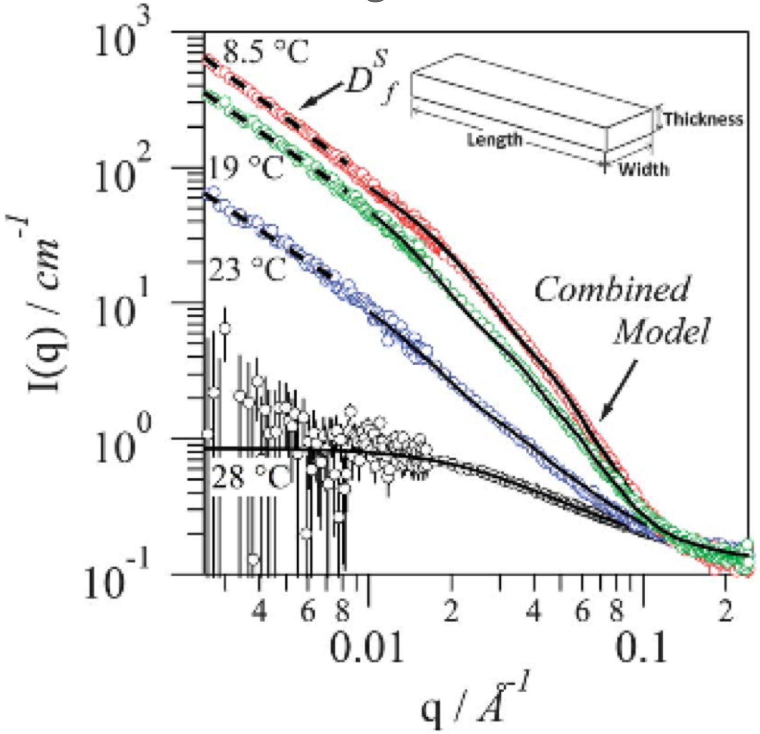
Example: Polymer solar cells

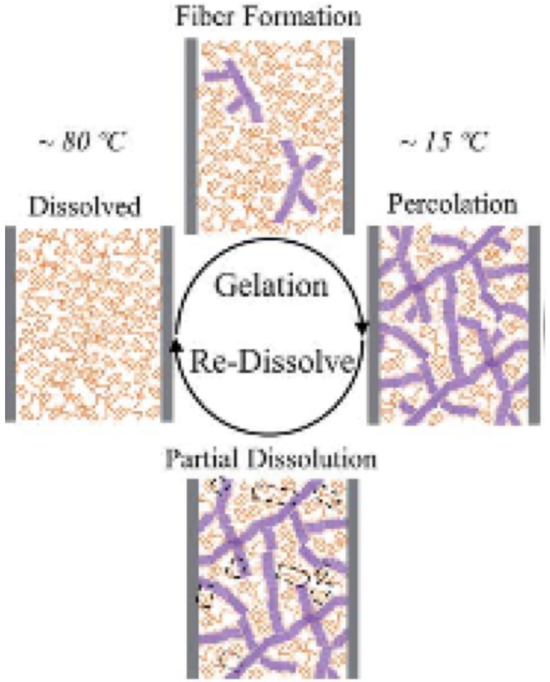
e.g. studying the structural properties of polythiophene for organic photovoltaics





