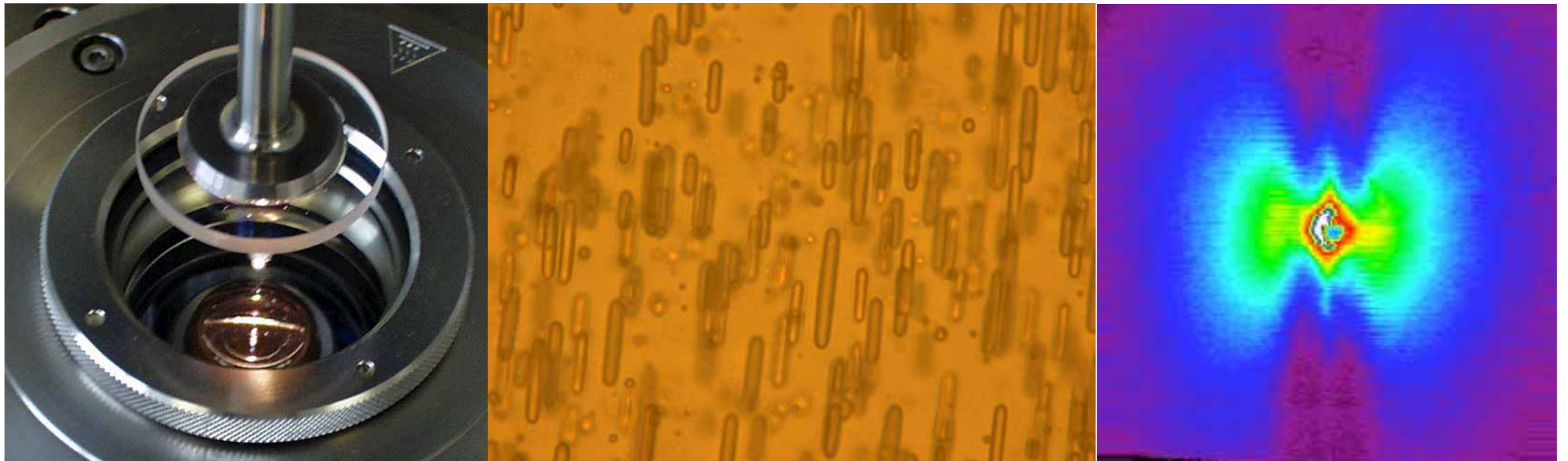

Rheology and scattering methods (SANS and SAXS under flow)

Peter Fischer¹ and Joachim Kohlbrecher²

¹ ETH Zurich, Institute of Food, Nutrition and Health, 8092 Zurich Switzerland

² PSI, Laboratory of Neutron Scattering and Imaging, 5232 Villigen, Switzerland



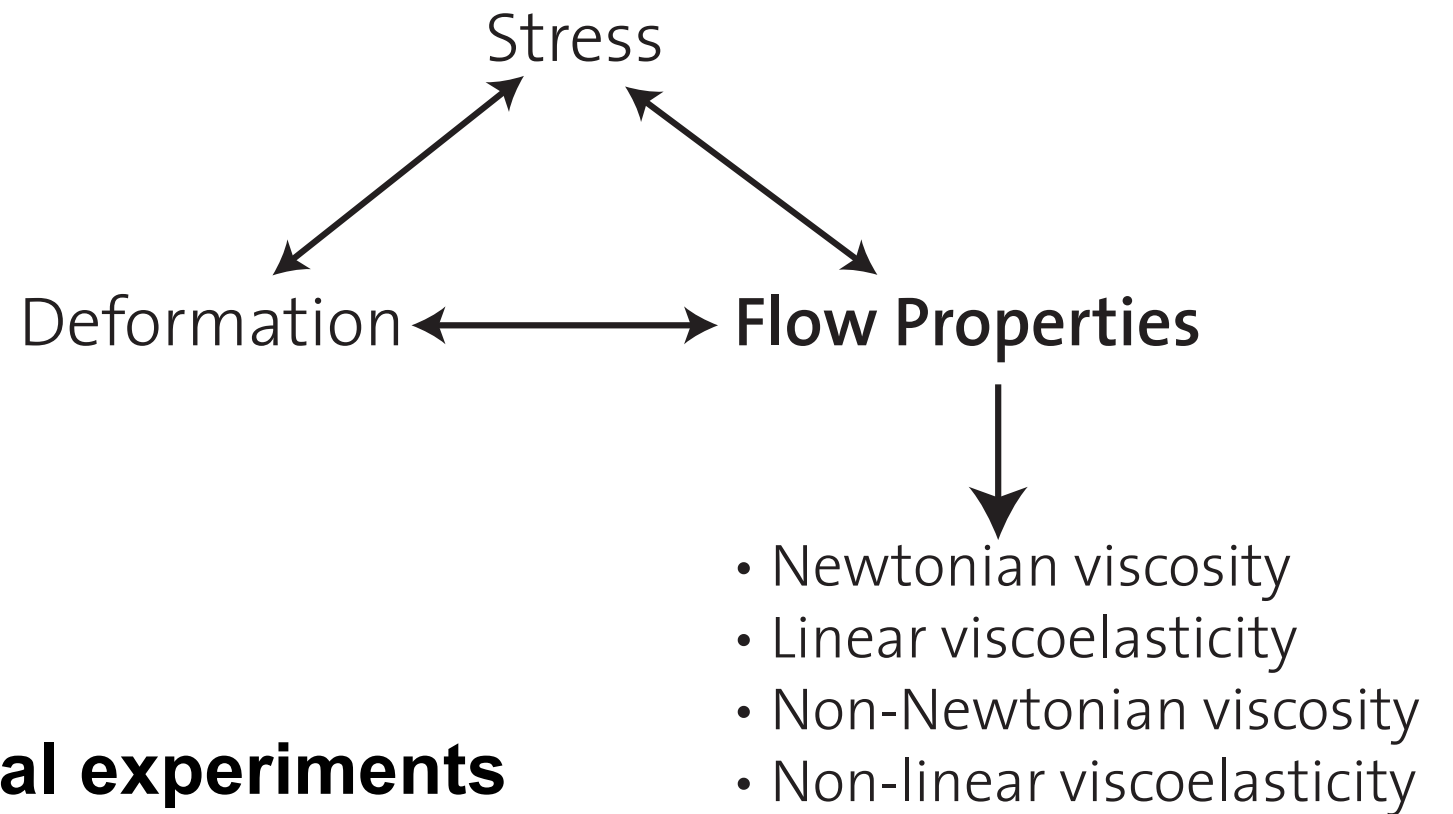
Rheology: Study of deformation and flow of matter¹

Constitutive Equation:

Stress = Flow Properties • Deformation

παντα ρει – **Everything flow²:**

Polymers, colloids, food & pharma,
biology, geology, ...



Information obtained from rheological experiments

1) Flow properties

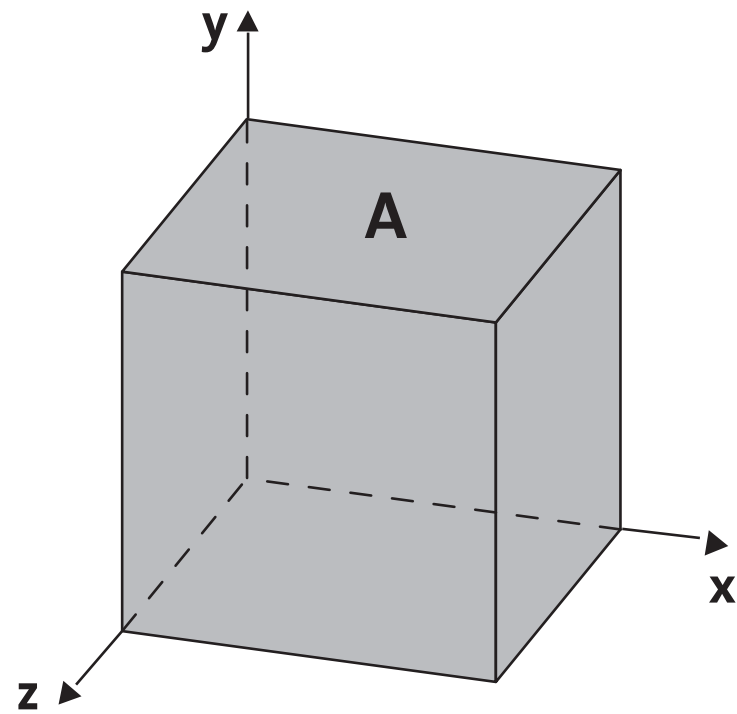
Macroscopic properties (viscosity, elasticity, viscoelasticity,)

2) Molecular Structure

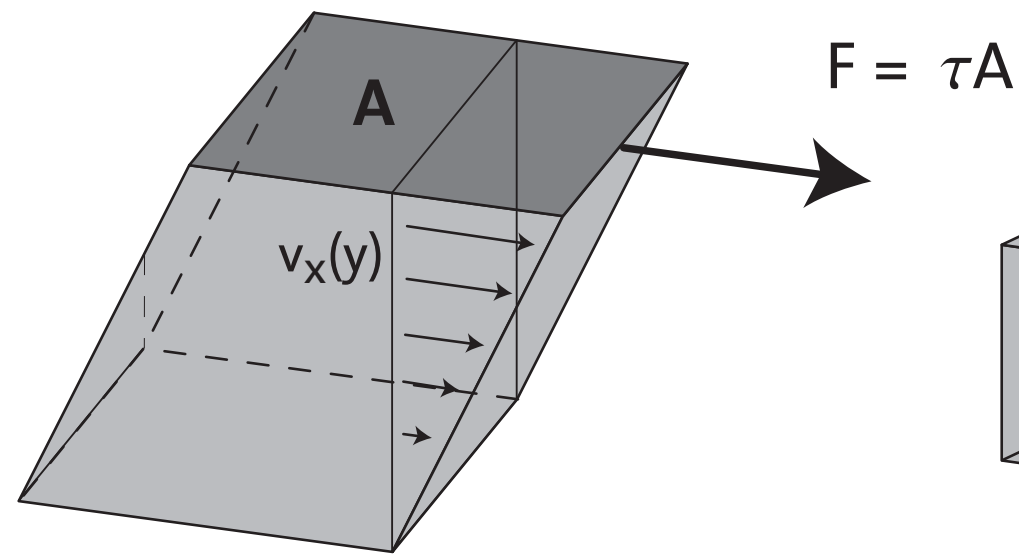
Flow as fingerprints of morphology, conformation, orientation,

3) Link between Structure development, process optimization, ...³

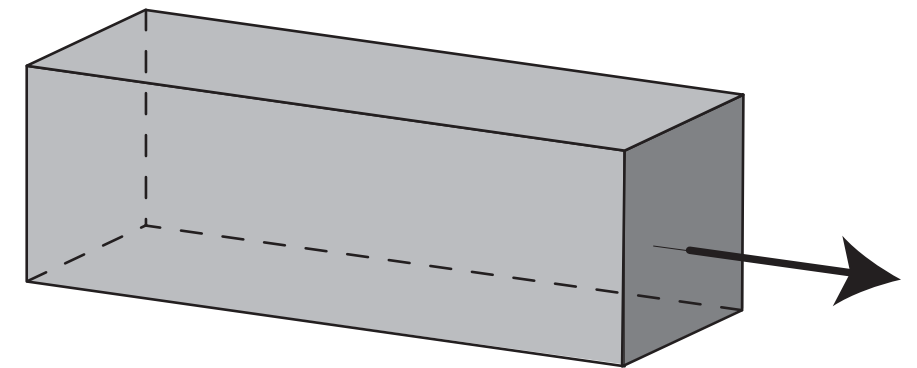
Rheology: Shear and elongation



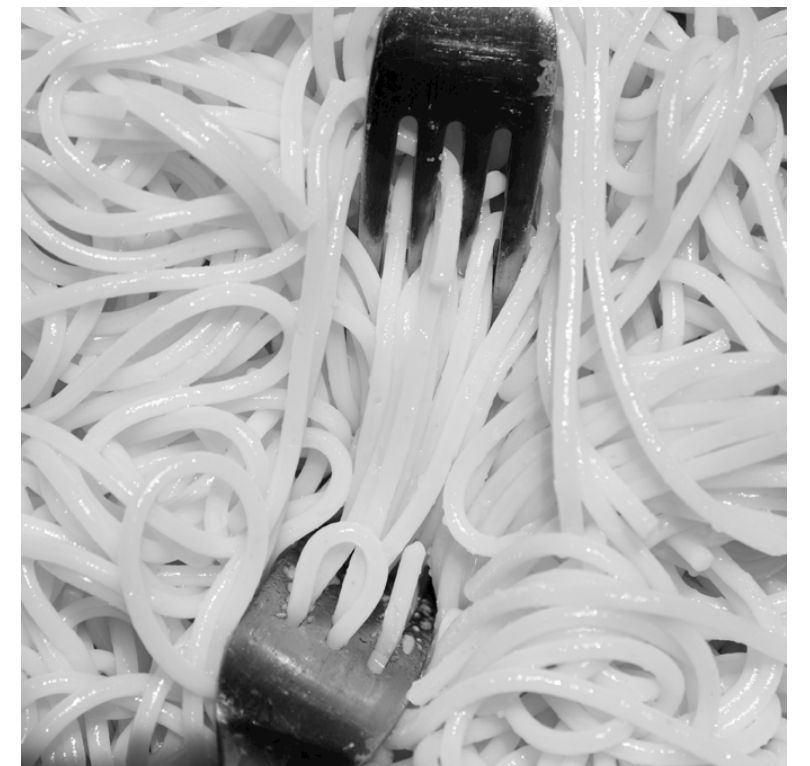
At Rest



Under Shear Flow



Under Elongational Flow



Rheology: Newtonian and non-Newtonian flow



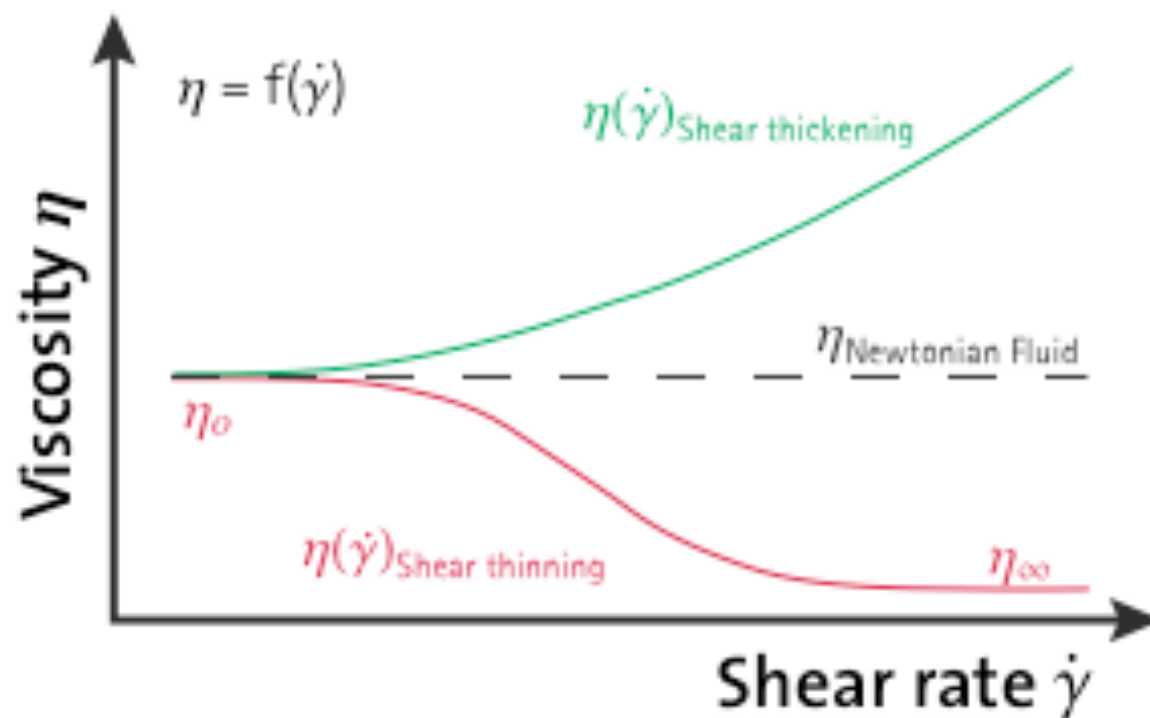
Structure at rest

$\dot{\gamma}$
• Rheology
• Process
• "Event"

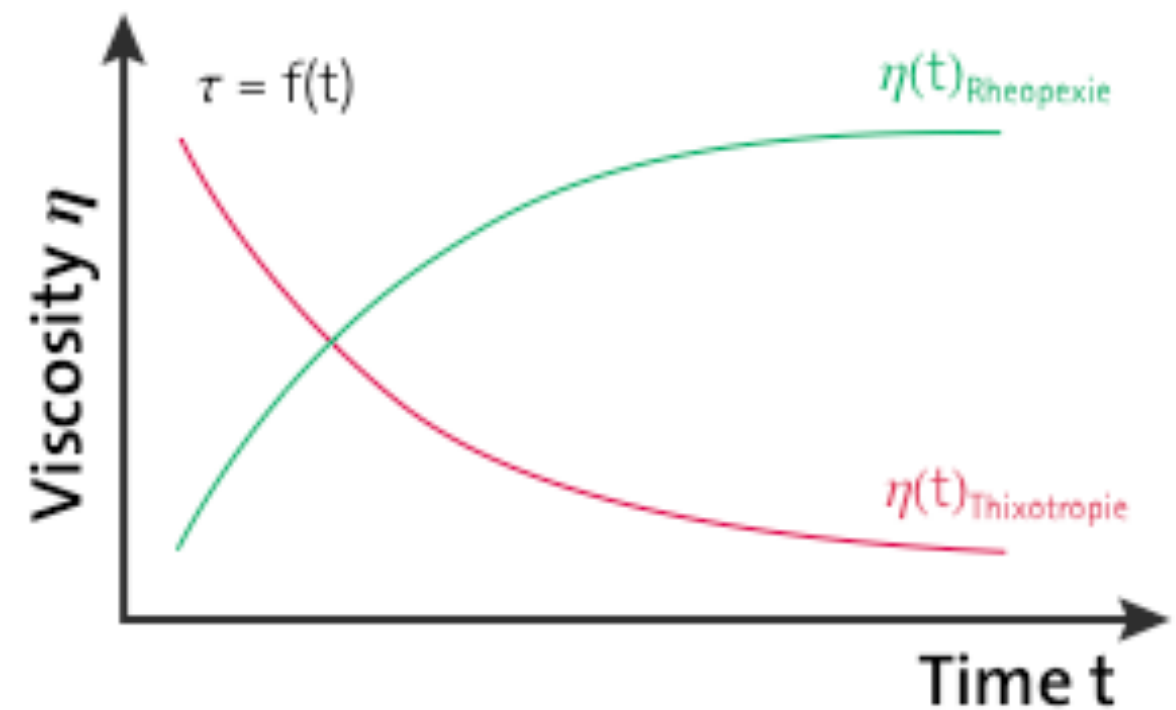


Shear-induced structure

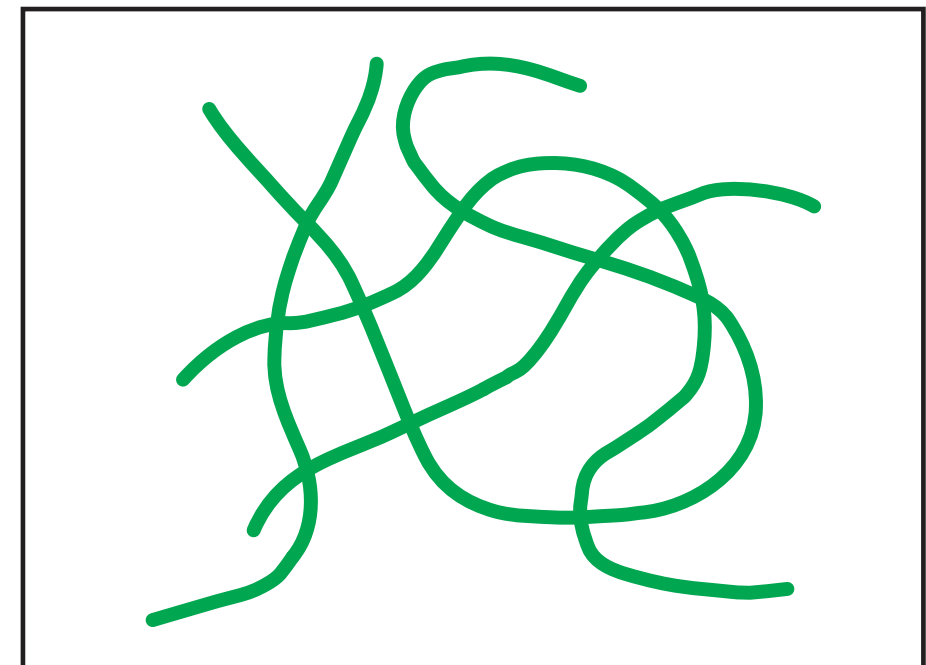
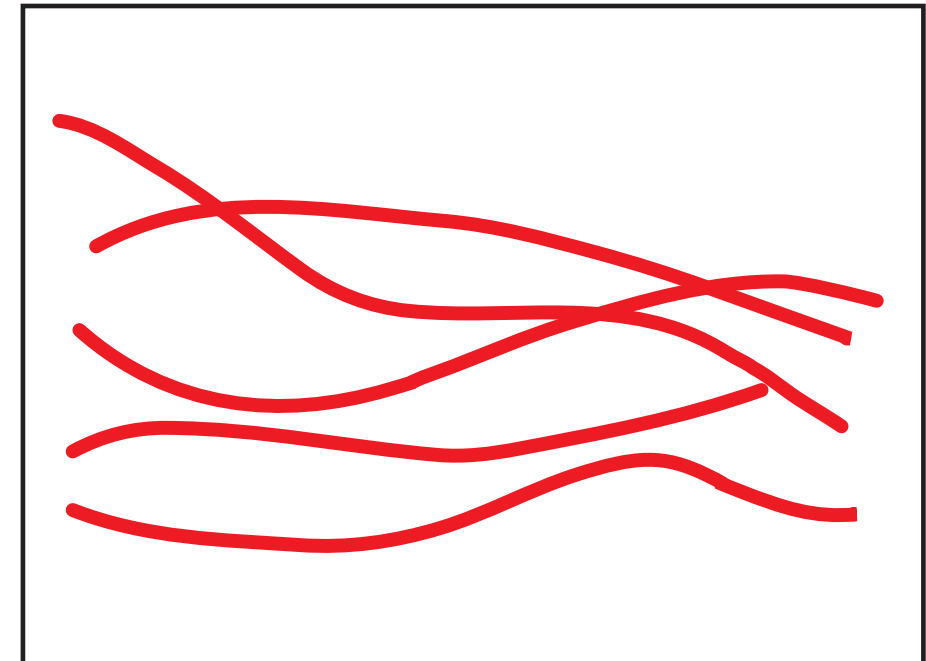
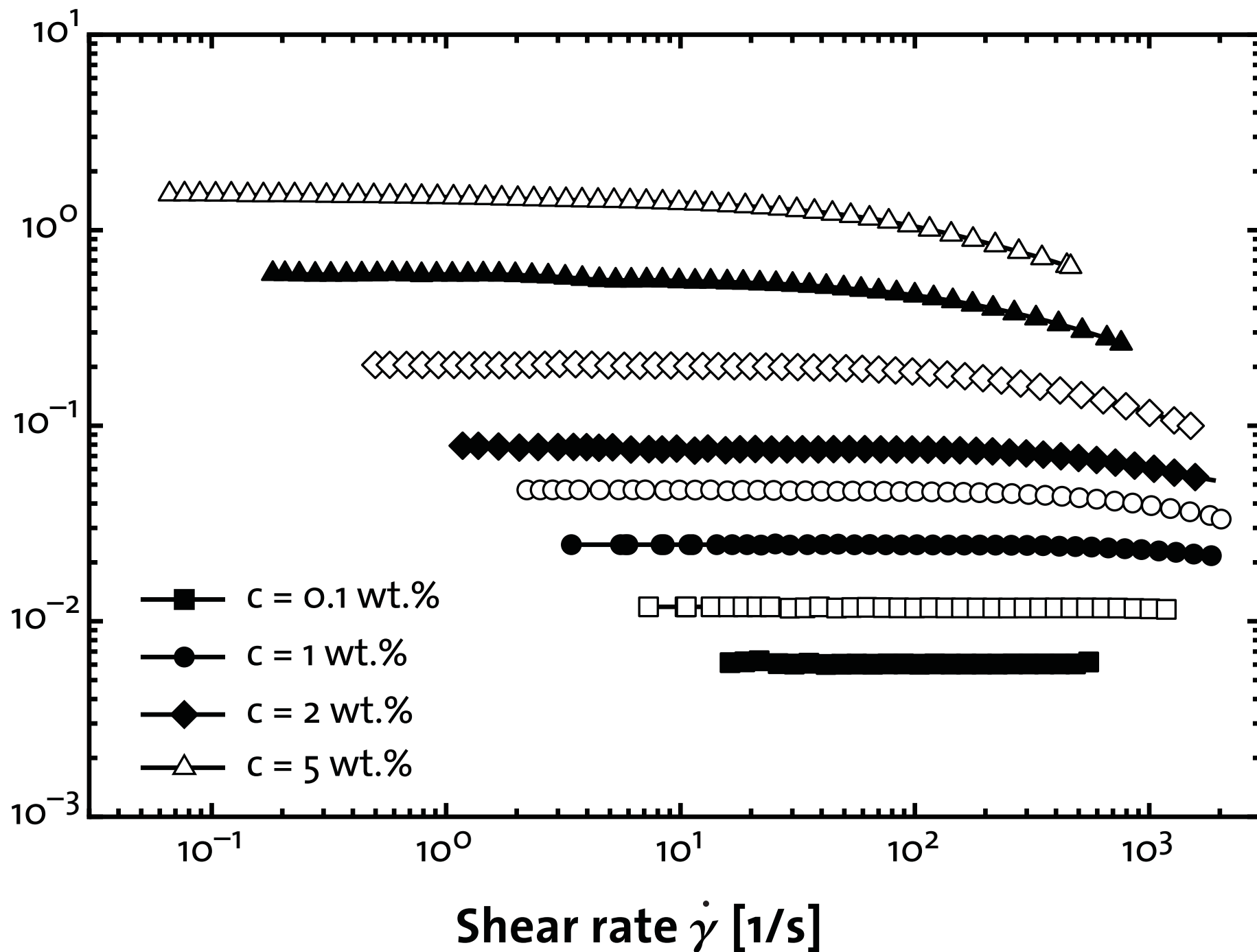
Effect of shear:



Effect of time:

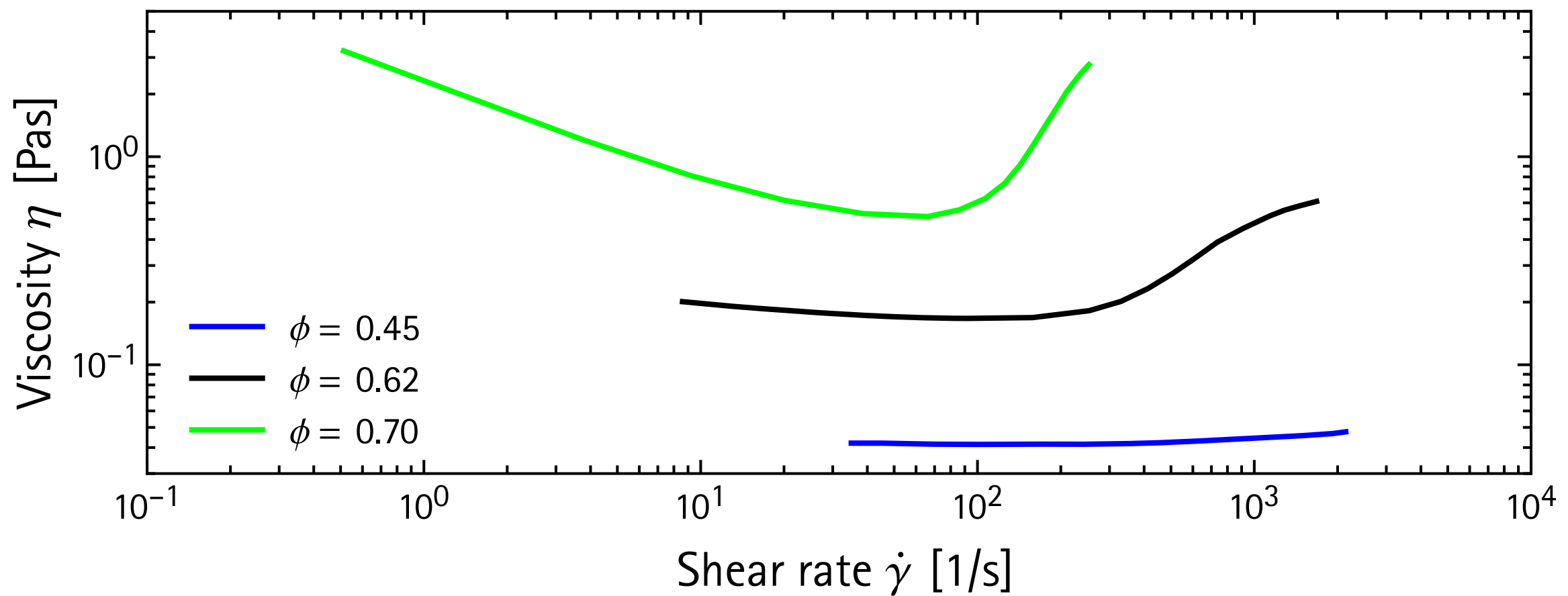
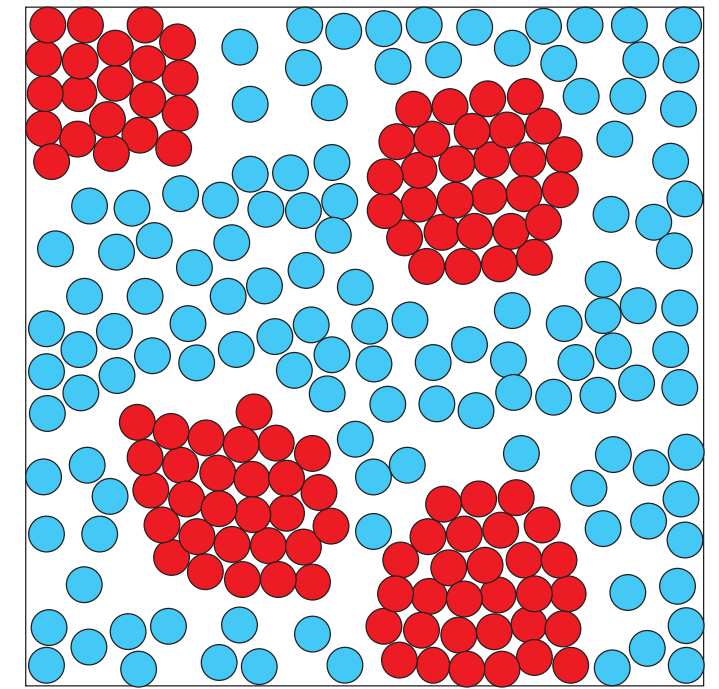
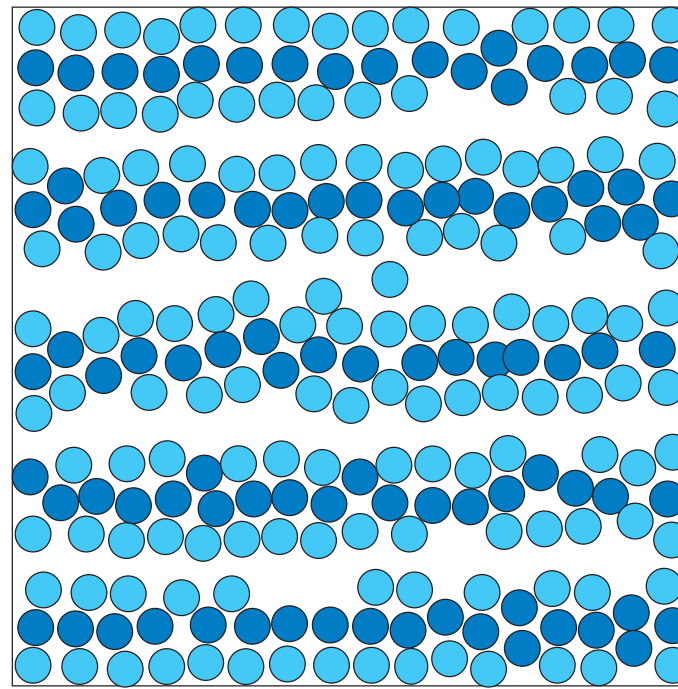
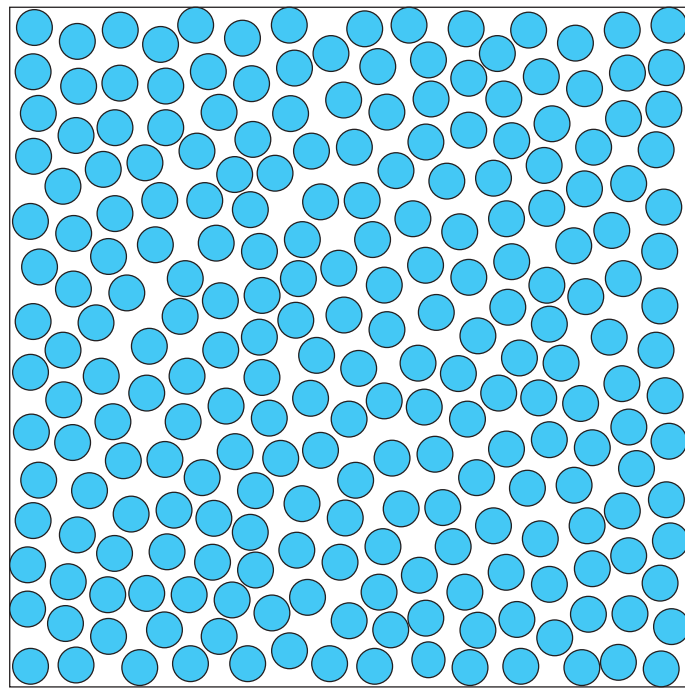


Rheology: Shear-thinning in polymer solutions



Flow curve of aqueous κ -carrageenan solution (concentration $c = 0.5$ to 6 wt%). The increase of concentration leads to an increase in viscosity and a shift of the onset of the shear thinning behavior (log-log plots are commonly used).

Rheology: Shear-thickening & dilatancy in suspensions

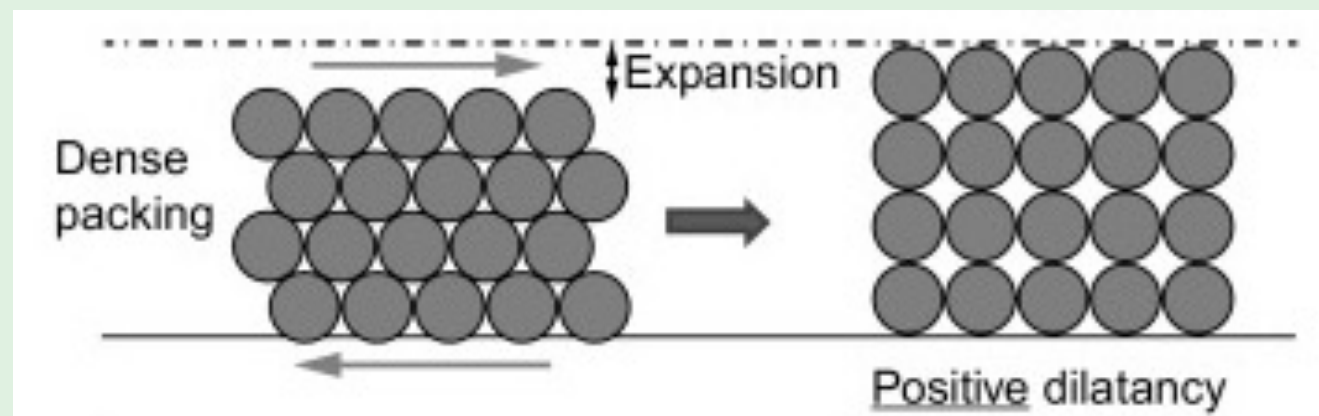


Rheo-Disaster: Dilatancy at the beach



Structure at rest: Sand fully saturated with water.

Rheology by foot: Sand structure disrupted, water “vanishes” in created voids.



http://mpegmedia.abc.net.au/science/articles/mp4/sand_experiment.mp4

Rheo-Disaster: Dilatancy during earthquakes

Körner ohne Kontakt: Was bei der Bodenverflüssigung passiert

Stabiler Boden

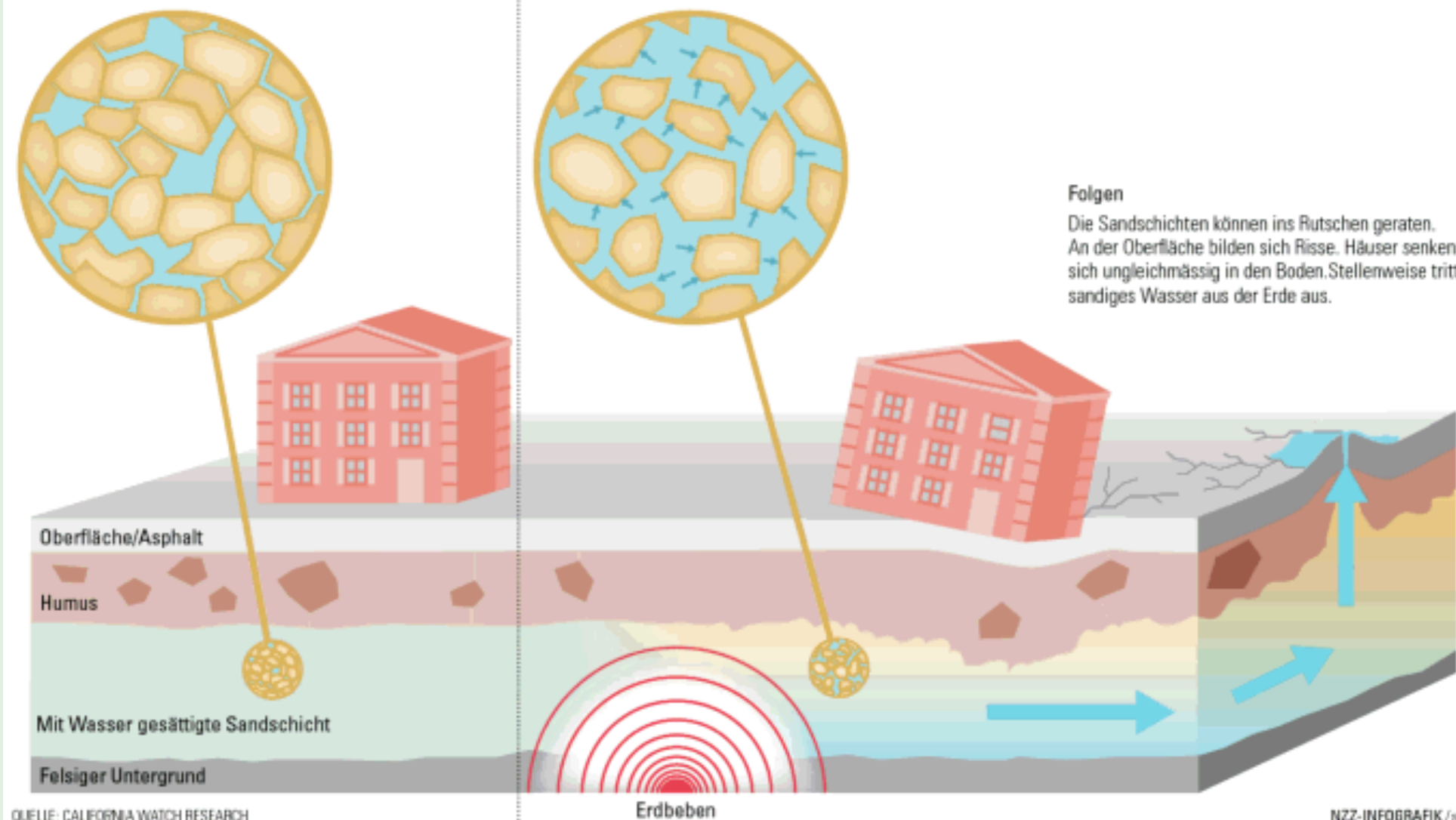
Lockere Sandböden sind fest, weil die Sandkörner sich berühren. Die Reibung der Körner aneinander macht den Boden tragfähig, obwohl die Poren mit Wasser gefüllt sind.

Verflüssigter Boden

Durch den Druck der Erdbebenwellen verändern die Sandkörner ihre Lage. Das Wasser kann nicht so schnell entweichen. Die Sandkörner verlieren den Kontakt und werden auseinandergepresst. Der Boden wird flüssig.

Folgen

Die Sandschichten können ins Rutschen geraten. An der Oberfläche bilden sich Risse. Häuser senken sich ungleichmässig in den Boden. Stellenweise tritt sandiges Wasser aus der Erde aus.



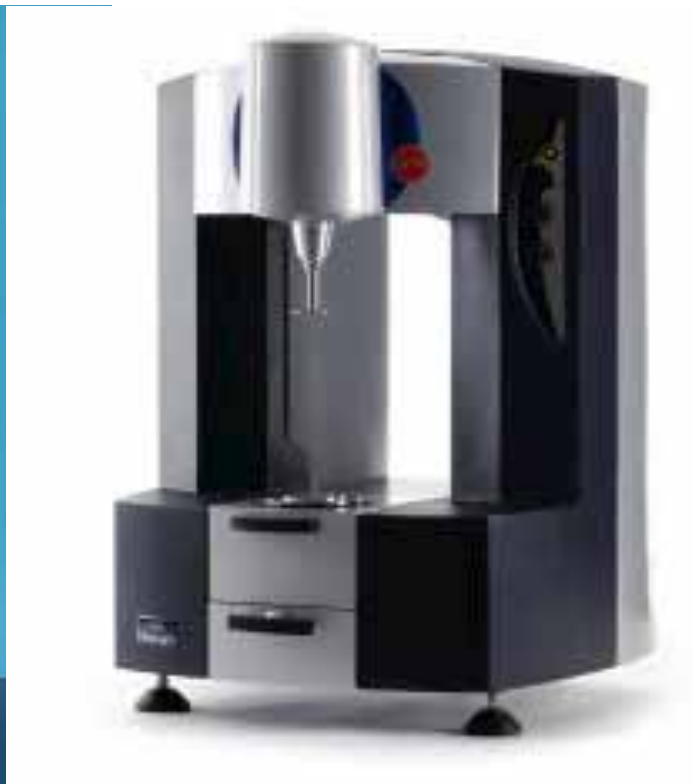
Christchurch/New Zealand



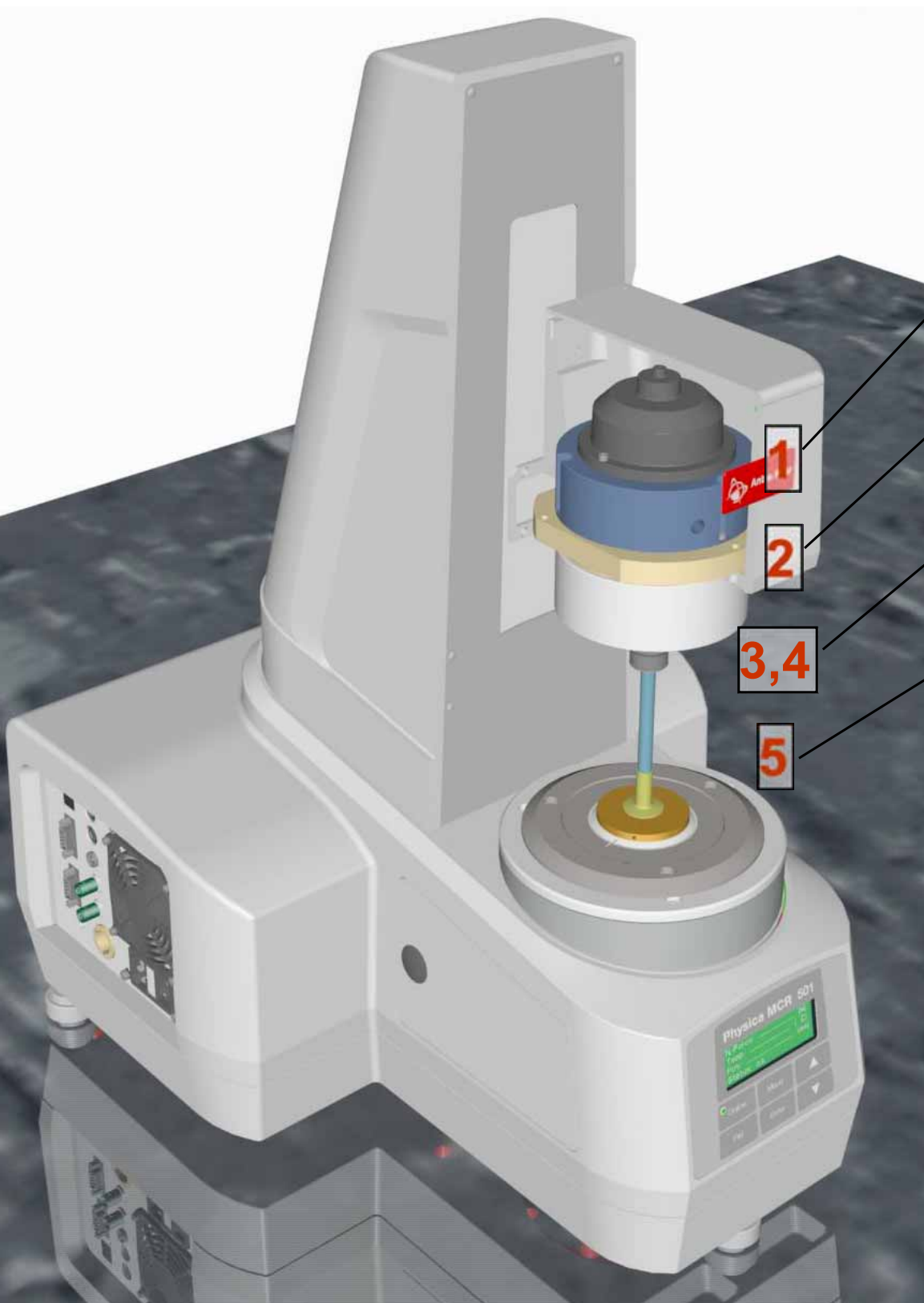
Niigata/Japan



Standard rotational rheometers



Design of a rotational rheometer



Optical Encoder

Motor (drag cup, EC)