Static SANS:
Gelation of the P3HT
microgel in toluene





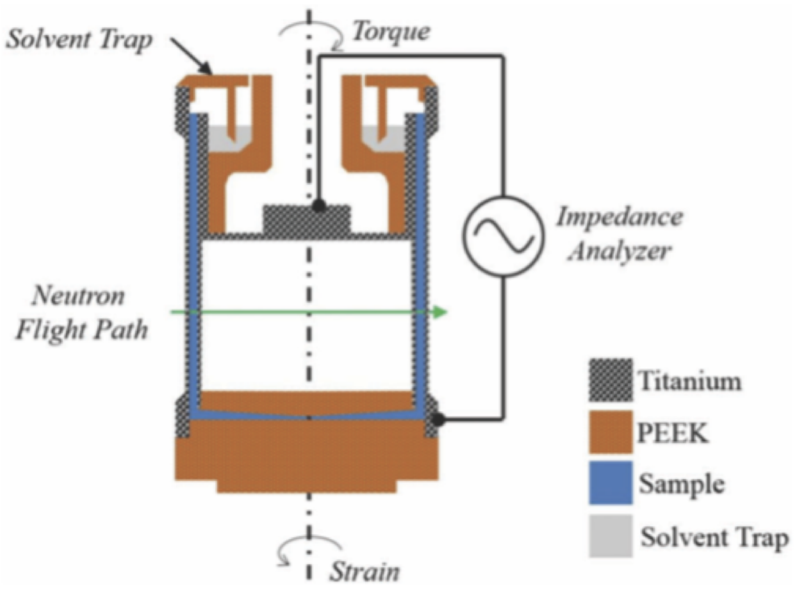
SANS show the structural features evolve through the gelation process and can be controlled by (i) partially redissolving, (ii) judicious selection of the aromatic solvent

Newbloom *et al.*, *Soft Matter*, 2012, **8**, 8854-8864

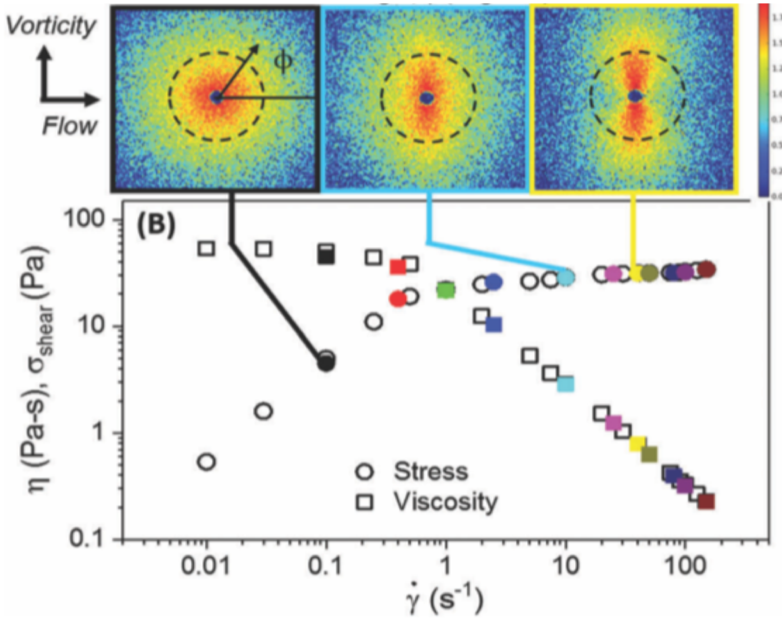
Example: Biomaterials, e.g. Lecithin

e.g. to untangle the branching behaviour in water-swollen reverse worm-like micelles

The electrical properties of these WLMs are independently sensitive to their topology and dynamics

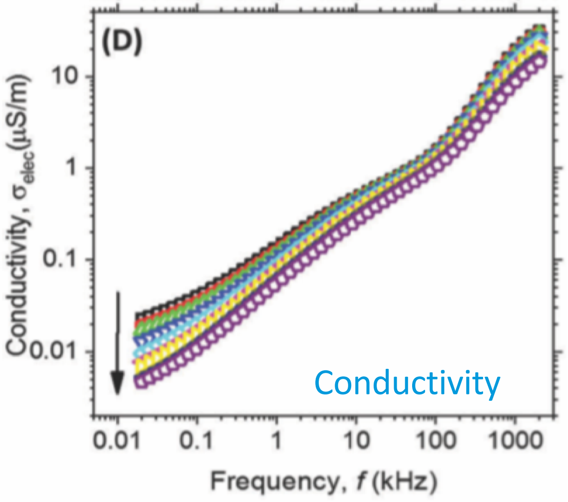


Small-angle neutron scattering:



Rheology: steady-sheer flow sweep

Dielectric spectroscopy:



- ➢ Branched WLMs show fast breakage times
- ➢ Unbranched WLMs show only subtle changes in their electrical properties.

Riley *et al.*, *Soft Matter,* 2018, **14**, 5344

Example 3: Proteins

NextBioForm: Centre for formulation and processing of biologics

…centre for competence development, innovation and development of formulations and process technologies for biologically based pharmaceuticals.

https://www.ri.se/en/nextbioform

Proteins & Surfactants

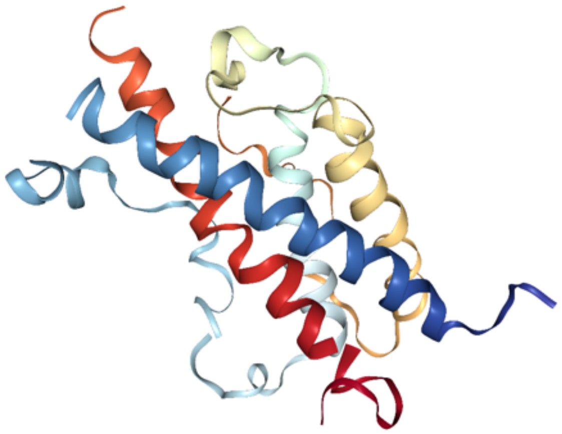
Adrian Sanchéz-Fernandéz (LU)

Proteins and surfactants **in formulated products** (drugs, cosmetics, food, detergents…) and **analytical techniques** (SDS-PAGE)

The interactions between protein and surfactants play an important role in the stability and performance of formulated products.

OUR GOAL:

Develop integrative approach to understand the **conformational and colloidal stability** of protein-surfactant systems.



Source: RCSB-PDB

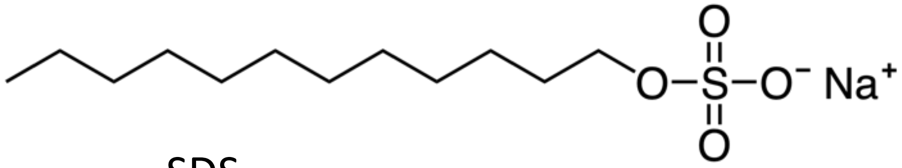
Model system:

- **Human growth hormone** (hGH) in 10 mM, pH 7 phosphate buffer.
- **Anionic surfactant** (SDS)

FERRING PHARMACEUTICALS

Implementation of advanced characterisation techniques:

- **Contrast variation small-angle neutron scattering** – constrained structural modelling.