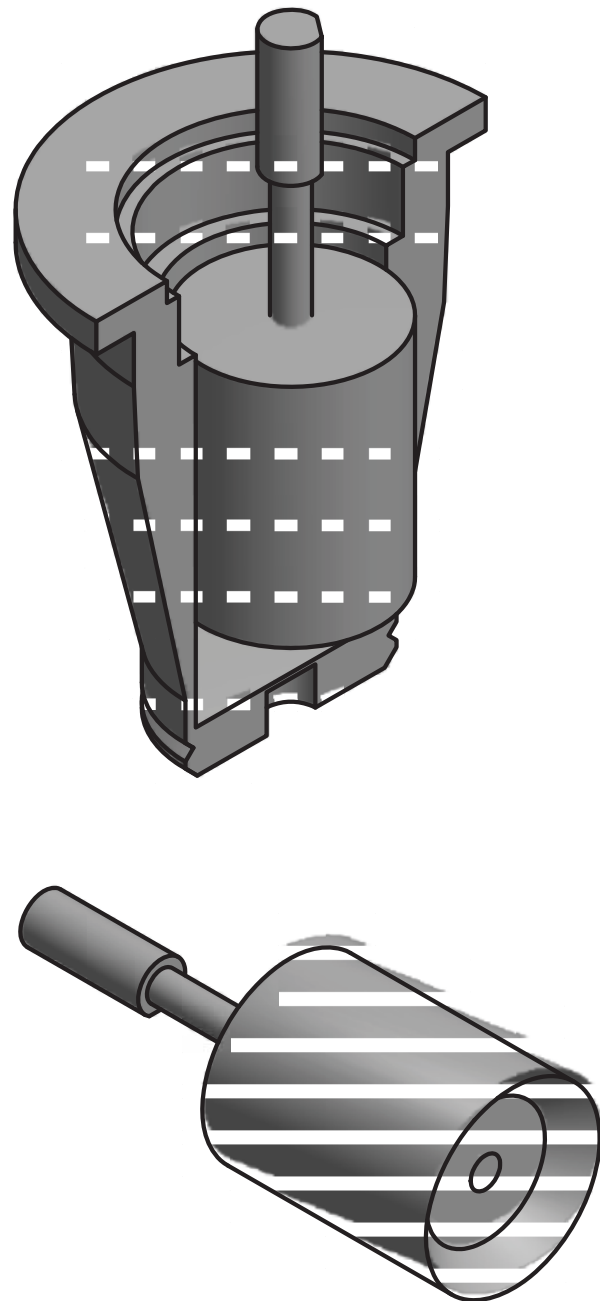
Air Bearing & Normal Force Sensor

Measuring geometry



Standard measuring geometries

Couette / Searle



Cone-Plate

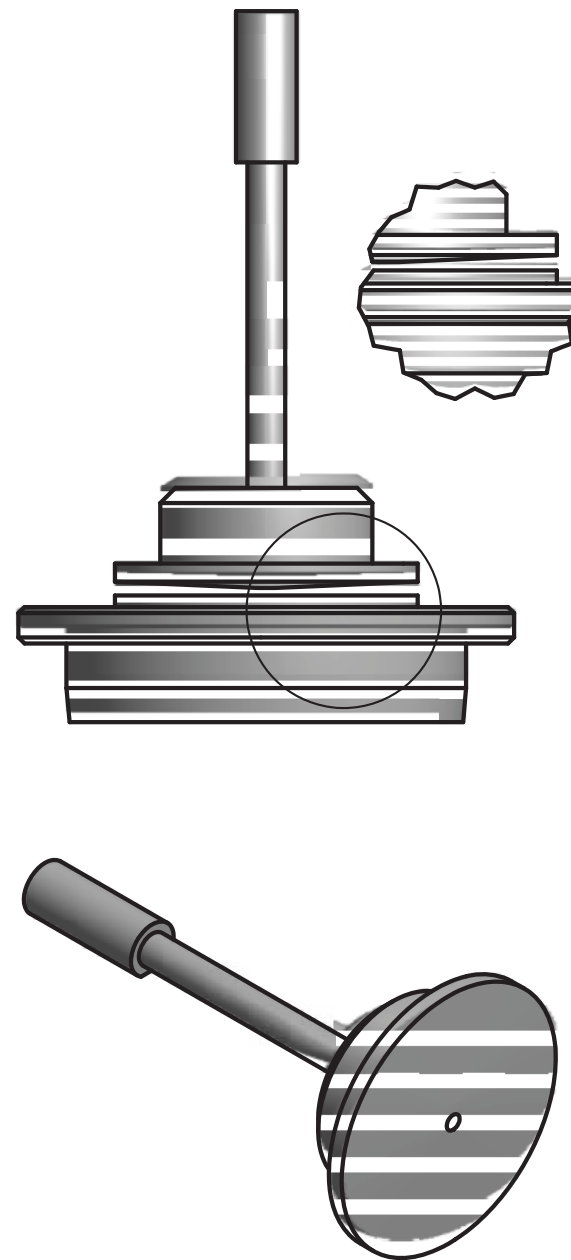
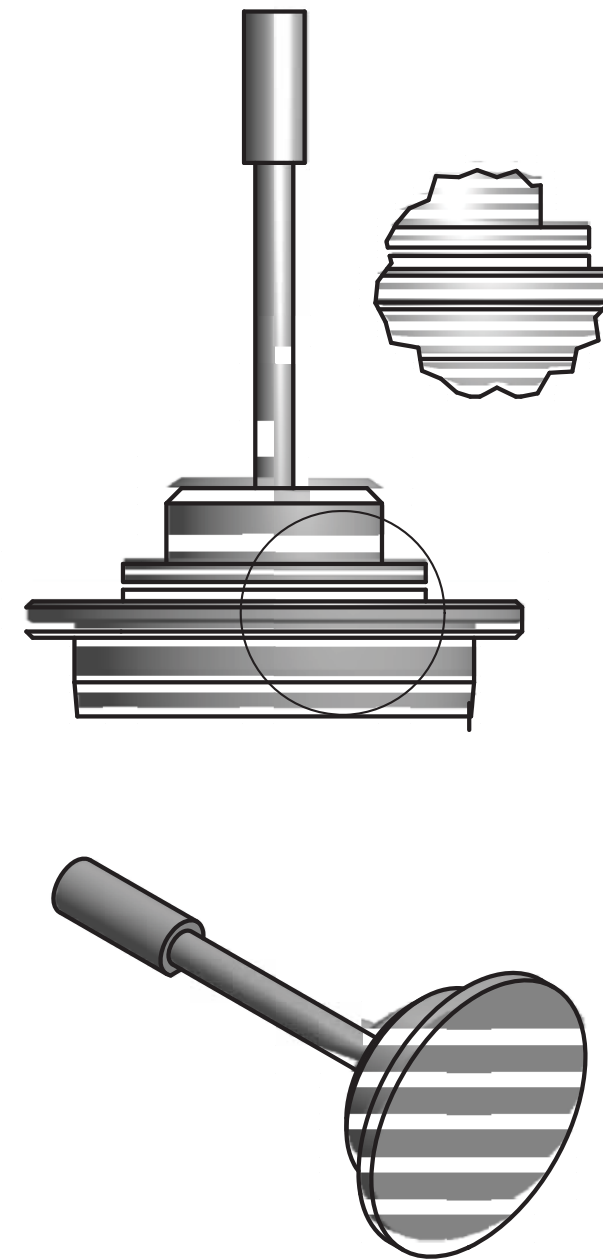


Plate-Plate



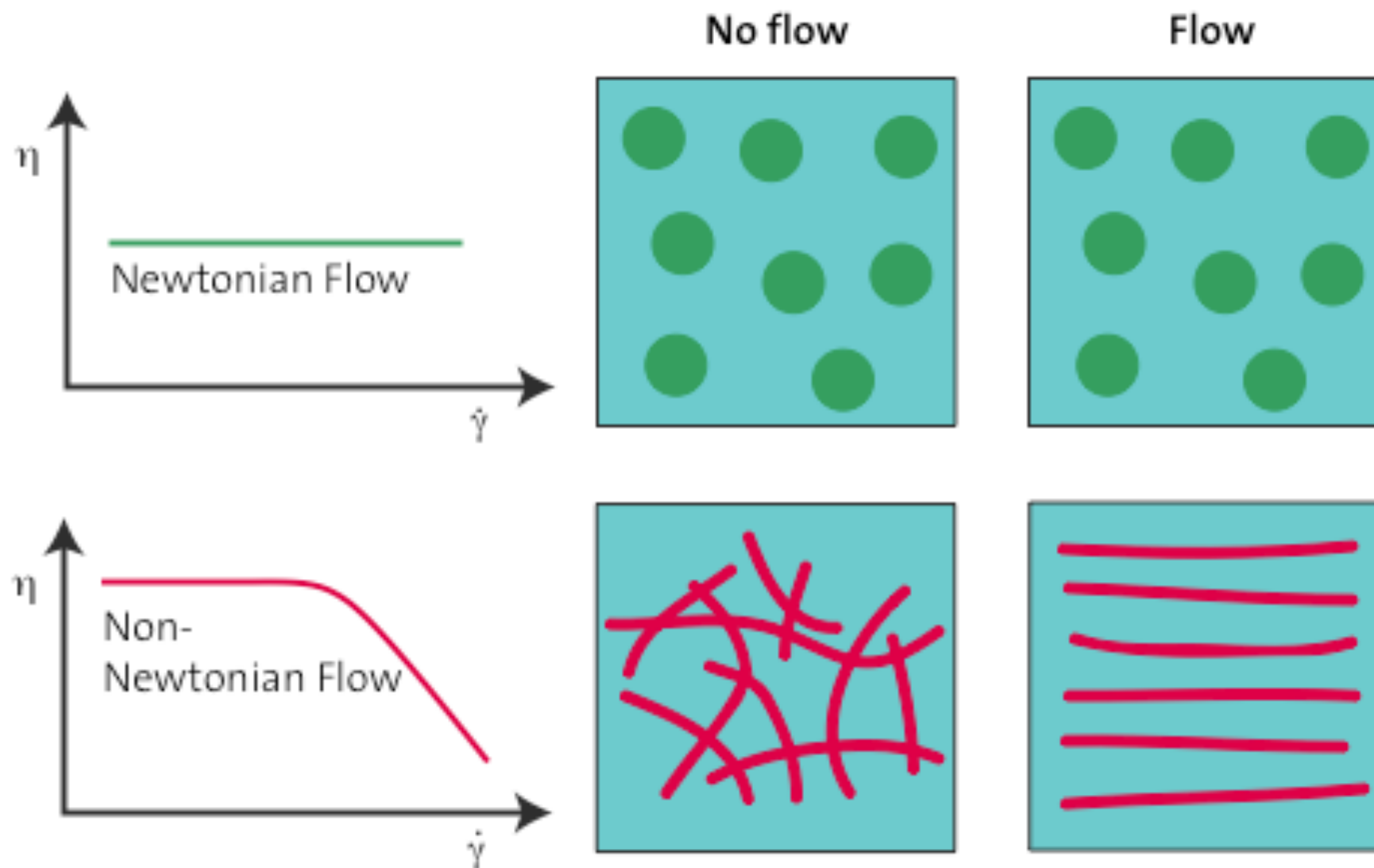
Raw data such as torque, normal torque, angular velocity, and angular displacement are transferred into rheological data via geometry factors

Coupling flow and flow induced structures I

Rheological properties result from a material deformation on micro- or nano-mechanical level (macroscopic rheology: microscopic dynamics and structure of complex fluids)

Macroscopic
Material Functions
(Rheometry)

Microscopic
Structure Parameters
(Scattering methods)



Rheo-Scattering Approach:

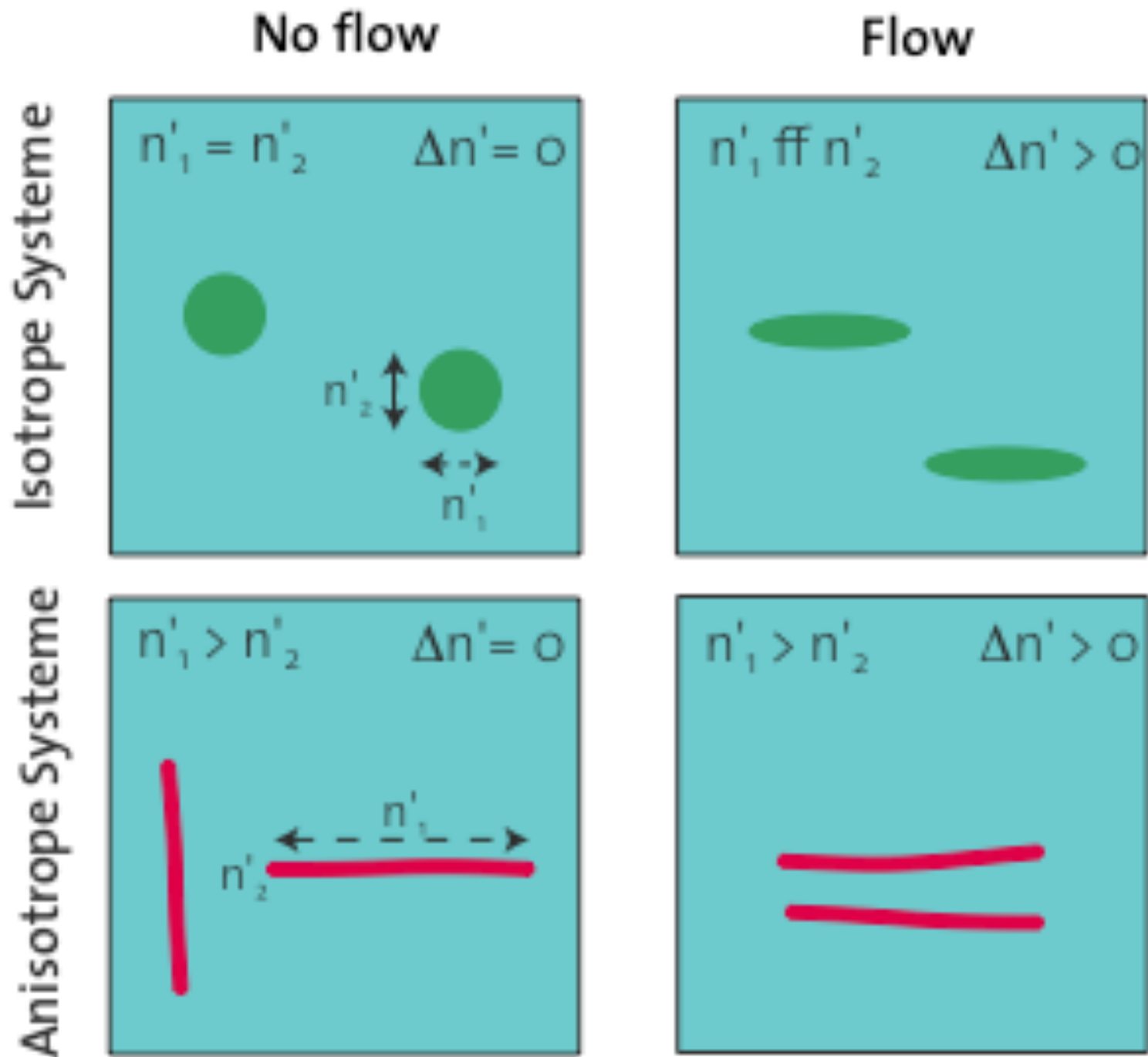
Superposition of rheology and an external field

Quantitatively measure of rheological properties

Qualitatively interpret of rheological behavior in microstructural terms

Coupling flow and flow induced structures II

Intrinsic & flow induced anisotropy of particle, droplets, and polymers



Changes in form or changes in alignment are used to investigate orientation effects in flow fields

- Deformable object like droplets or bubbles align and deform under flow. The optical properties change in line with the deformation.

- Anisotropic shaped particle or polymers align in flow and sum up their intrinsic optical properties.

Rheo-Scattering methods (SALS, SANS, SAXS)

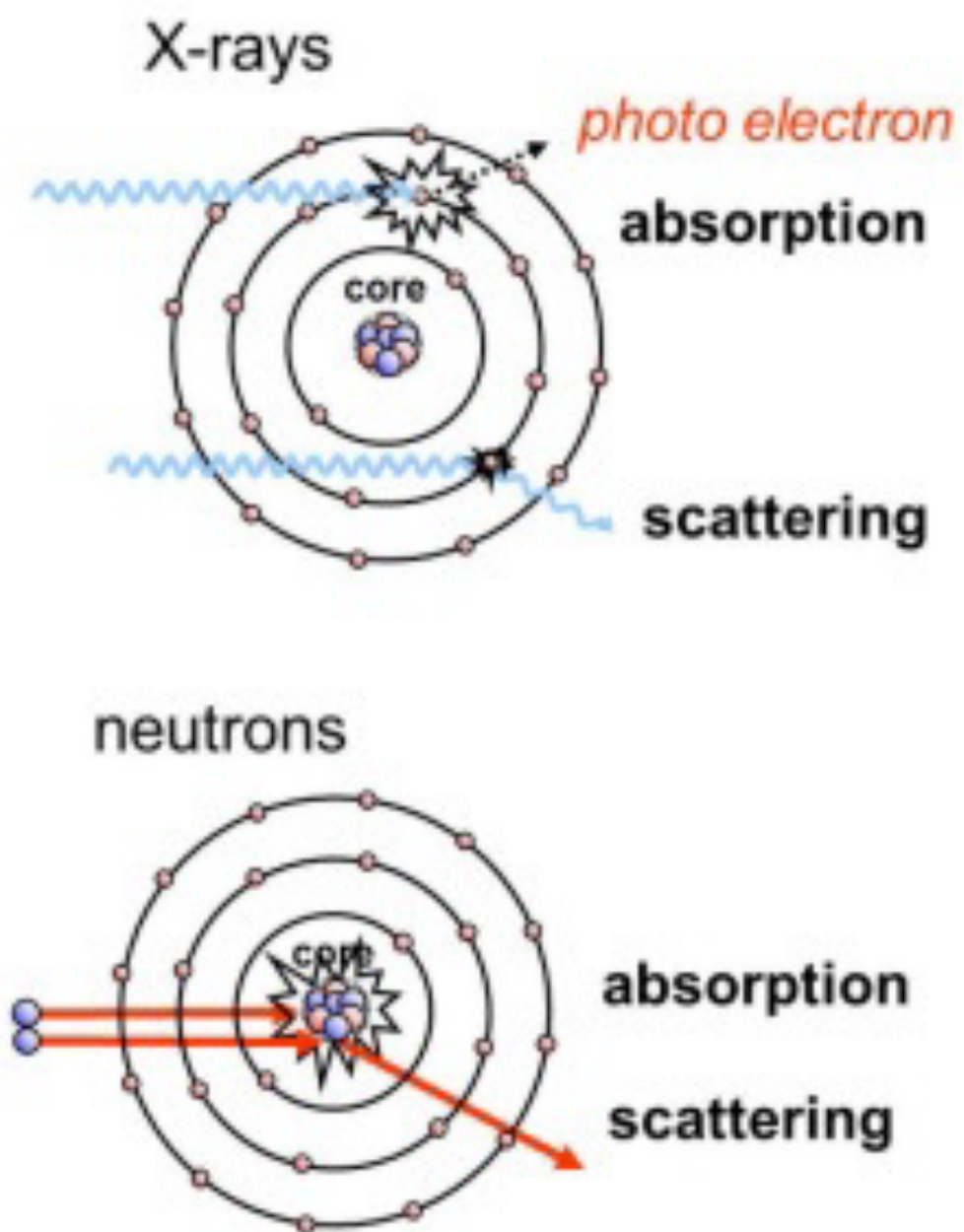
Small Angle Neutron Scattering (SANS)
Small Angle X-Ray Scattering (SAXS)
Small Angle Light Scattering (SALS)



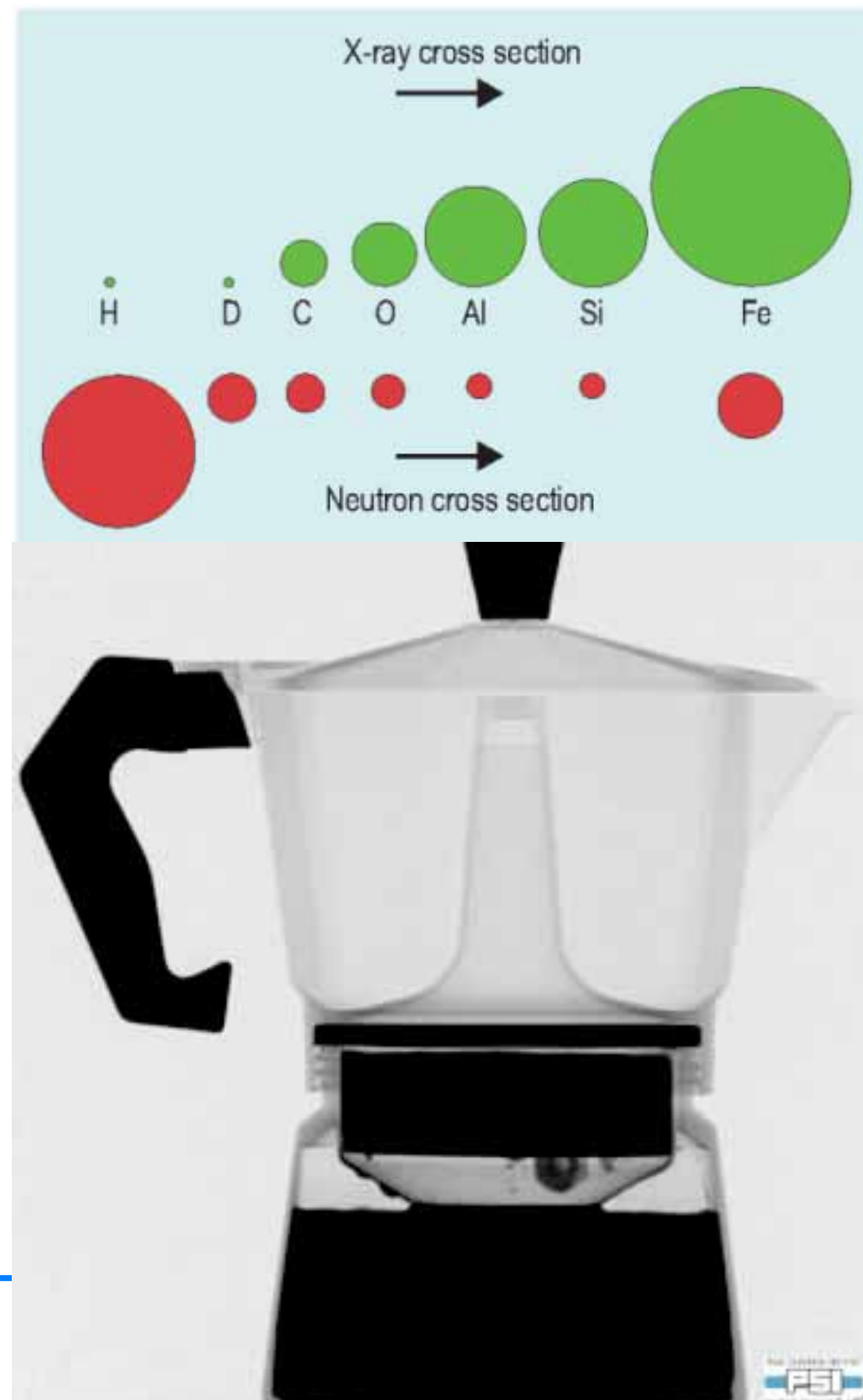
Neutron and X-ray scattering

Interactions with matter:

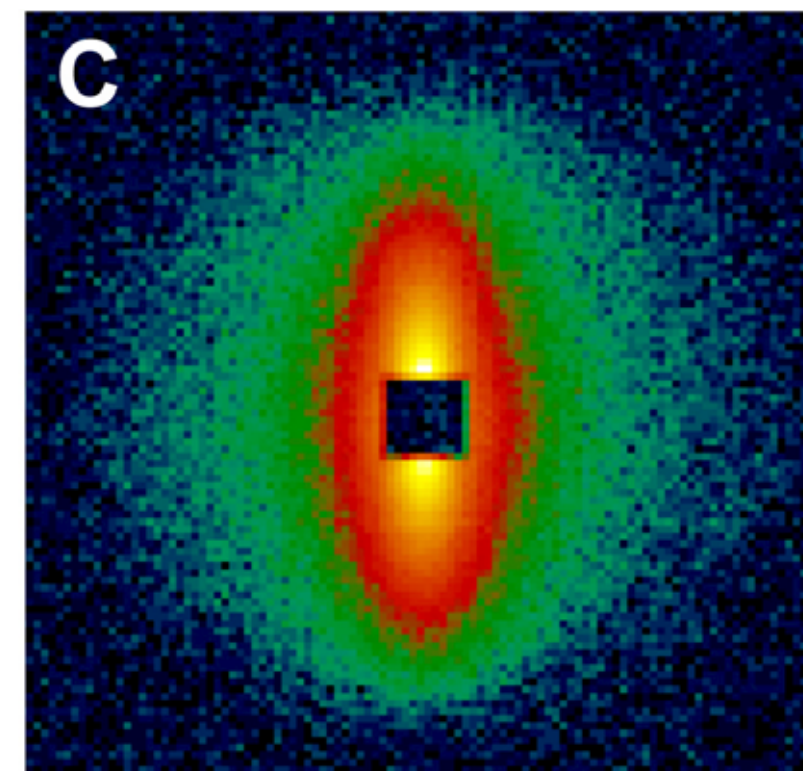
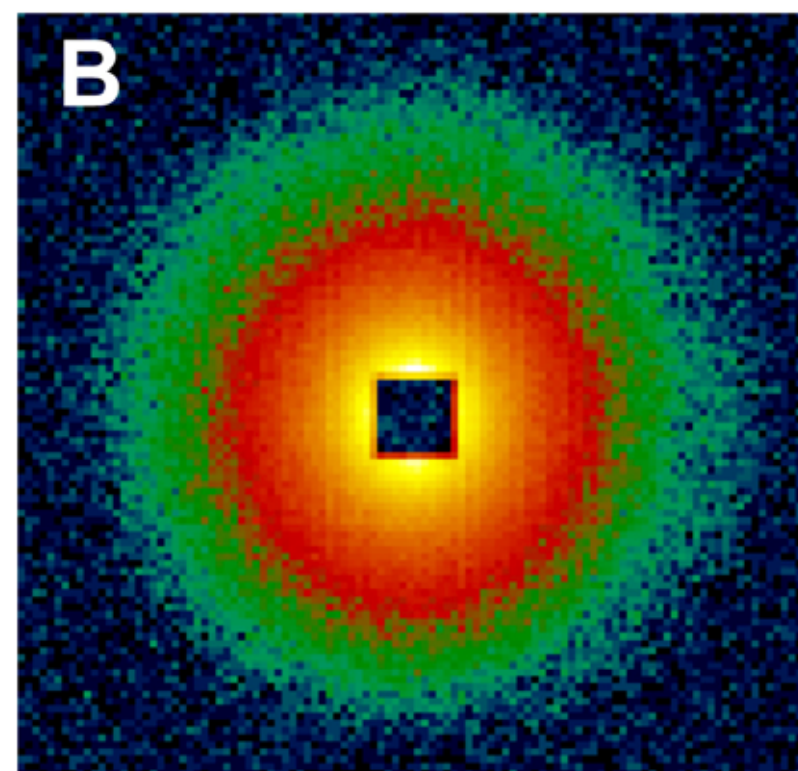
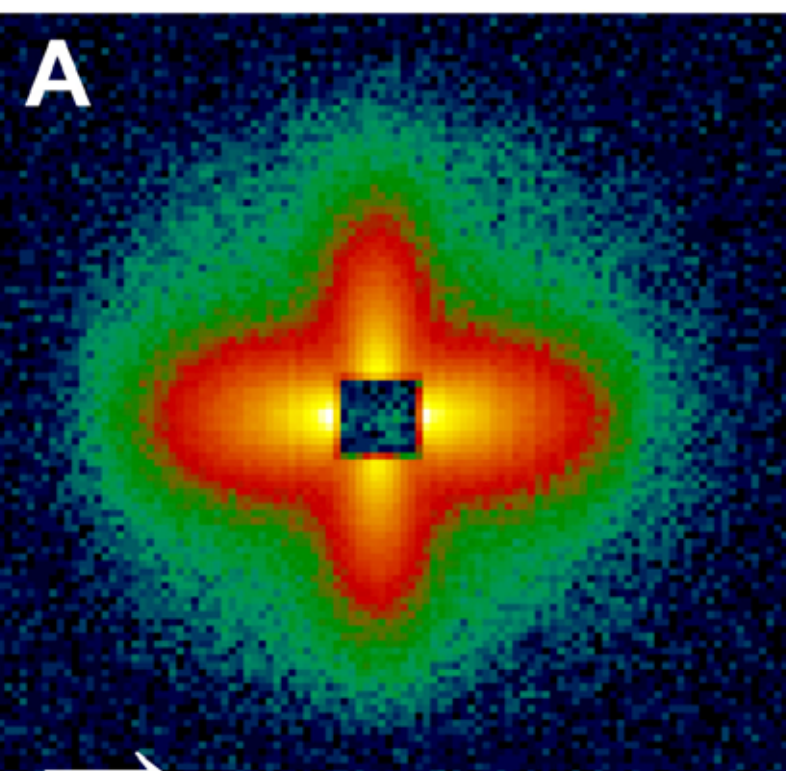
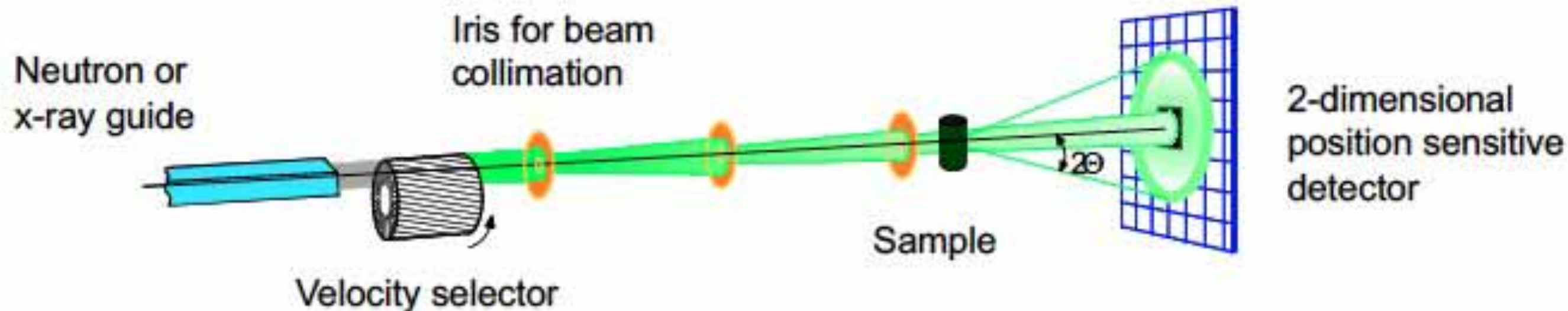
- X-rays: electron density
- Neutrons: nucleus (isotope contrast)



Neutron imaging



Principle setup and the obtained data

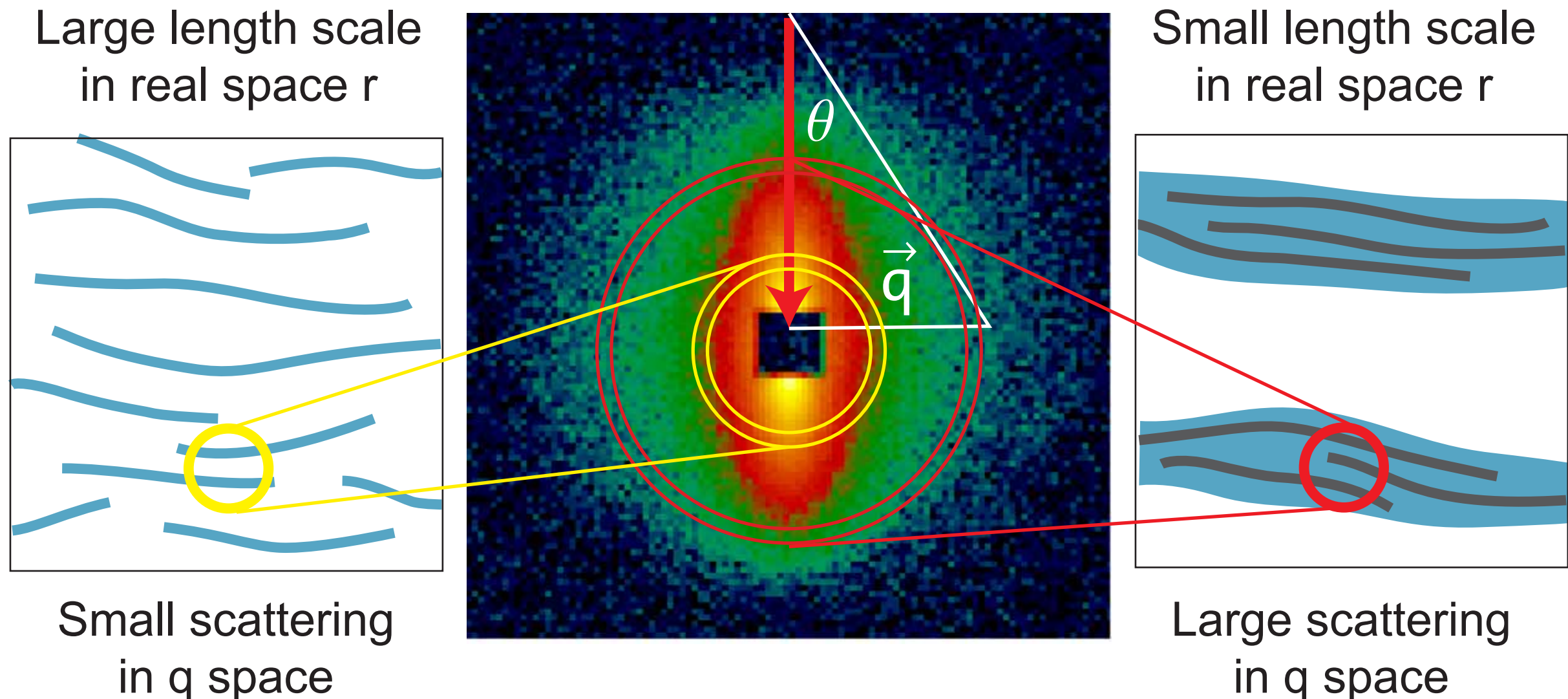


Color code correspond to scattering intensity, i.e. amount of neutrons or photons detected per unit area (yellow- high intensity, blue – low intensity)

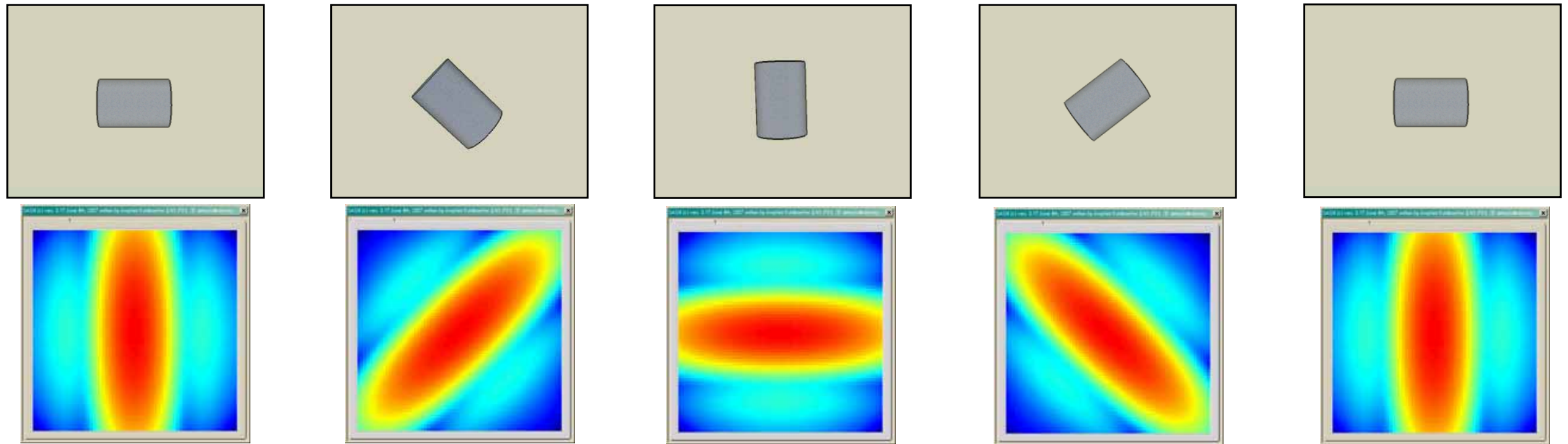
Real $h(r)$ and reciprocal space $I(q)$

Scattering patterns are **2D Fourier transformation** of the **real space** size r [m] in the **inverse space** expressed by the scattering vector q [1/m]. Consequences are:

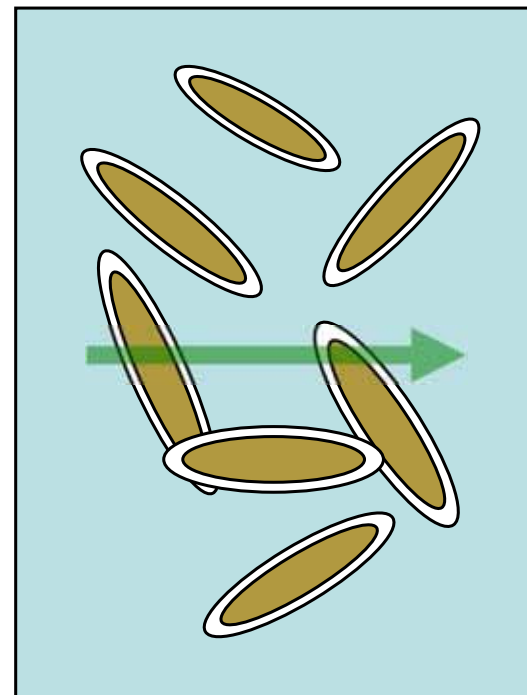
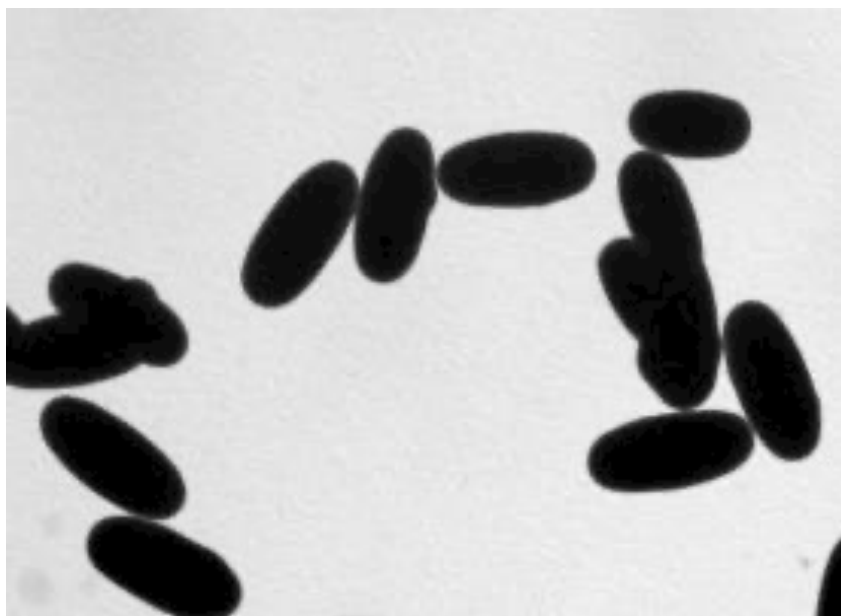
- Large structures lead to small scattering angles (small scattering vectors)
- Small structures lead to large scattering angles (large scattering vectors)
- Object shape is tilted by 90° in the scattered image



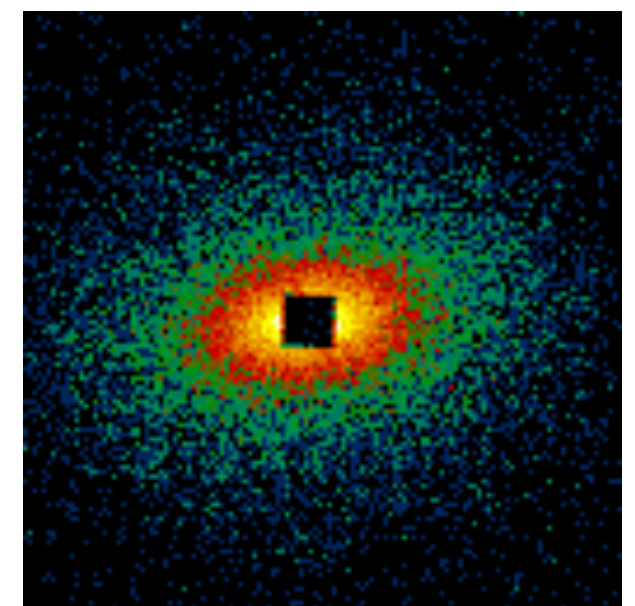
Scattering of anisotropic particles I



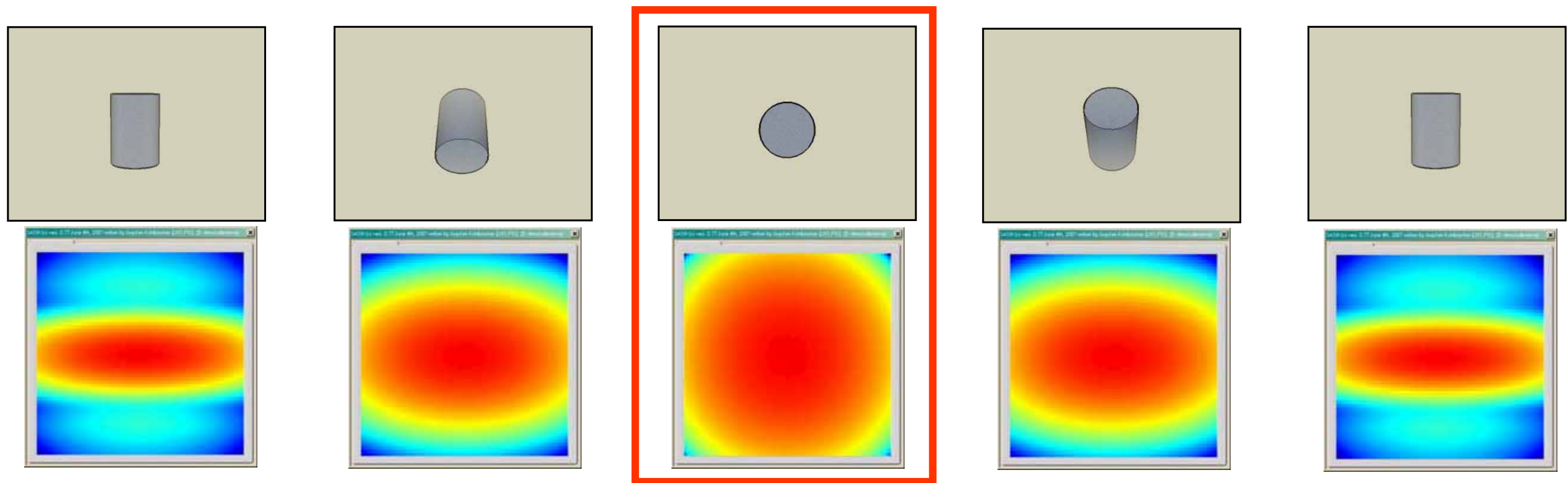
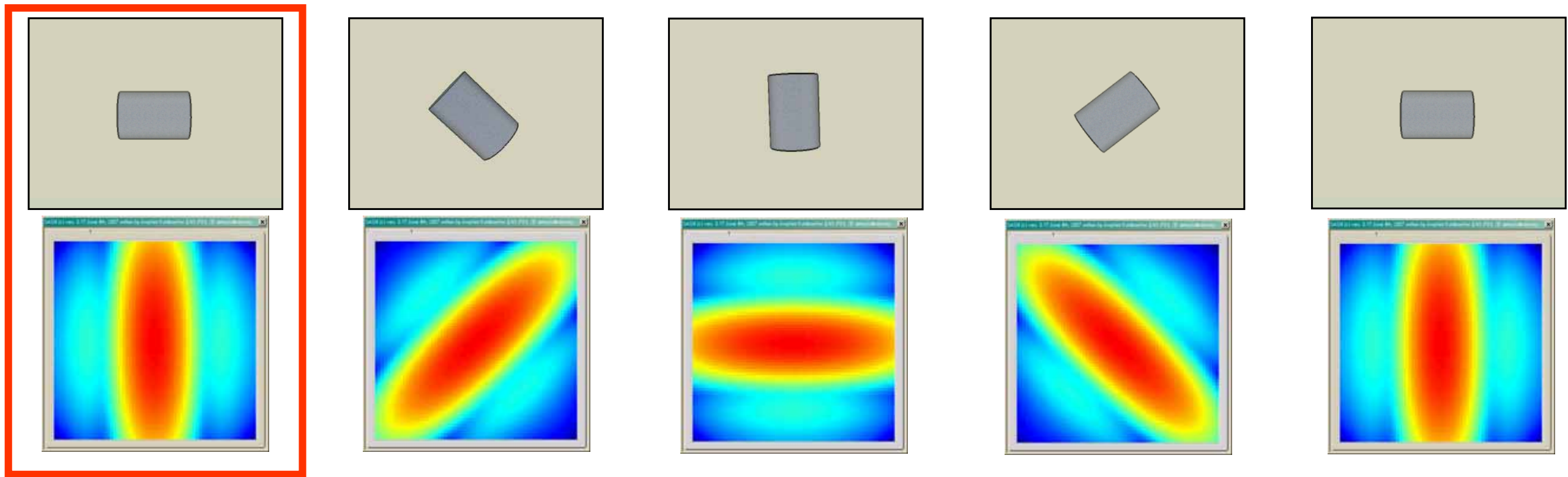
Silica coatings on $\alpha\text{-Fe}_2\text{O}_3$ particles



$f=10\text{Hz}$ $B=5\text{mT}$



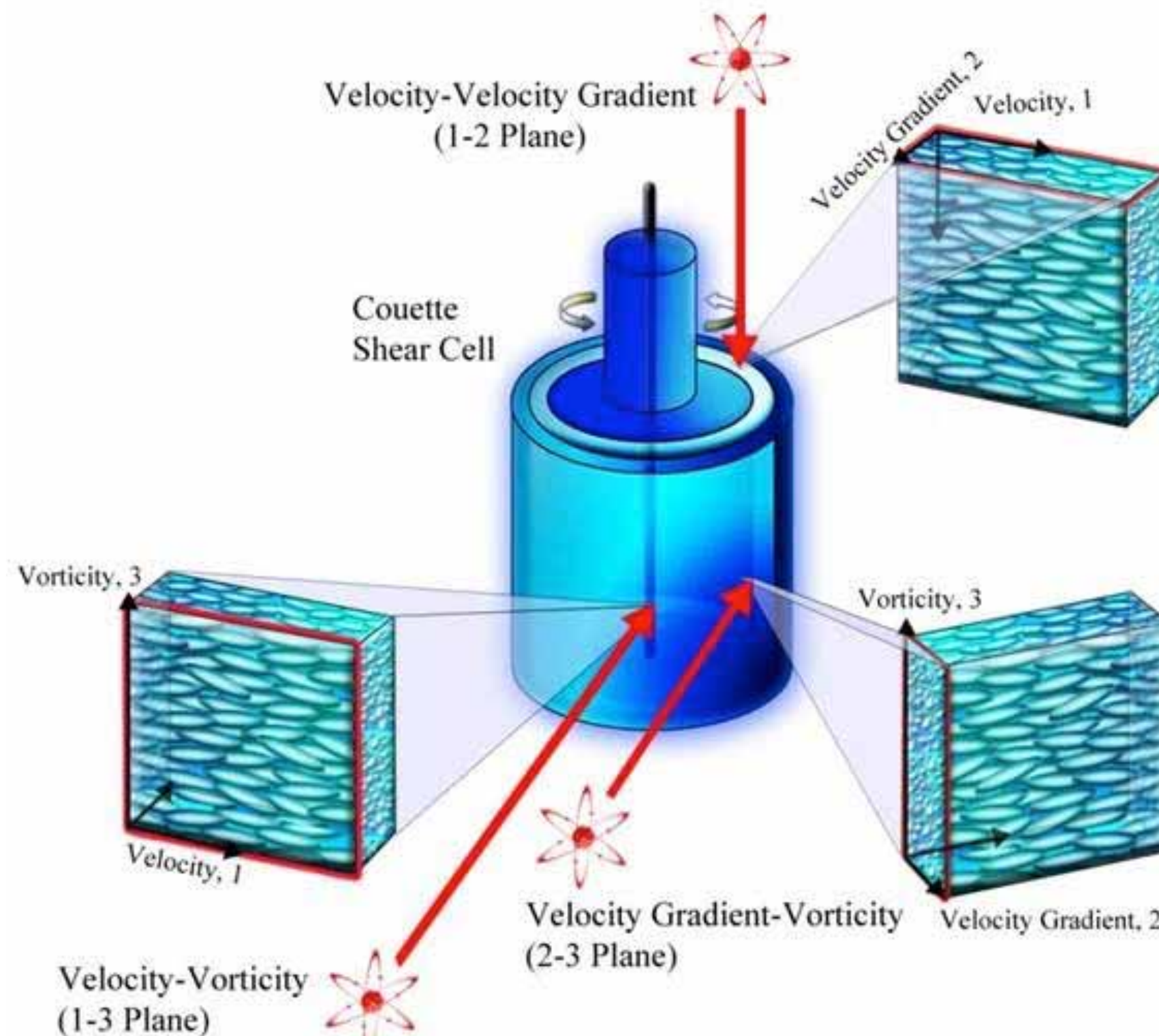
Scattering of anisotropic particles II



<http://www.lookingatnothing.com/index.php/archives/349>

Scattering of anisotropic particles III

Flow induced orientation and how the corresponding scattering pattern look like?



Rheometer and flow cells I

In situ rheometric shearing apparatus at the NIST Center for Neutron Research¹

G.C. Straty^a, C.D. Muzny^{a,*}, B.D. Butler^a, M.Y. Lin^b, T.M. Slaweki^b,
C.J. Glinka^b, H.J.M. Hanley^a

^aPhysical and Chemical Properties Division, National Institute of Standards and Technology Boulder, CO, 80303 USA

^bNIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA

Received 12 August 1997; received in revised form 4 November 1997

Apparatus for the investigation of liquid systems in a shear gradient by small angle neutron scattering (SANS)

P. Lindner (*) and R. C. Oberthür

Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France

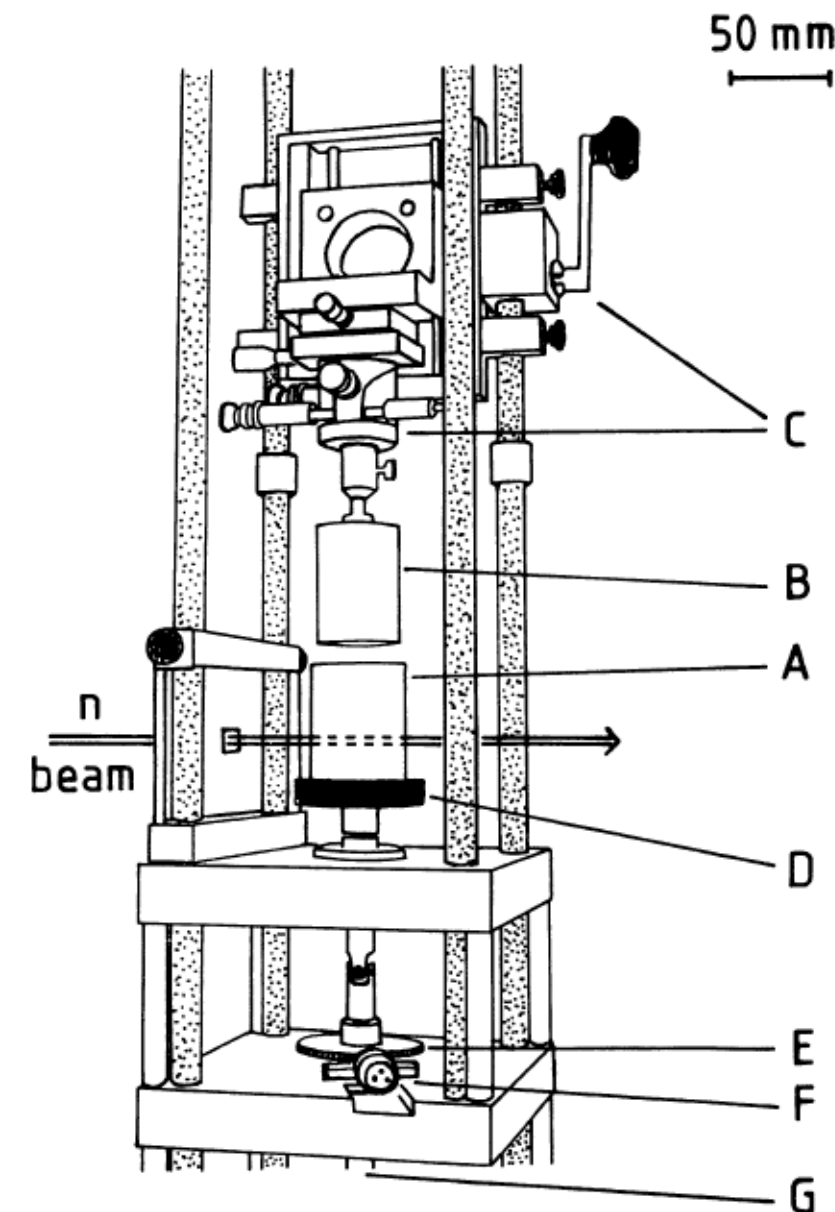


Fig. 2. — Schematic view of the central part of the apparatus. A : quartz-glass rotor, B : stator, C : support for adjustment, D : fixation with screw crap on turn-table, E : rotating cog, F : magnetic detector, G : connection to motor drive (not shown).

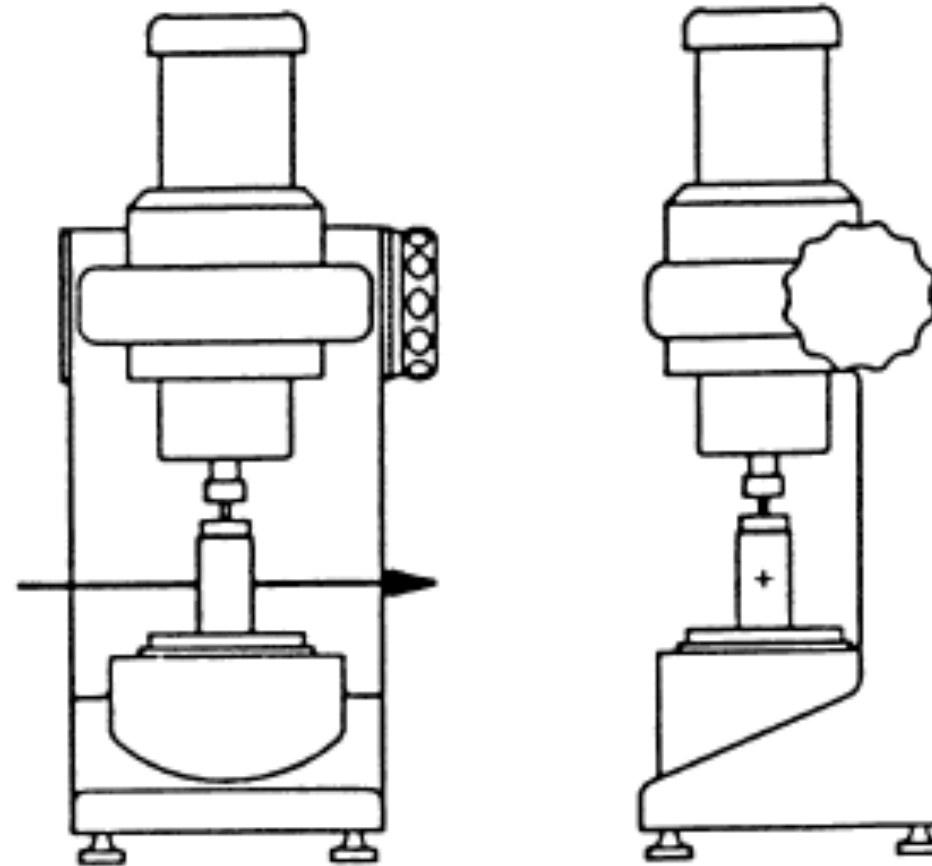


Fig. 1. Rheometer showing position of cell and beam direction.

Small-angle neutron scattering of sheared concentrated dispersions: Microstructure along principal flow axes

C. G. de Kruif, J. C. van der Werff, and S. J. Johnson
Van't Hoff Laboratory, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands
R. P. May
Institut Laue-Langevin, Grenoble, France

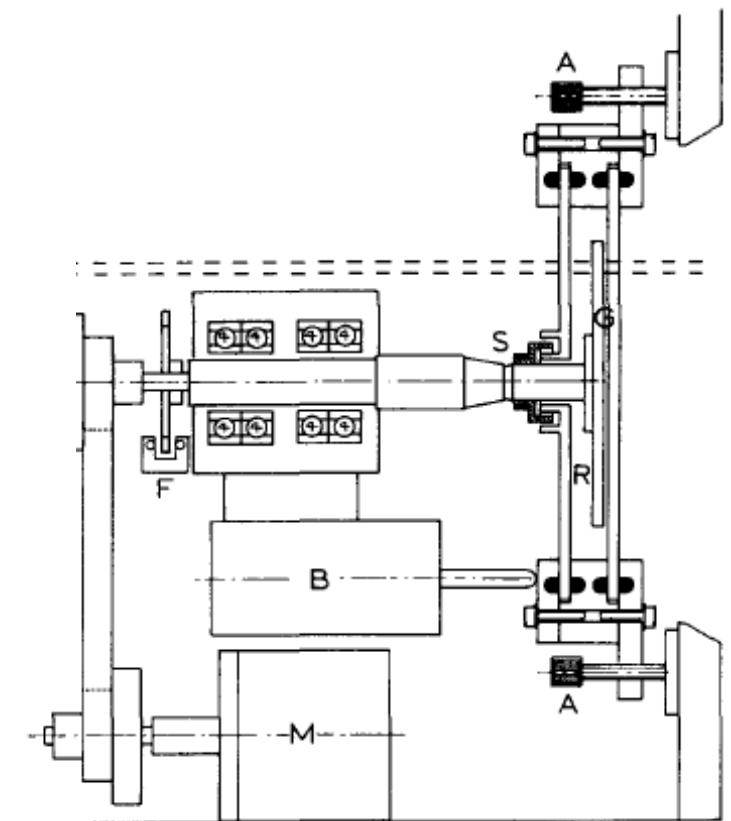
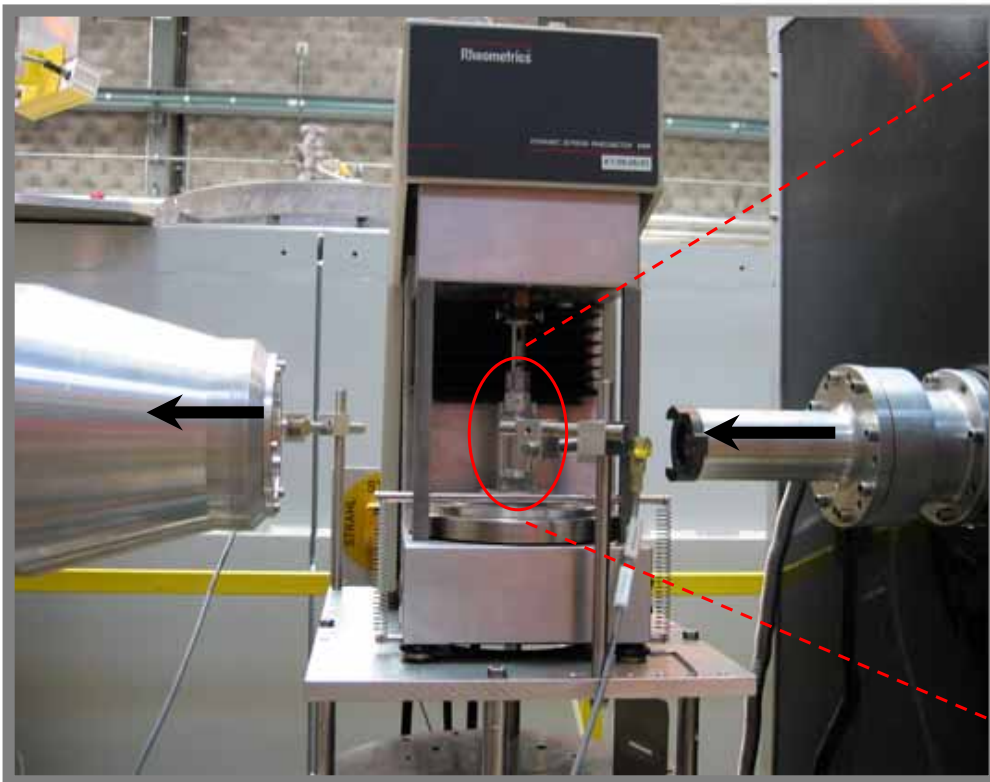
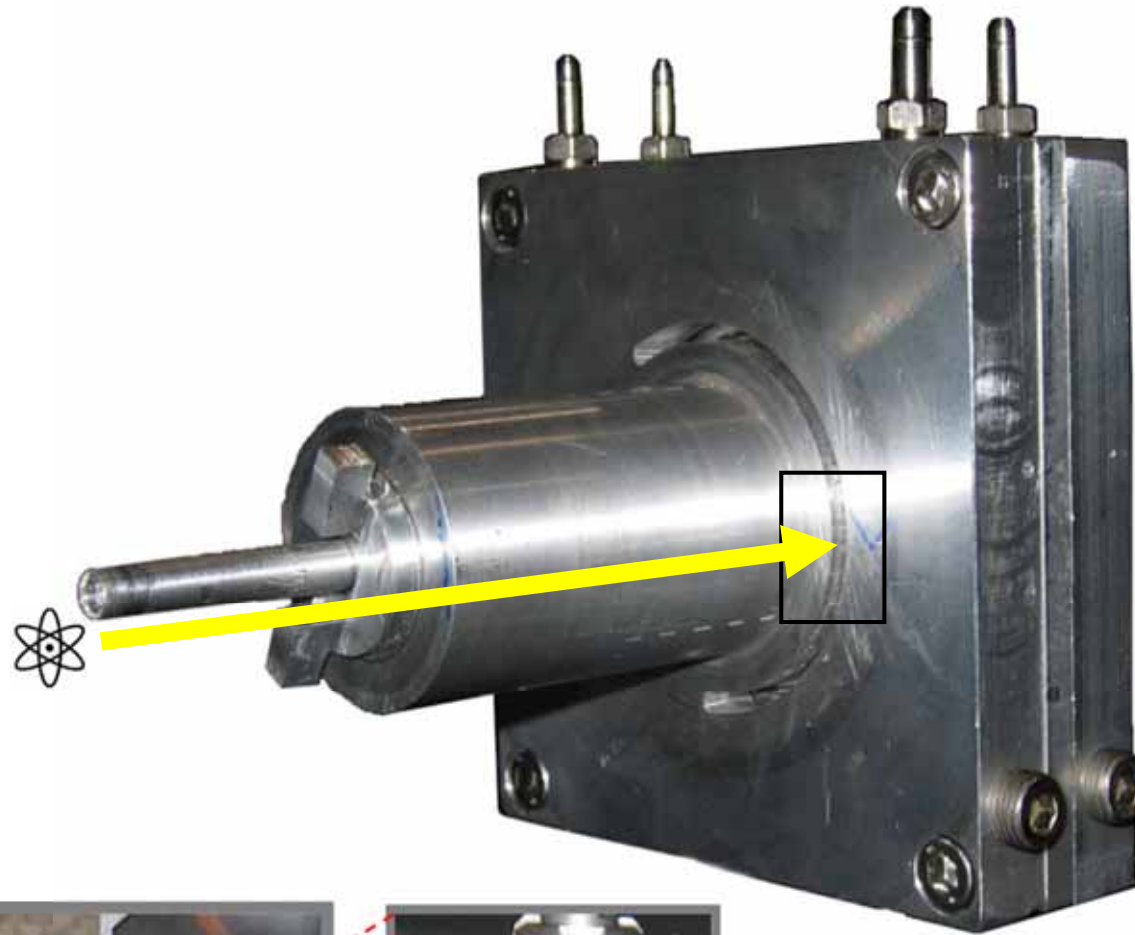


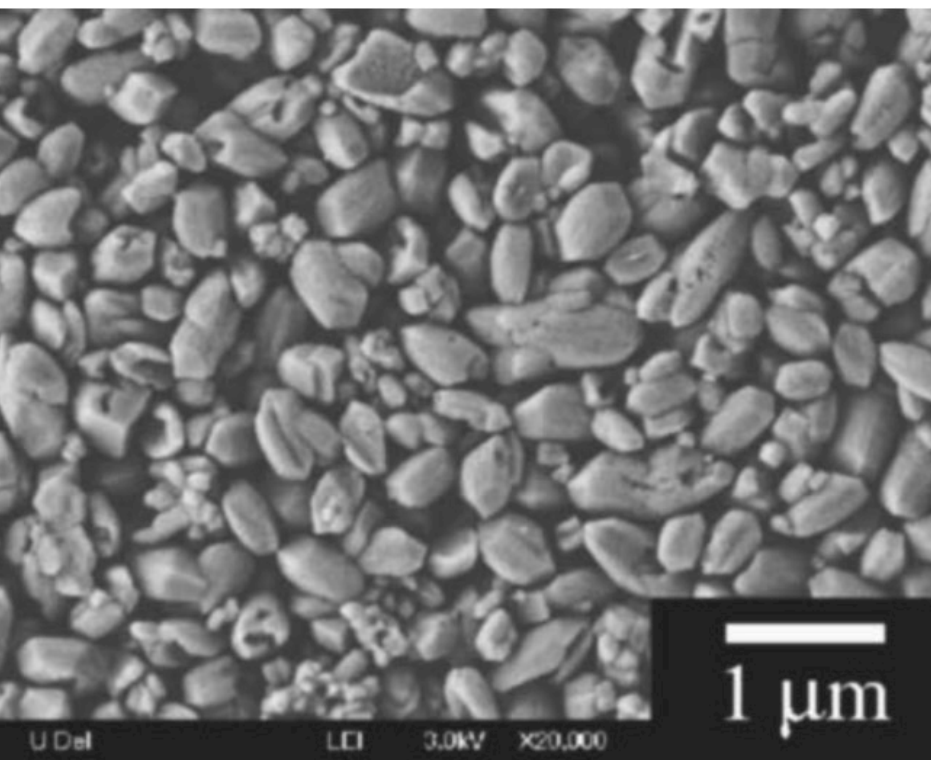
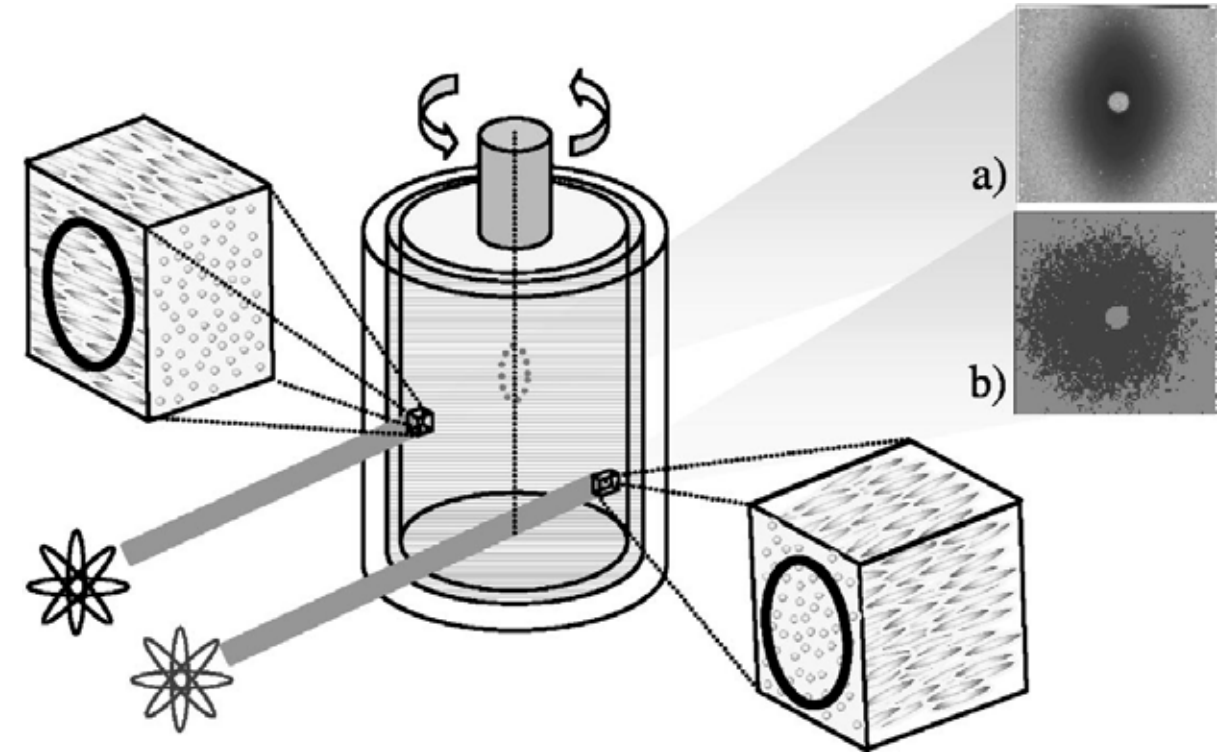
FIG. 1. Schematic diagram of the vertically mounted, parallel-plate flow cell: A, micrometer adjustment screws; B, micrometer distance sensor; C, position of incident neutron beam; F, encoder disk for angular velocity measurement; G, gap containing the sample; M, dc motor; R, rotating quartz disc; and S, drive shaft.

Rheometer and flow cells II

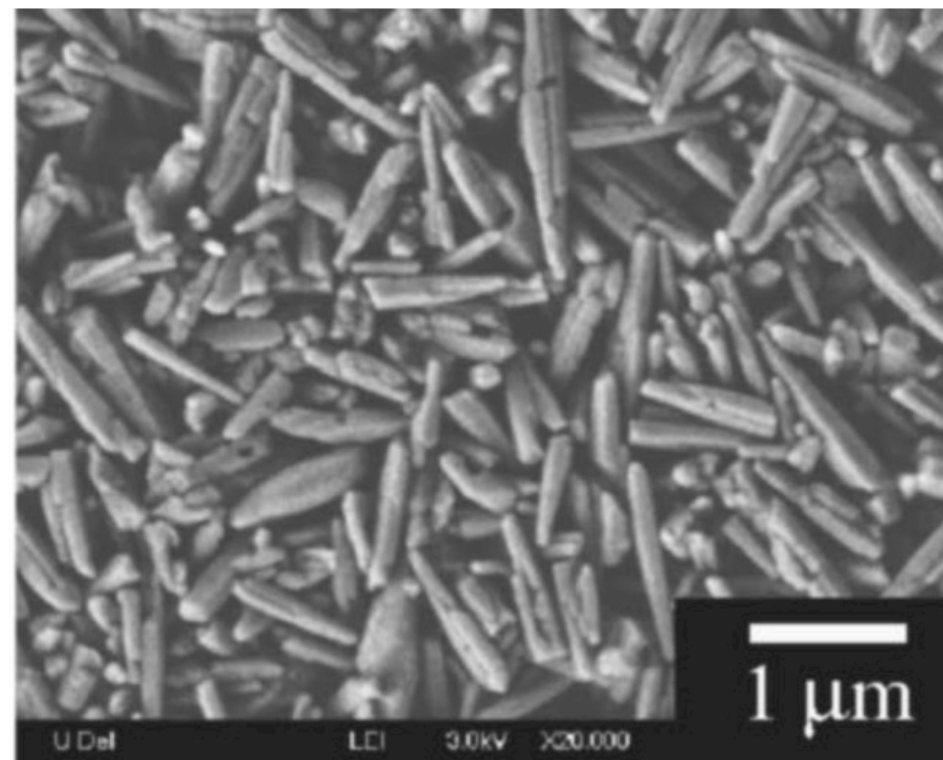


Example: Shear induced structure in suspensions I

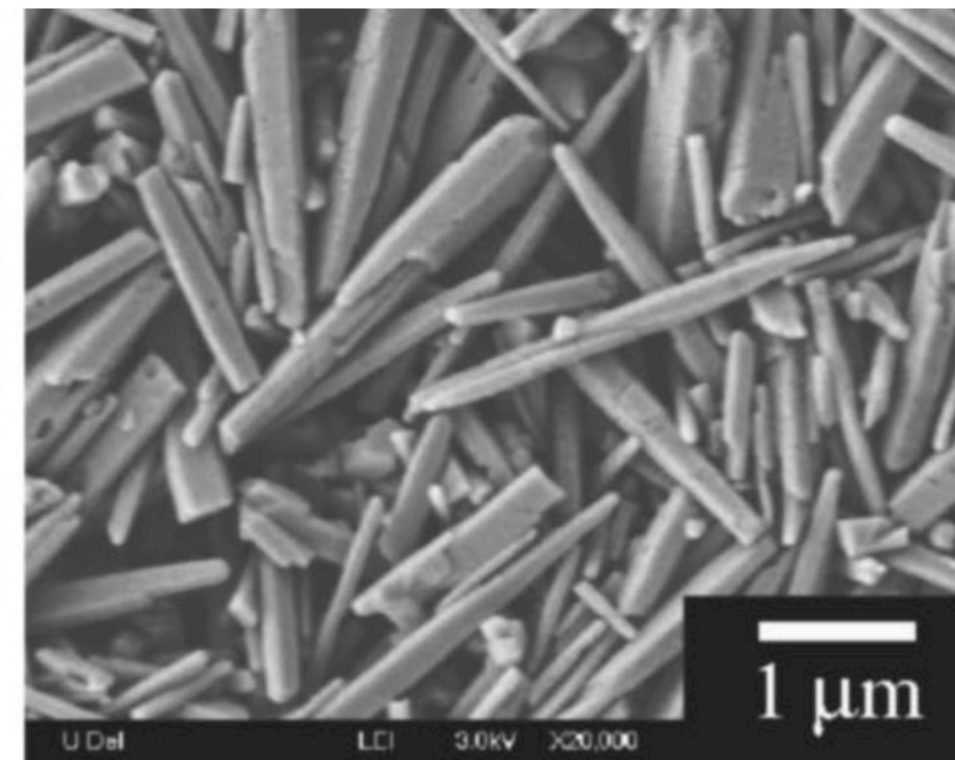
Precipitated calcium carbonate (PCC) particles of varying particle aspect ratio (nominal L/D: 2, 4, 7) suspended in polyethylene glycol (PEG)