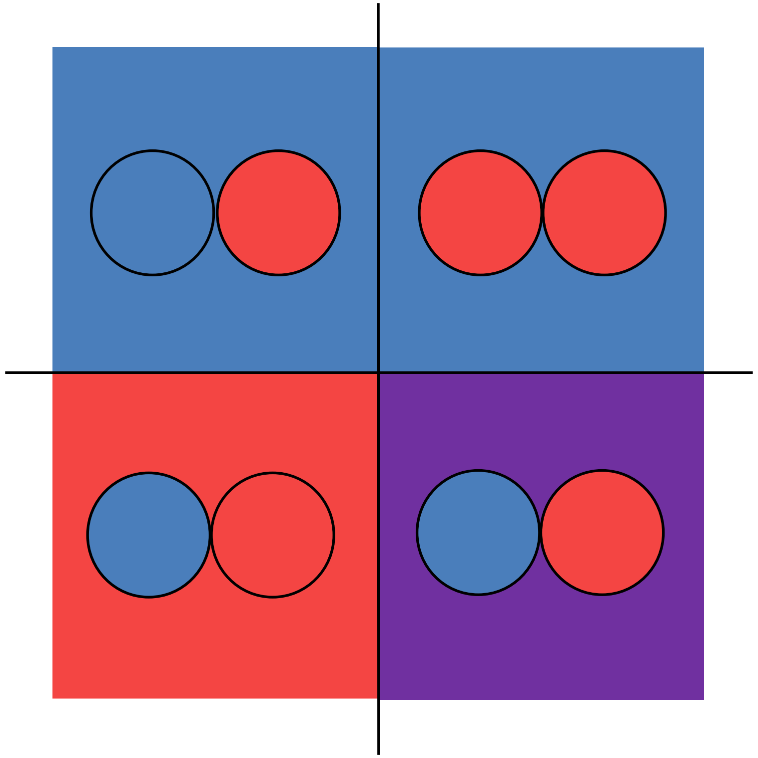
SDS

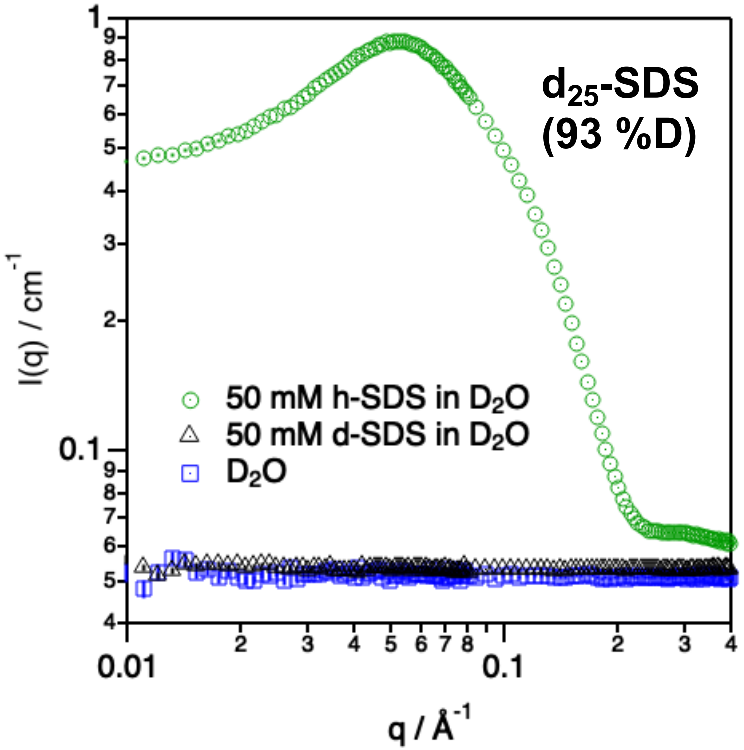
Small-angle neutron scattering with contrast variation

Probing hGH-SDS complexes…

1. Surfactant-solvent matched – protein backbone.
2. Protein-surfactant matched – complex.
3. Protein-solvent matched – surfactant.
4. Zero-average contrast condition – ZAC.

Component	SLD / $\times 10^{-6}$ Å^{-2}
$C_{12}H_{25}$	-0.39
$C_{12}D_{25}$	6.98
SO_4	4.32
D_2O	6.37