L/D: 2



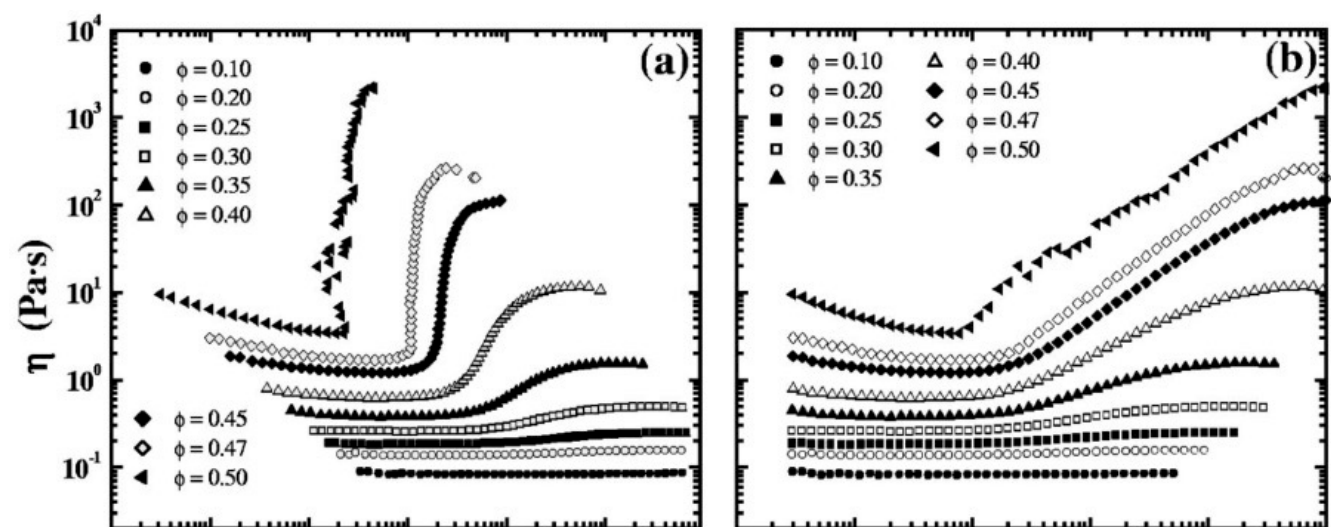
L/D: 4



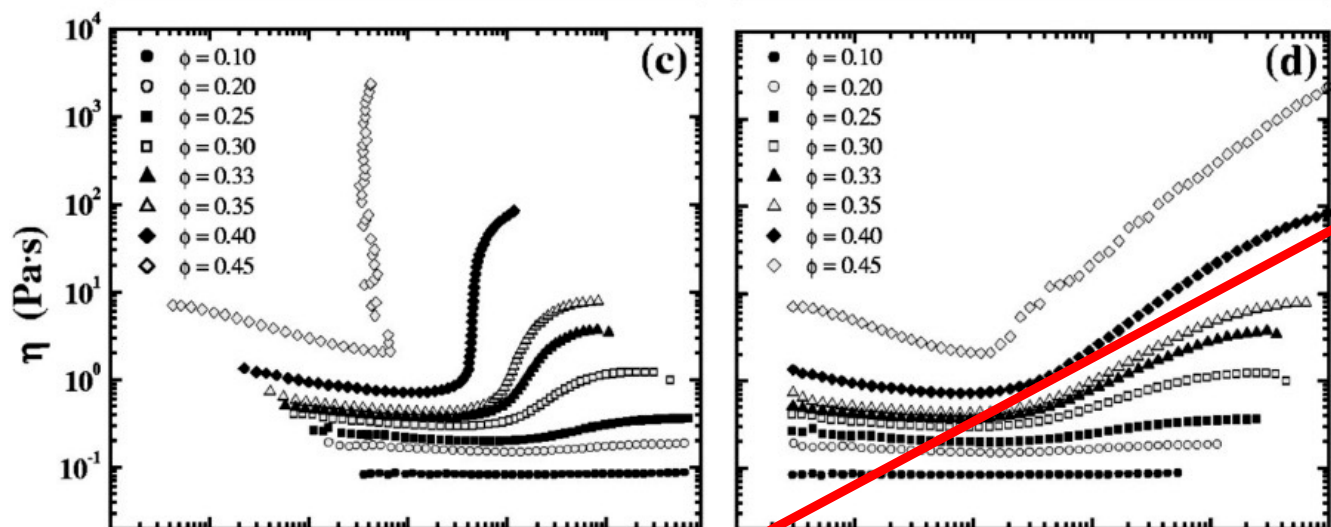
L/D: 7

Example: Shear induced structure in suspensions II

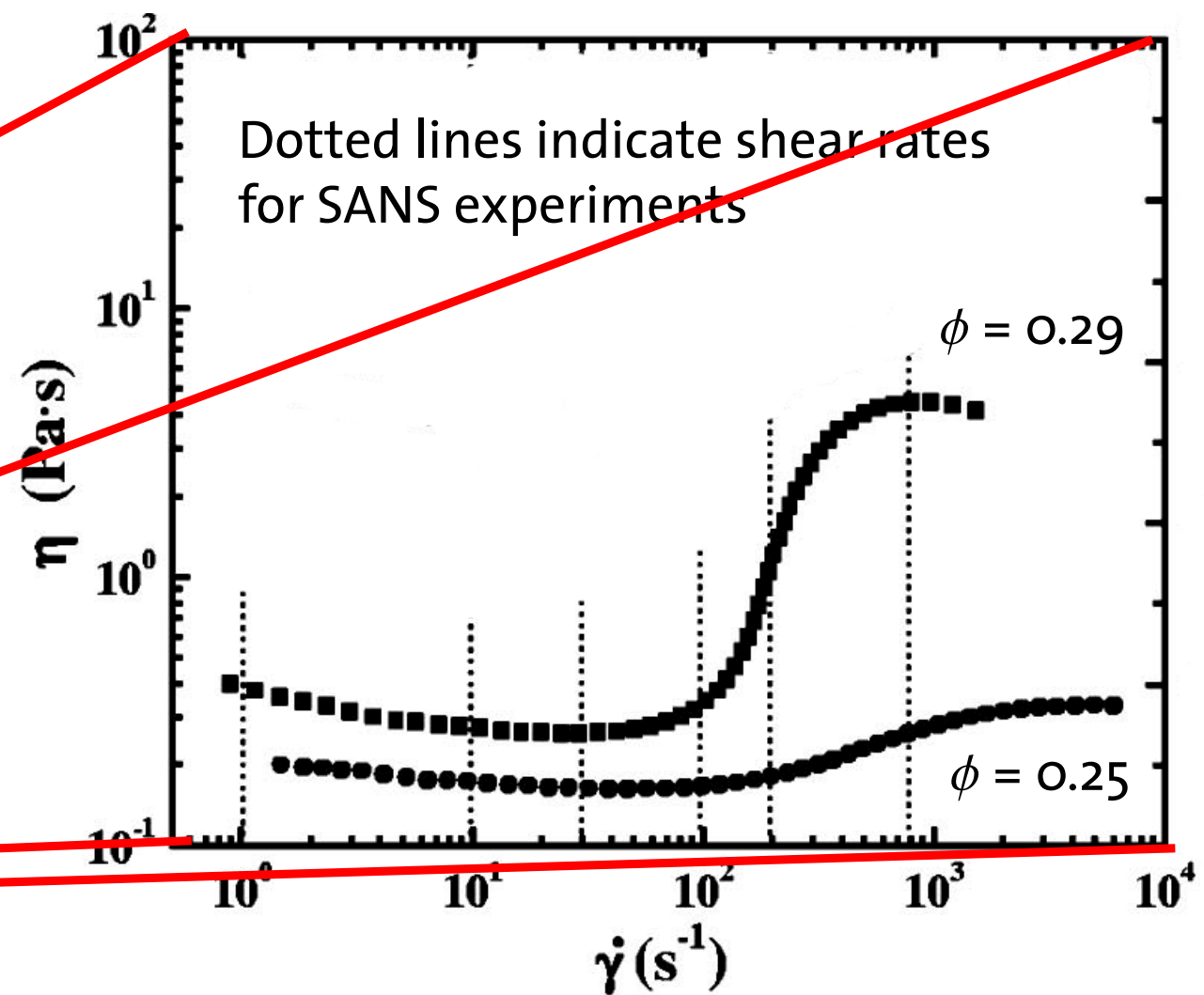
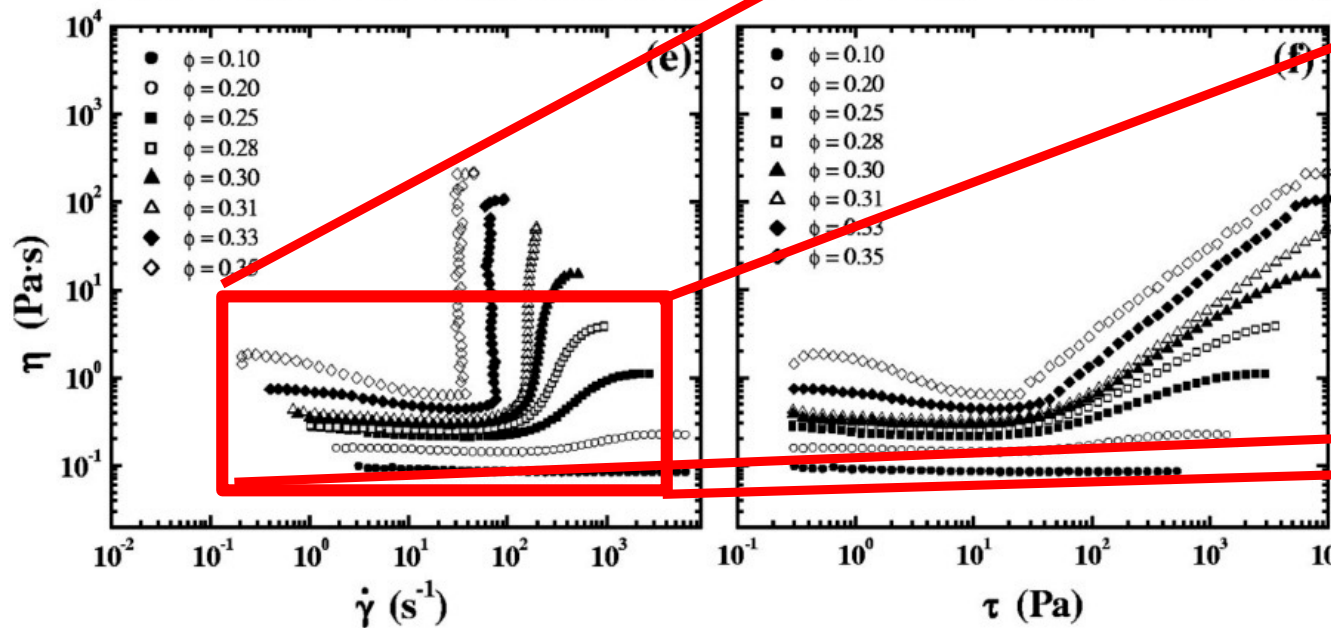
L/D: 2



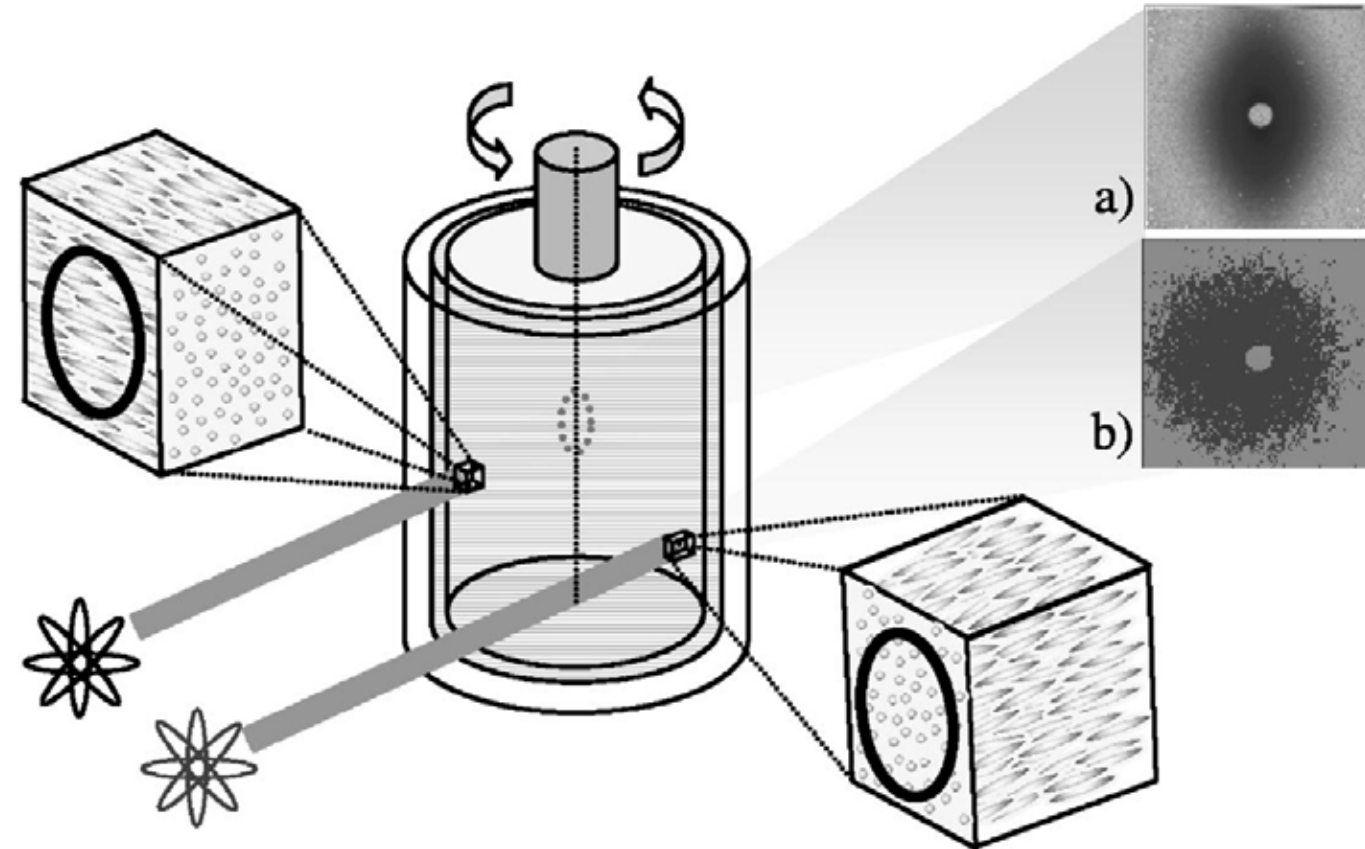
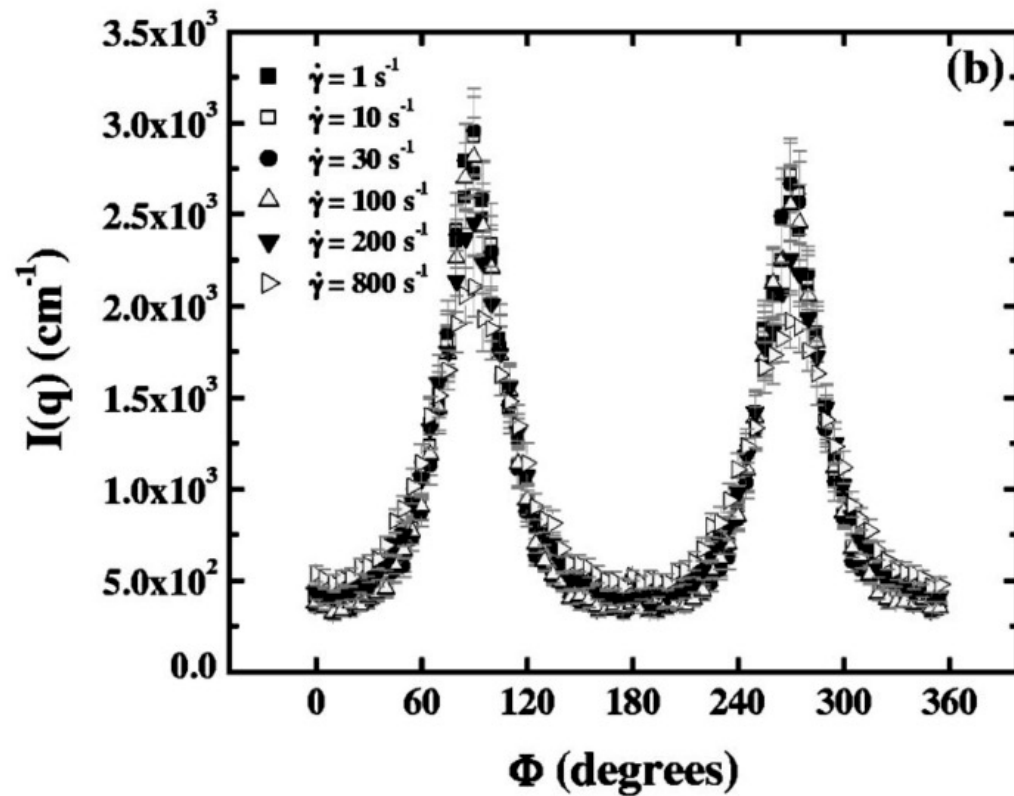
L/D: 4



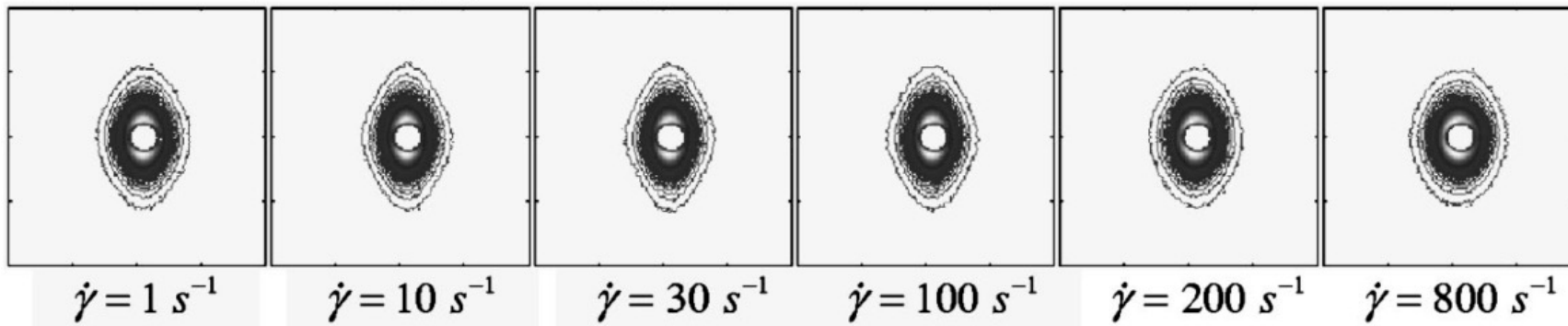
L/D: 7



Example: Shear induced structure in suspensions III



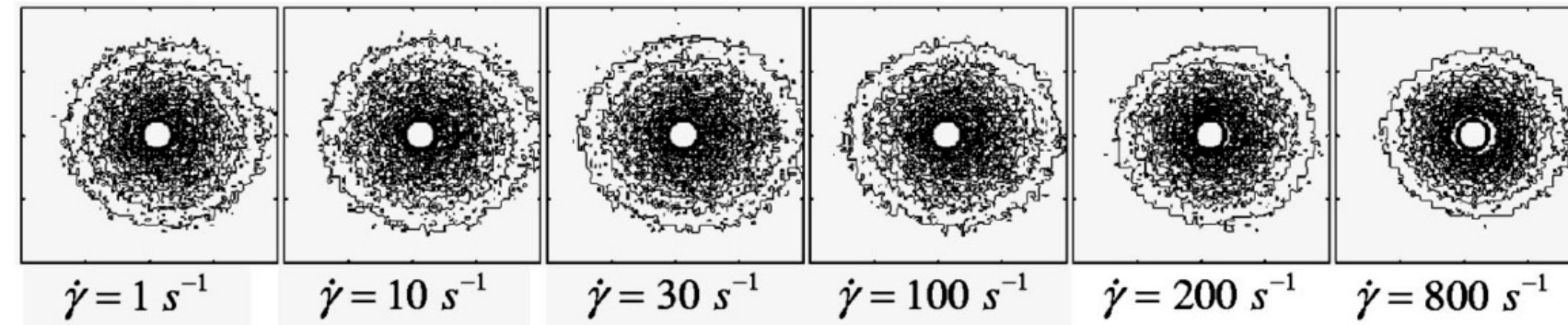
(c) Radial (x-velocity, y-vorticity)



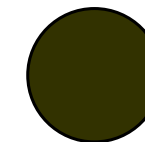
Orientation of rods (radial view)