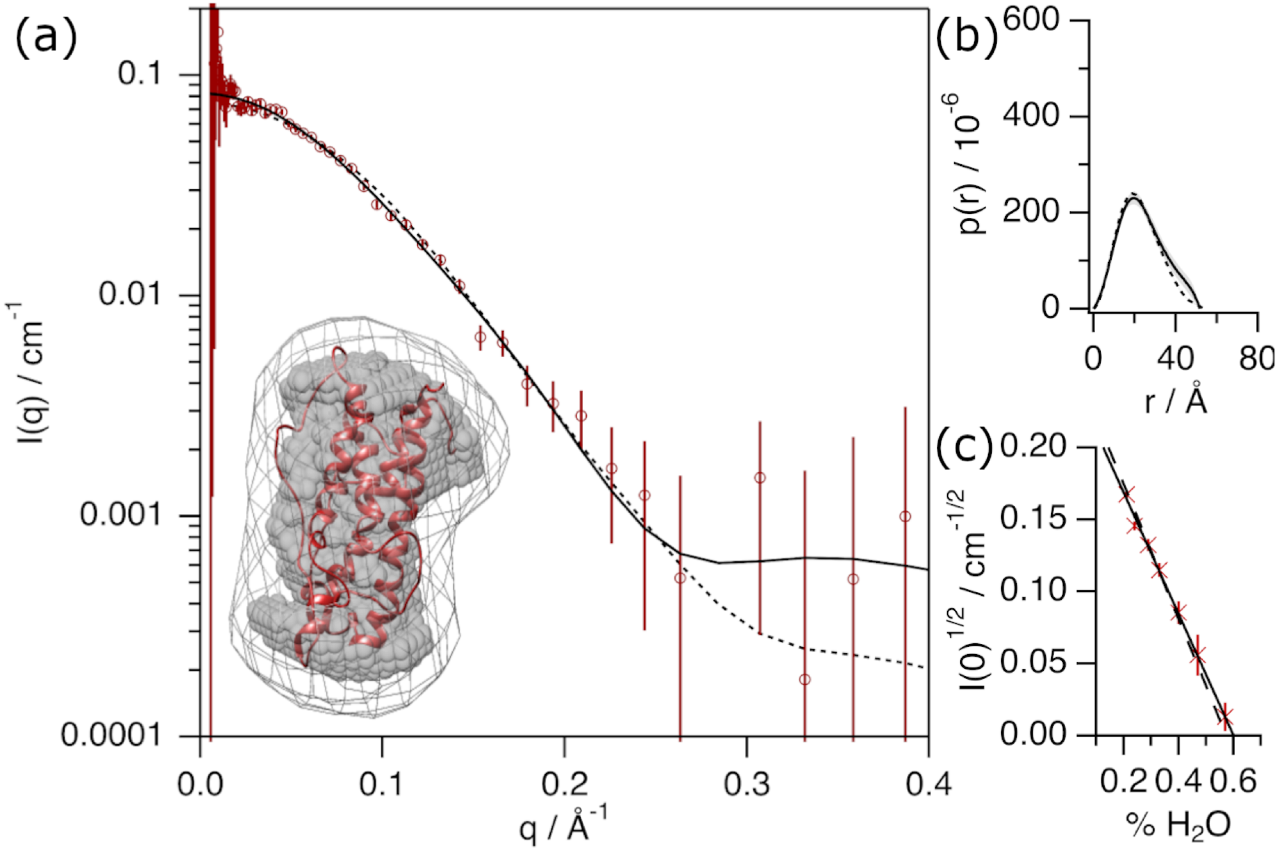




SANS2D, ISIS (UK)
D11, ILL (FR)

Structural characterisation of hGH

Pure hGH (0.154 mM) in buffered D_2O



Globular protein:

- D_{max}= 51.7 Å
- R_g = 18.4±0.3 Å
- I(0) = 0.079±0.012 cm^{-1}
- Monomer in solution
- Contrast match point: 60.1±2.1% H_2O.