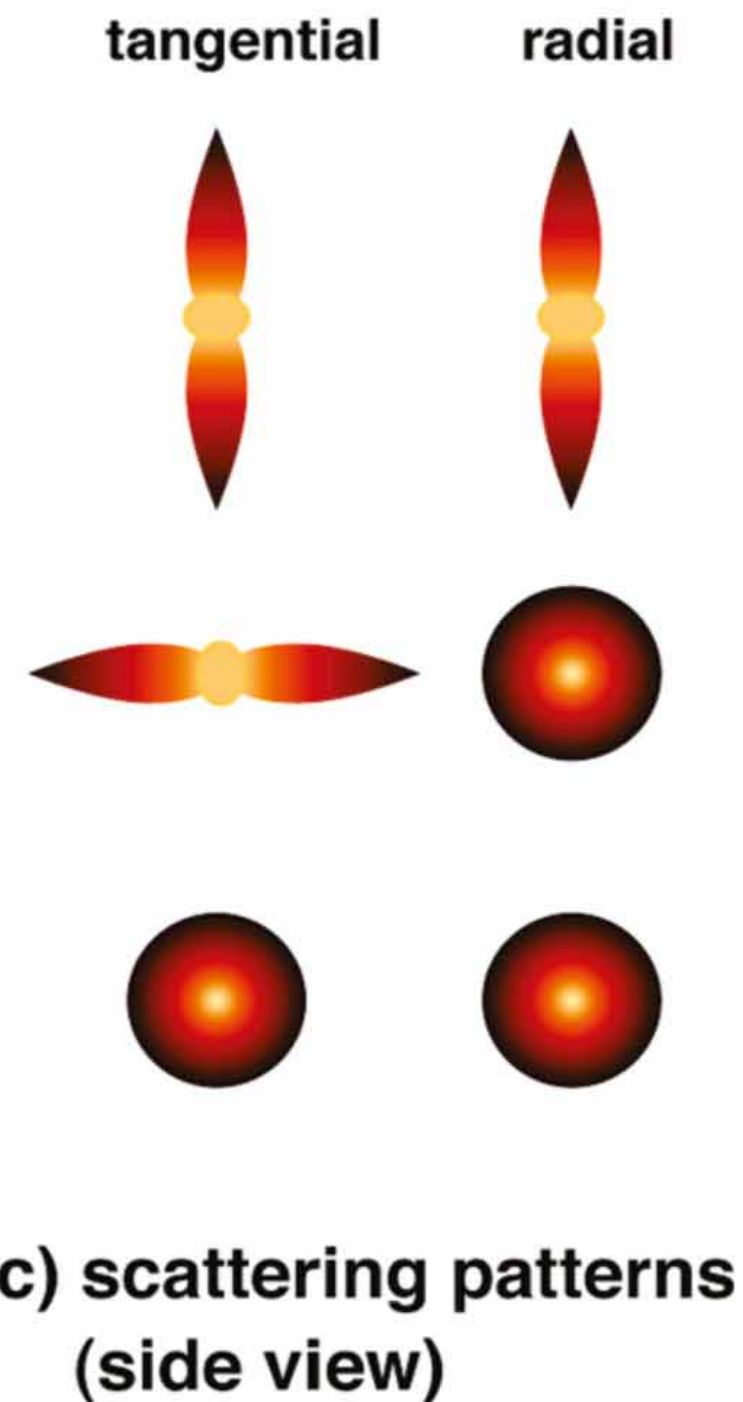
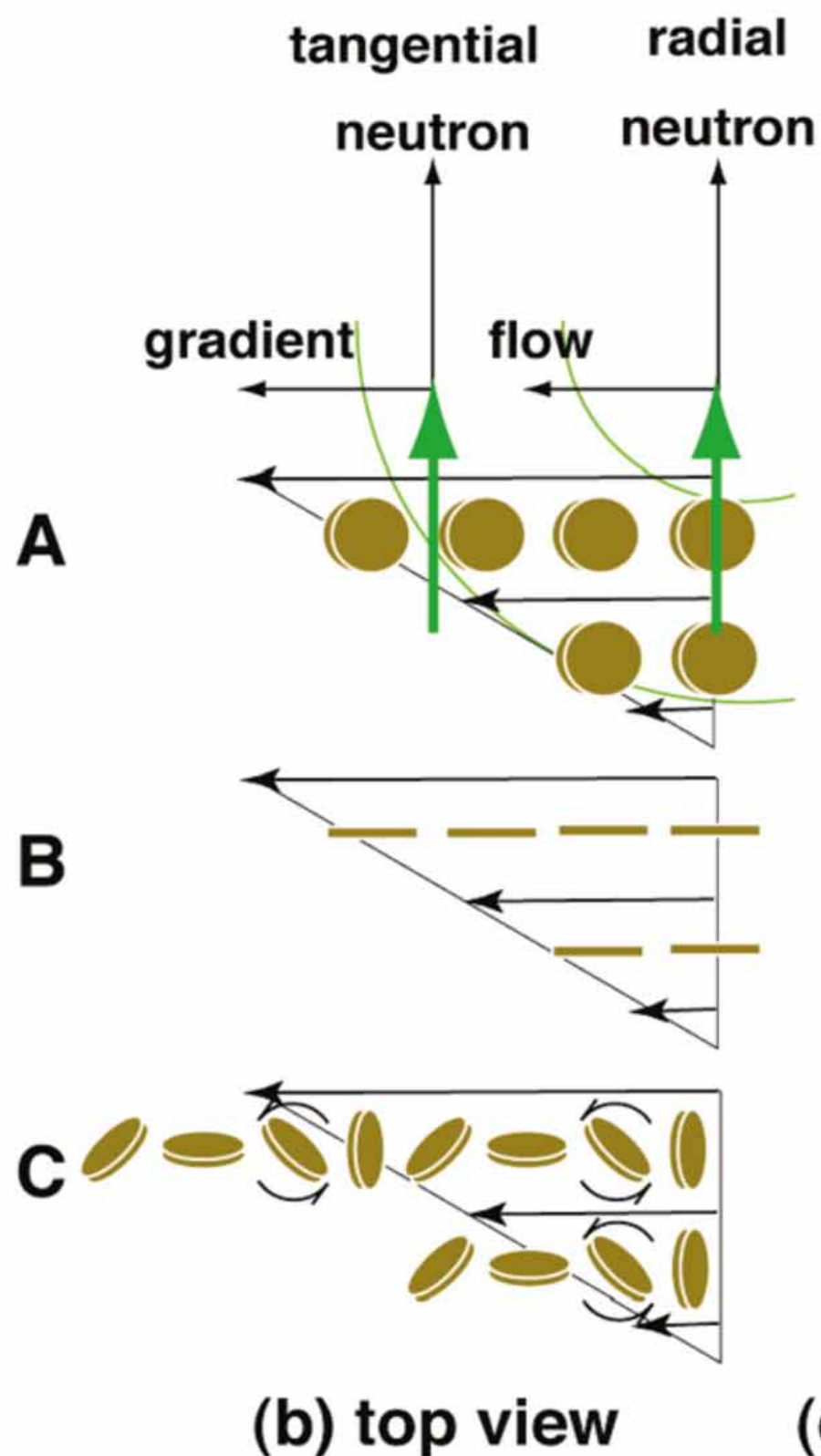
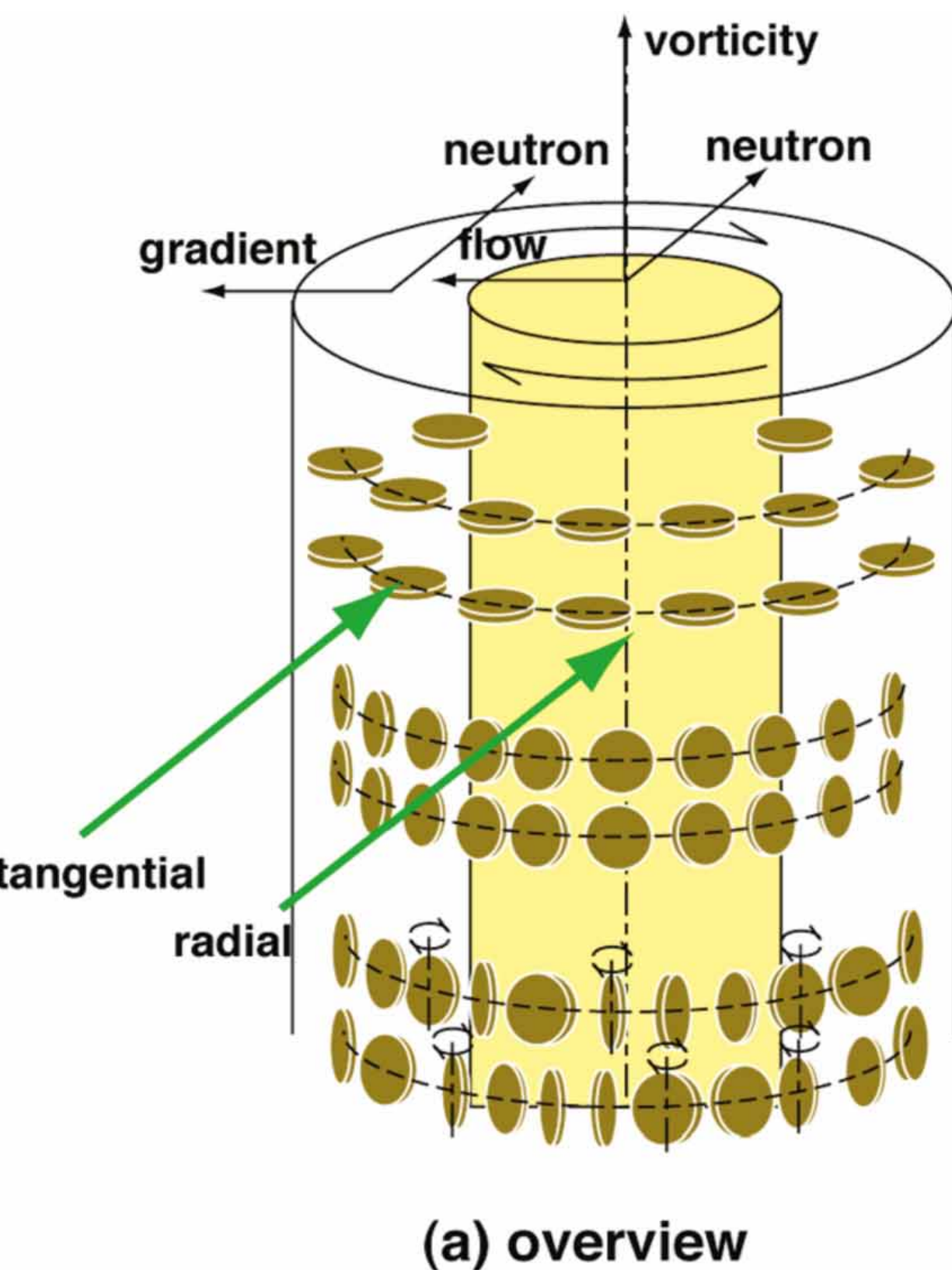
(d) Tangential (x-velocity gradient, y-vorticity)



Orientation of rods (tangential view)



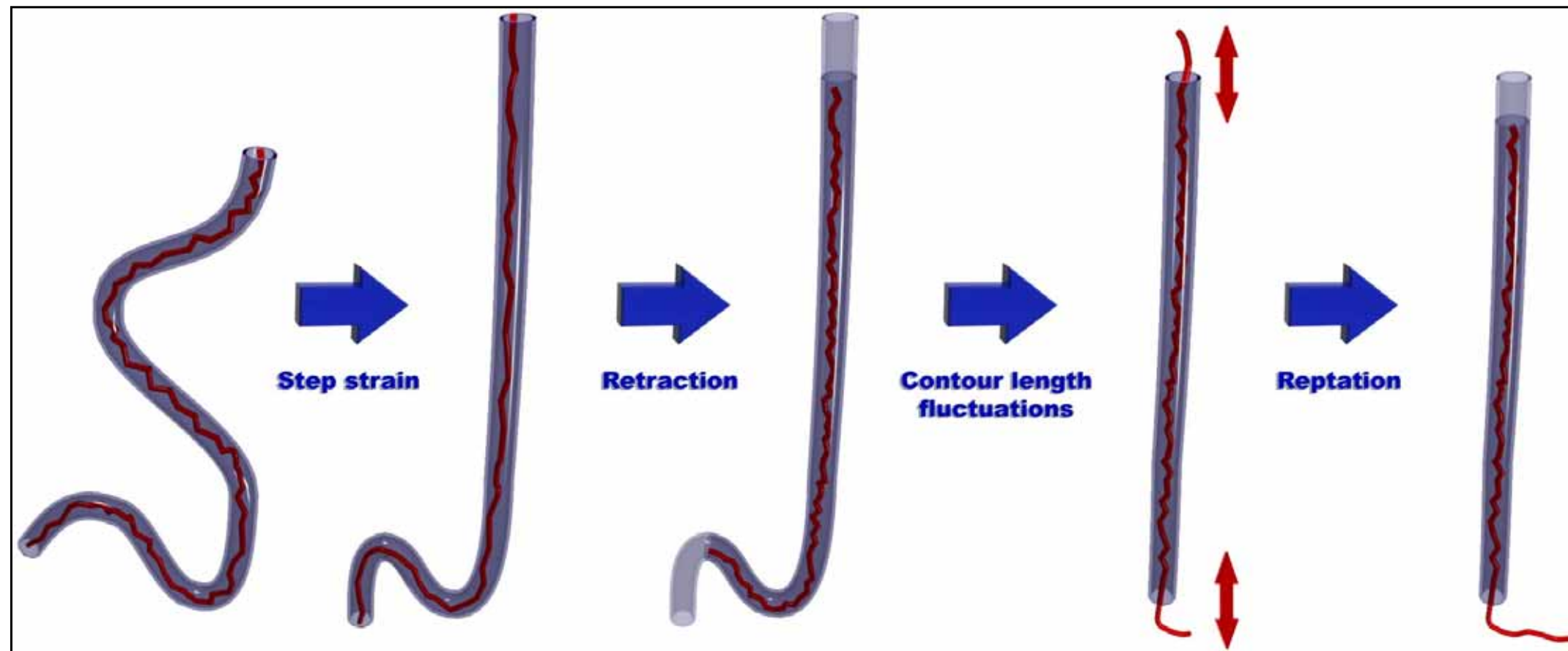
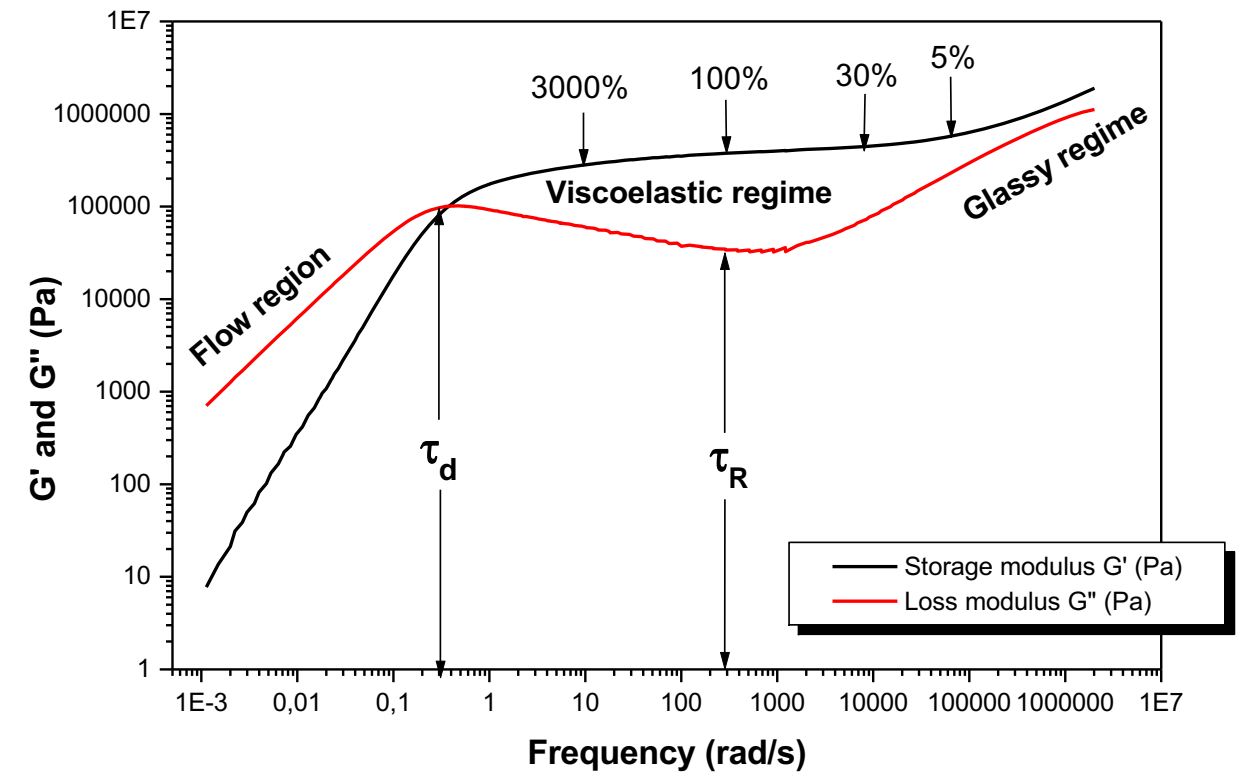
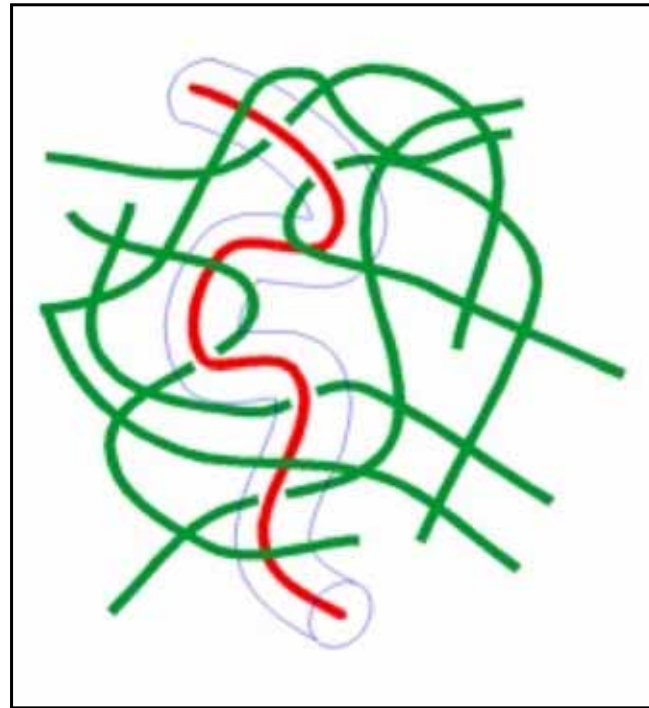
Summary: Probing different shear planes



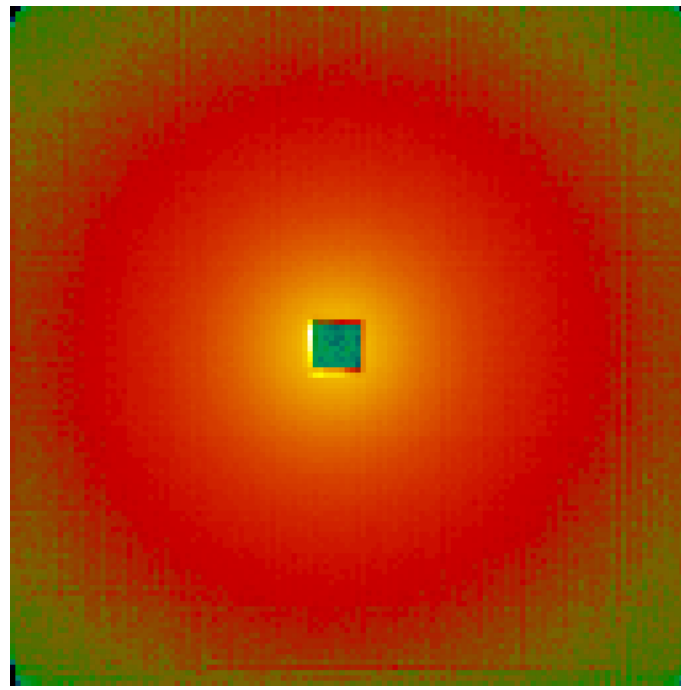
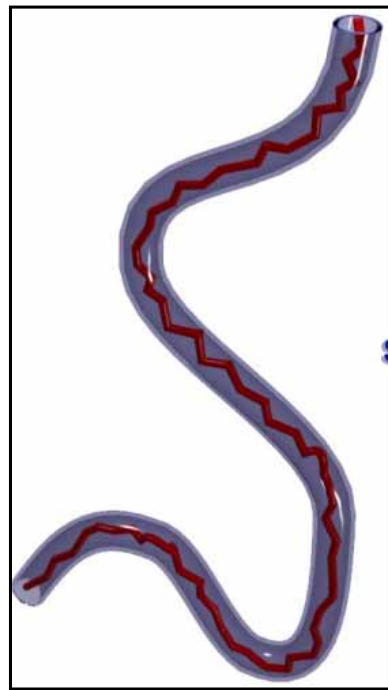
Example: Polymer relaxation (Anisotropic form factor) I

Linear polyisoprene melt:

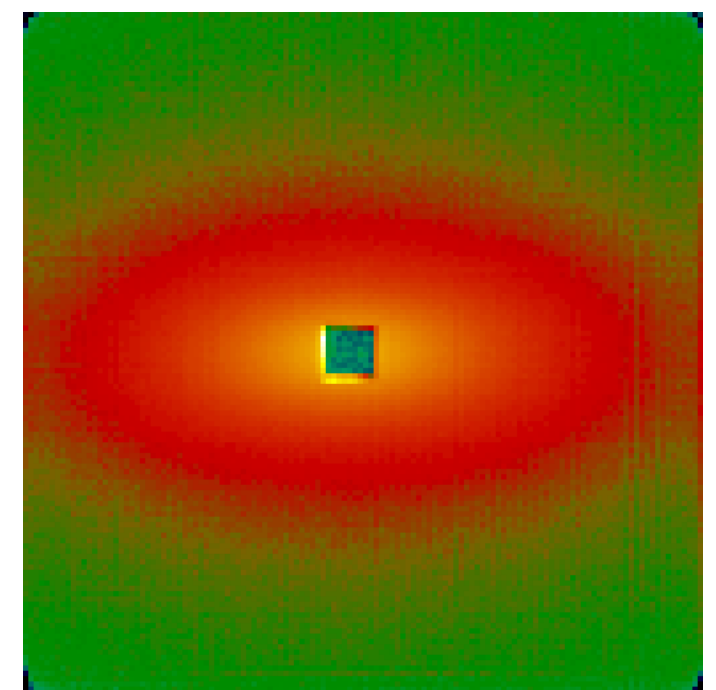
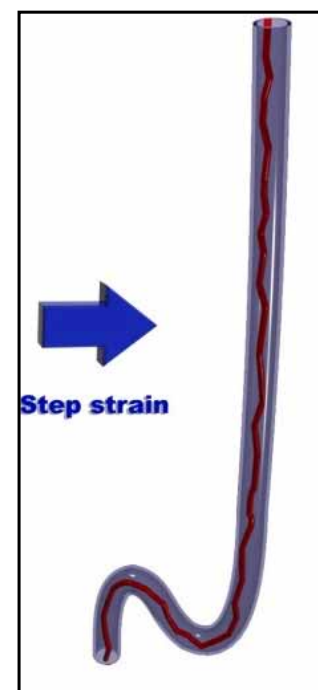
- $R_g \sim 175 \text{ \AA}$
- $t_d = 21 \text{ s}$
- $t_R = 0.02 \text{ s}$
- $G_0 = 410000 \text{ Pa}$



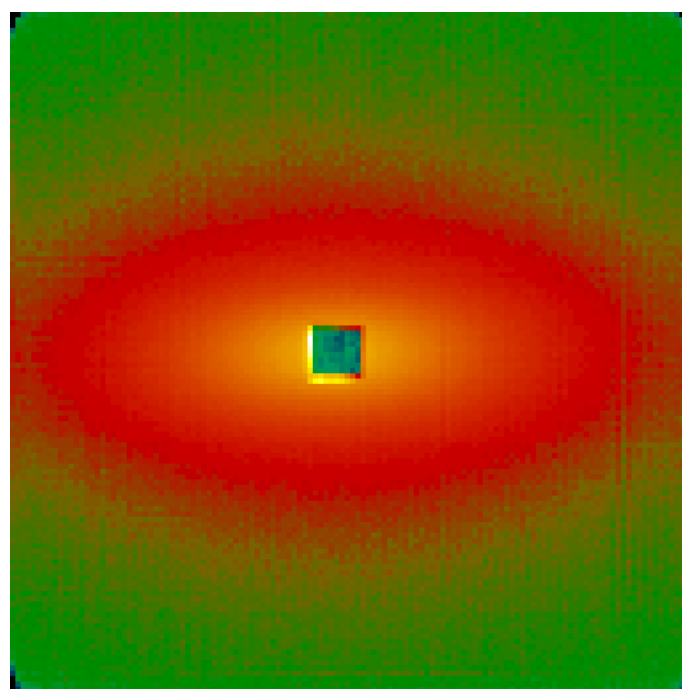
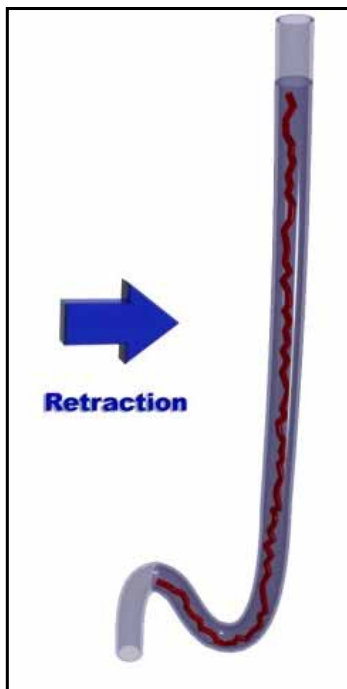
Example: Polymer relaxation (Anisotropic form factor) II