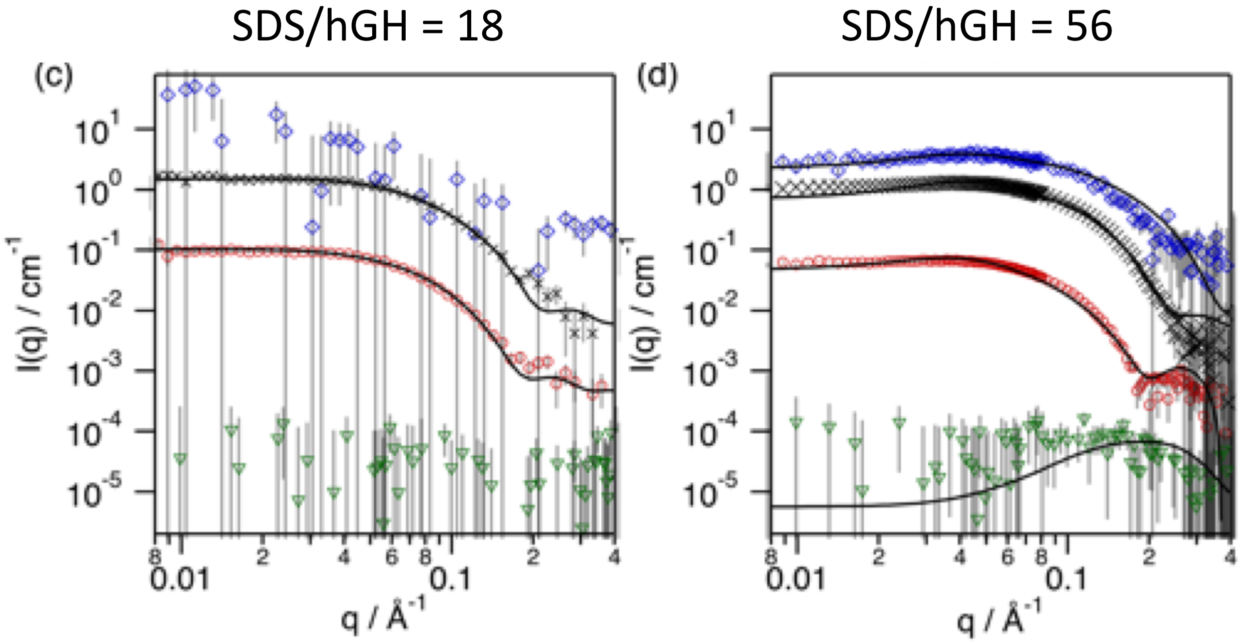
Contrast variation and SANS

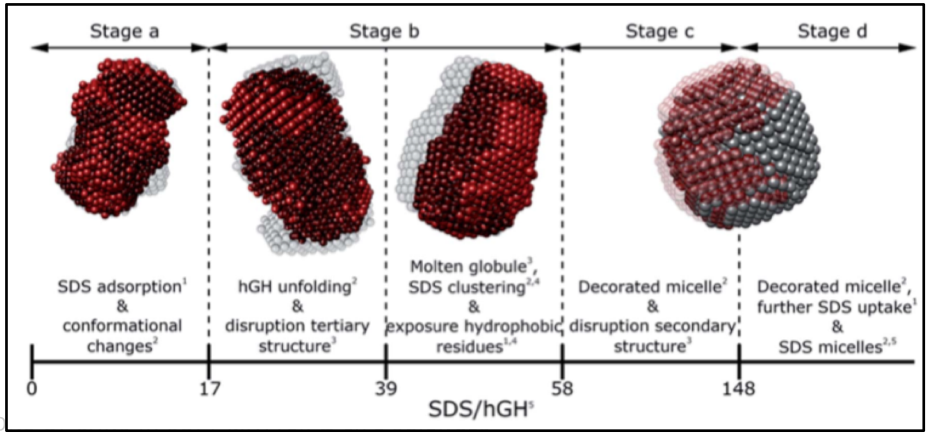
Changes in **structure and interactions** between complexes.

Surfactant phase – **various complexation stages: pre-CAC, pre-CMC and post CMC.**

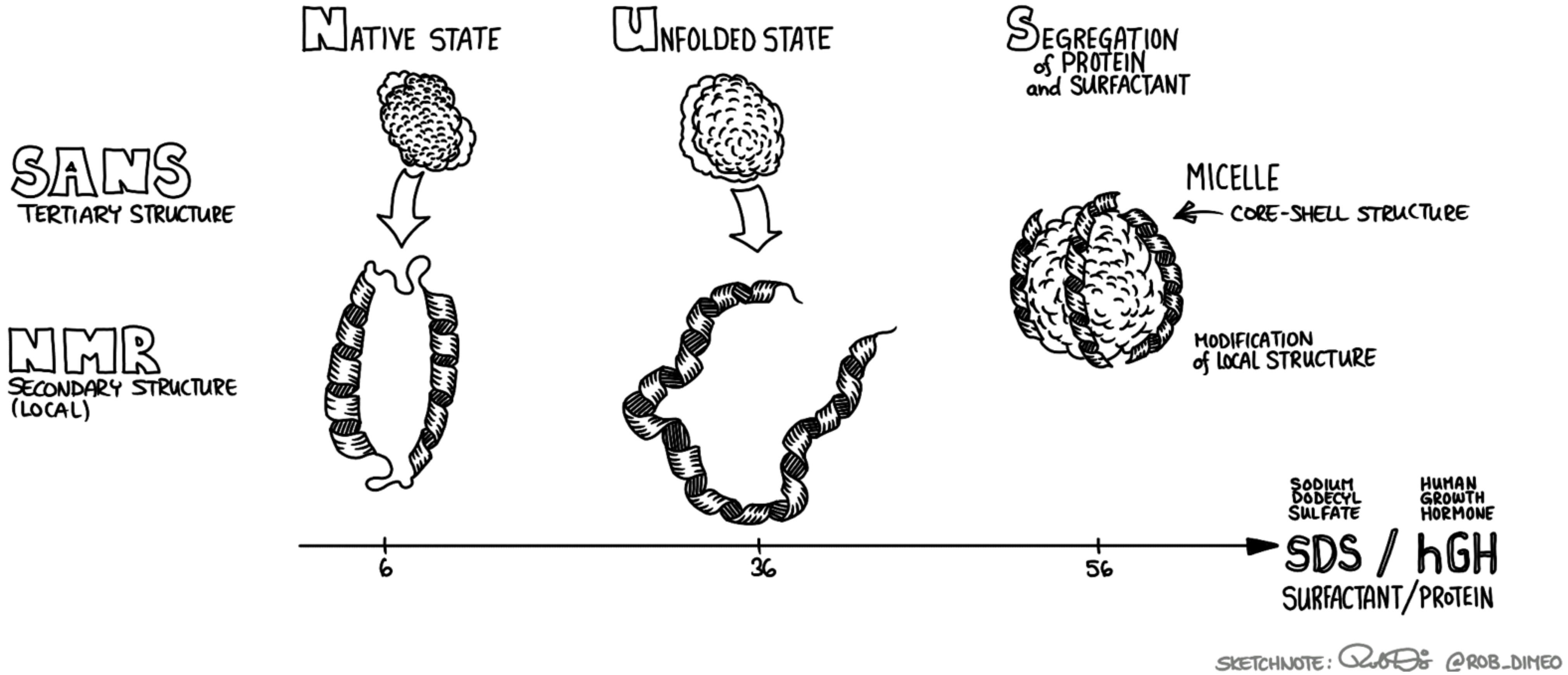
Model-based fitting:

- Low SDS/hGH mode **– unfolded protein with sparsely adsorbed surfactants.**
- High SDS/hGH mode – **decorated micelle morphology.**





Different interaction stages



Sequential
Parallel

Complex mechanism

Hydrophobic
Electrostatic

Connecting molecular origin and mesoscopic structure

A. Sanchéz-Fernandéz, C. Diehl, J. E. Houston, A. E. Leung, J. P. Tellam, S. E. Rogers, S. Prevost, S. Ulvenlund, H. Sjogren and M. Wahlgren, *Nanoscale Adv.*, 2020, **2**, 401