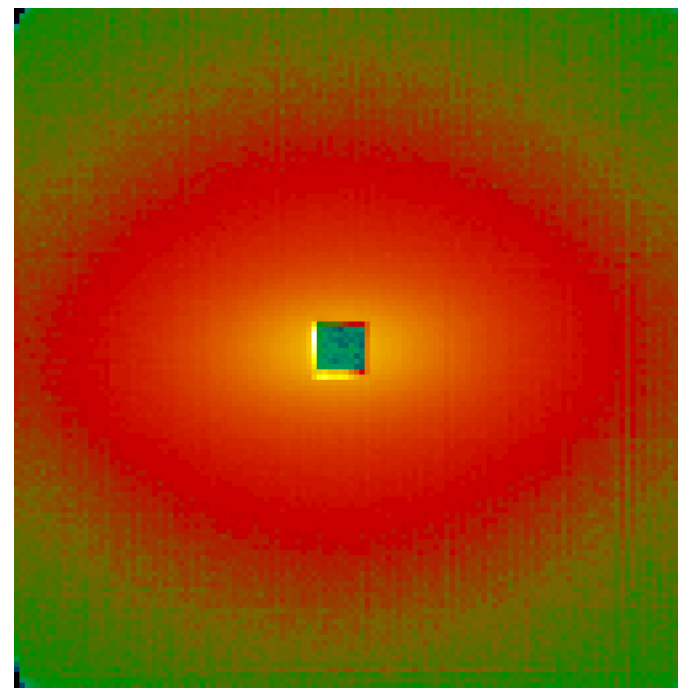
Isotrope



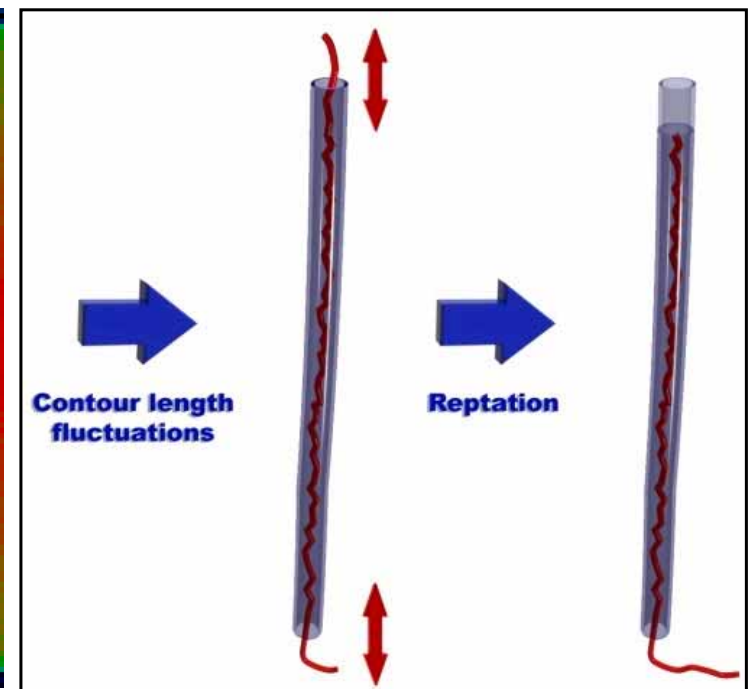
$\sim 0\%$ of τ_R



$\sim 100\%$ of τ_R



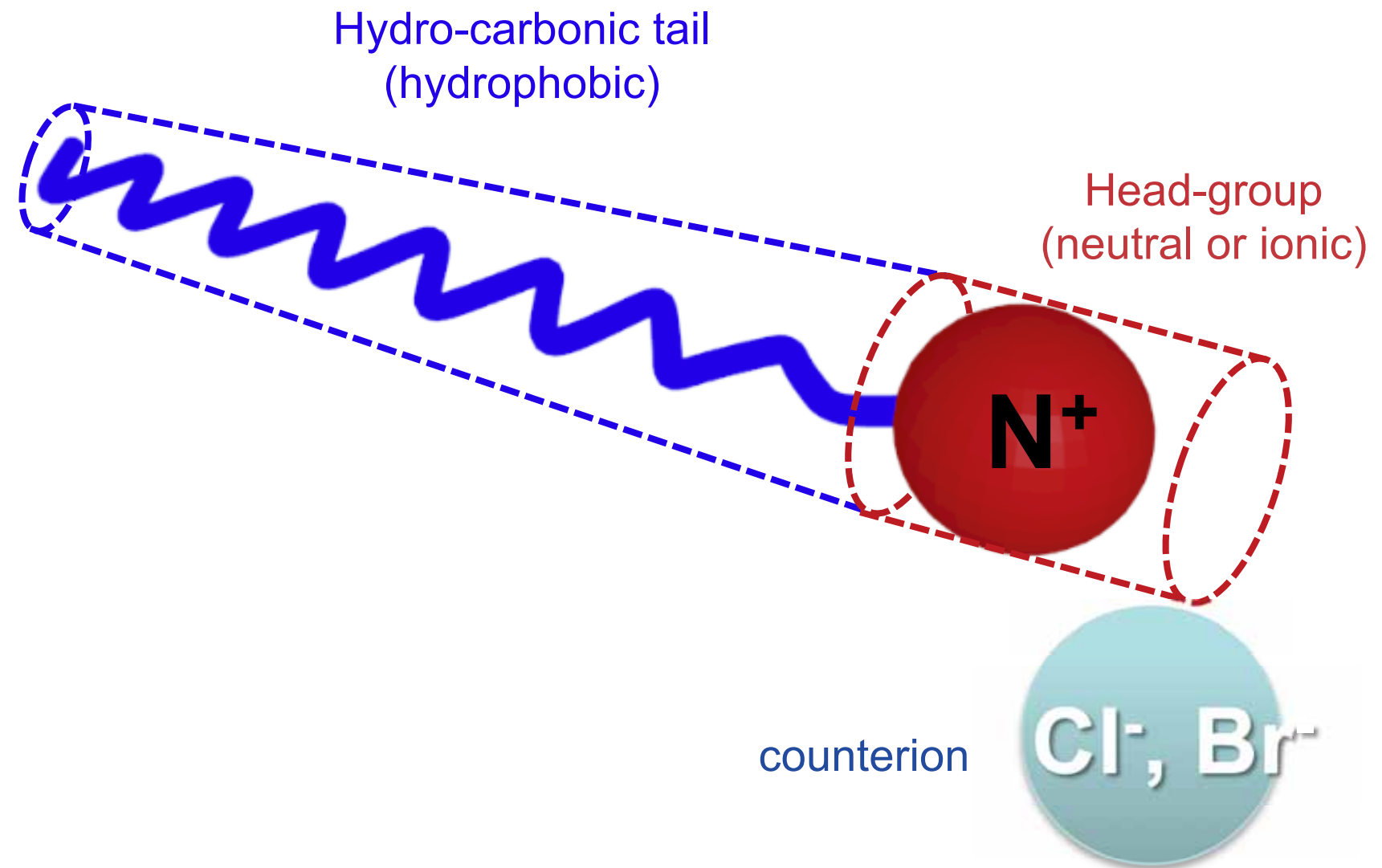
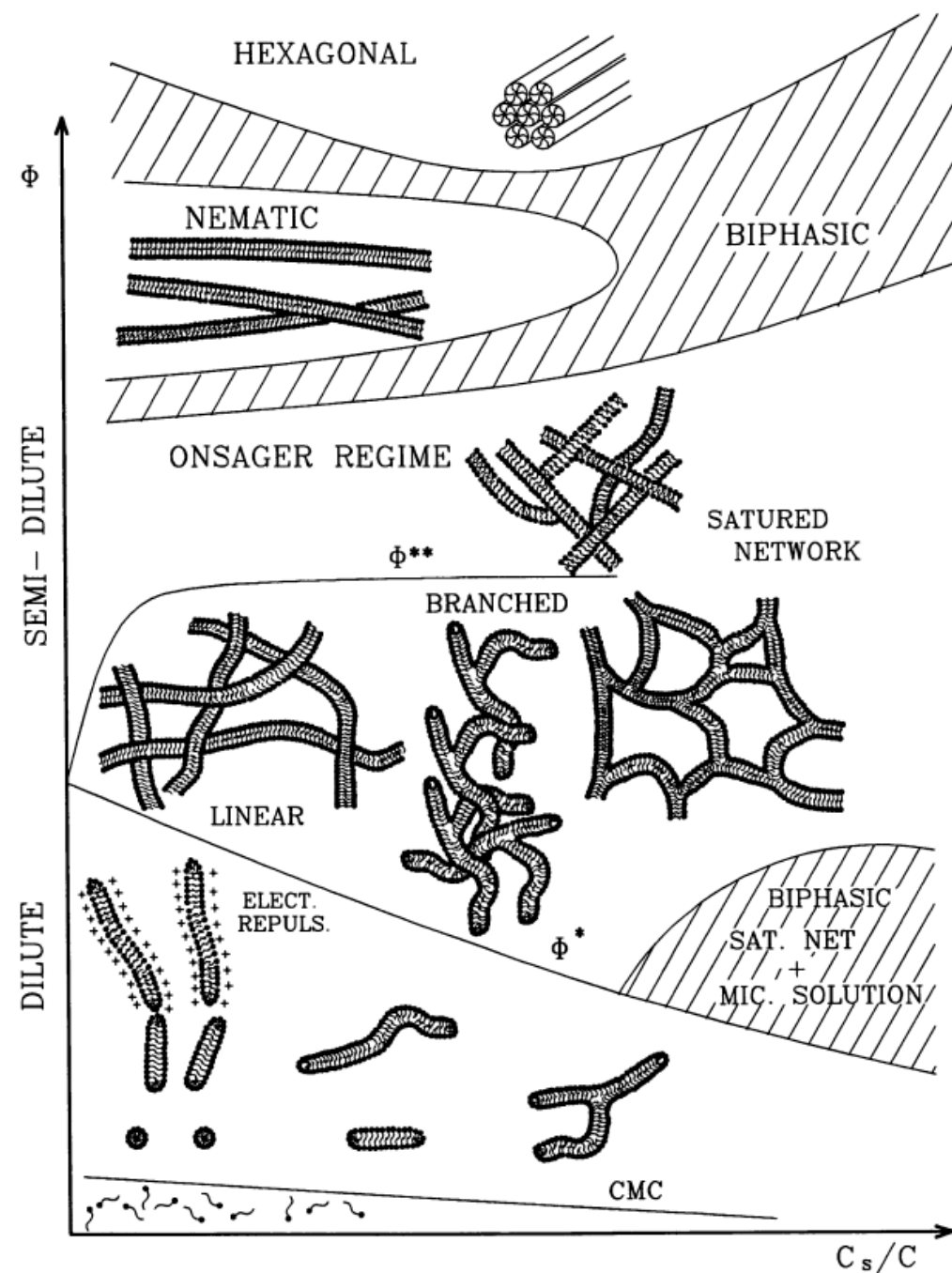
$\sim 1000\%$ of τ_R



Example: Shear banding in surfactant solutions I

Micellization is a balance of:

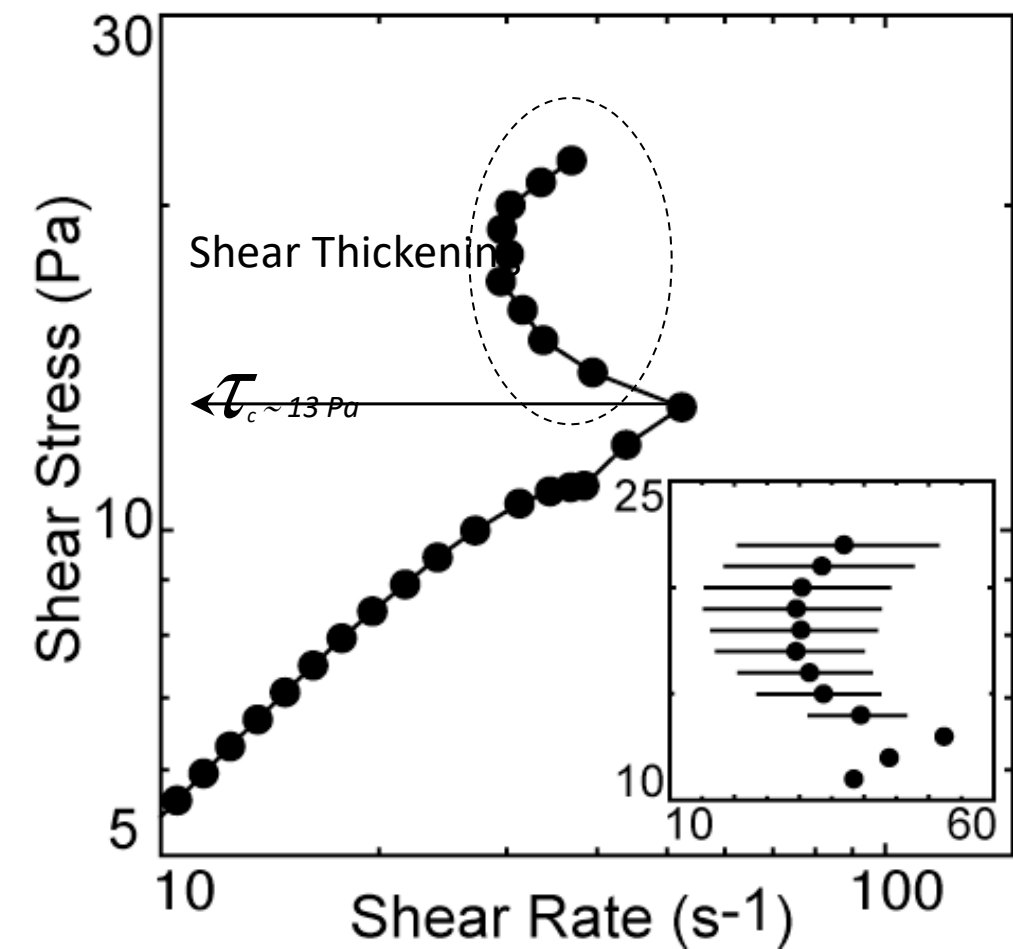
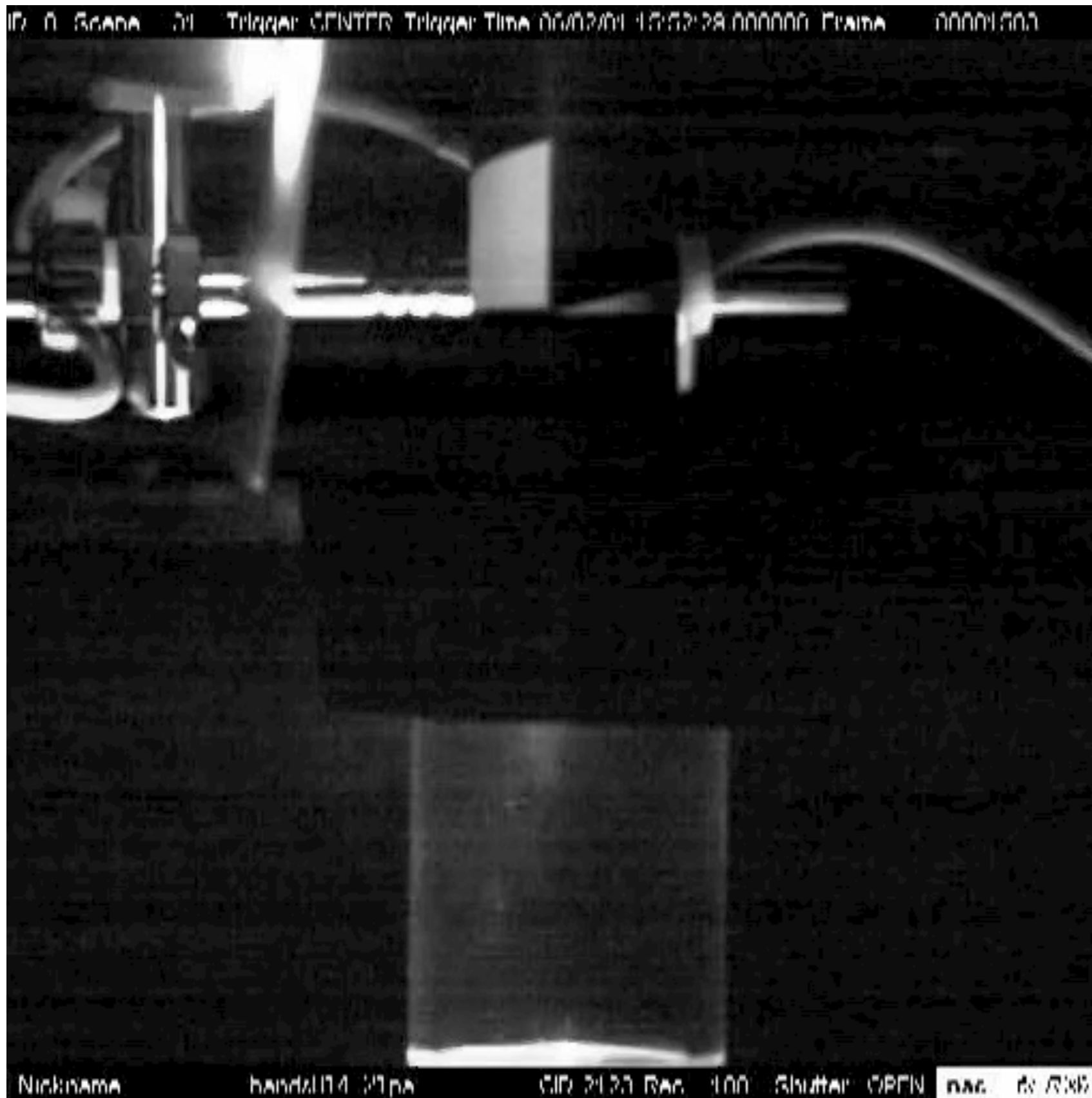
- Hydrophobic forces
- Electrostatics



Phase diagram defined by

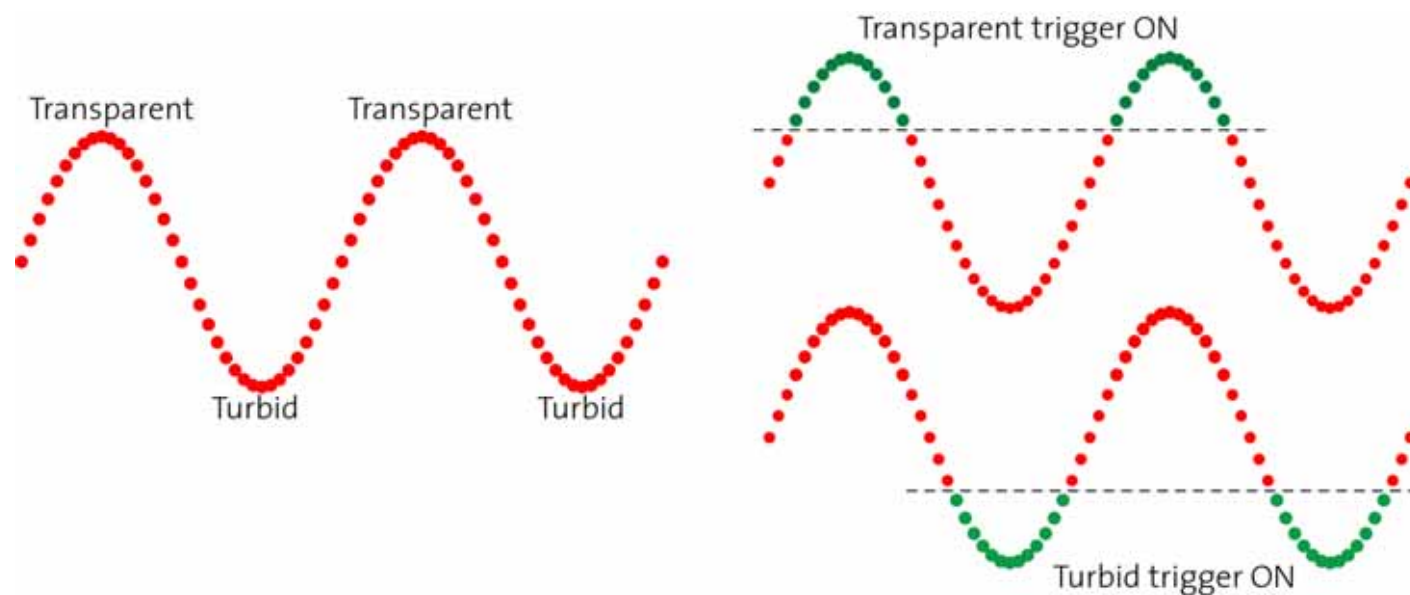
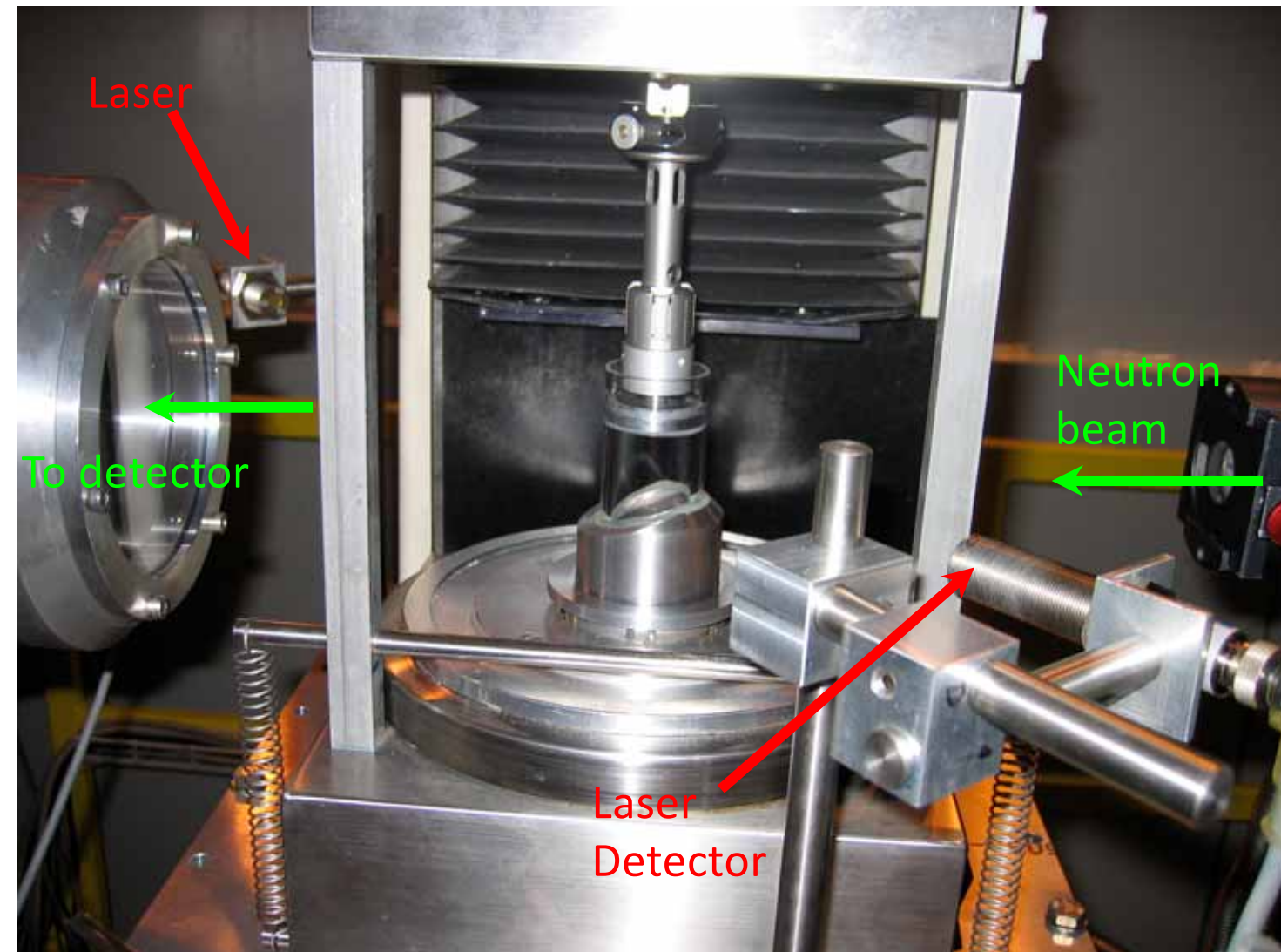
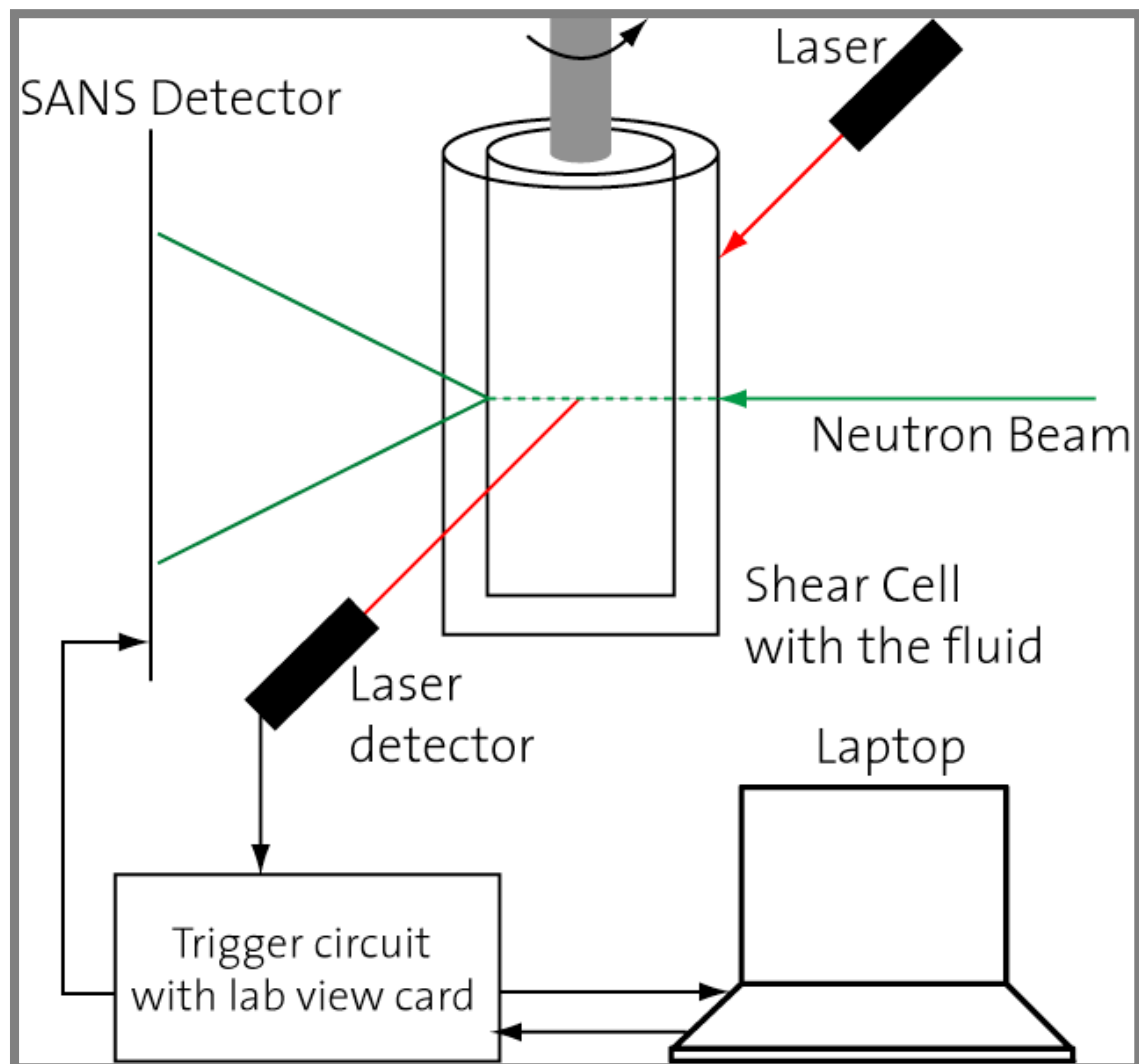
- Surfactant and counterion
- Concentration and its ratio
- Packing parameter
- Additional components

Example: Shear banding in surfactant solutions II



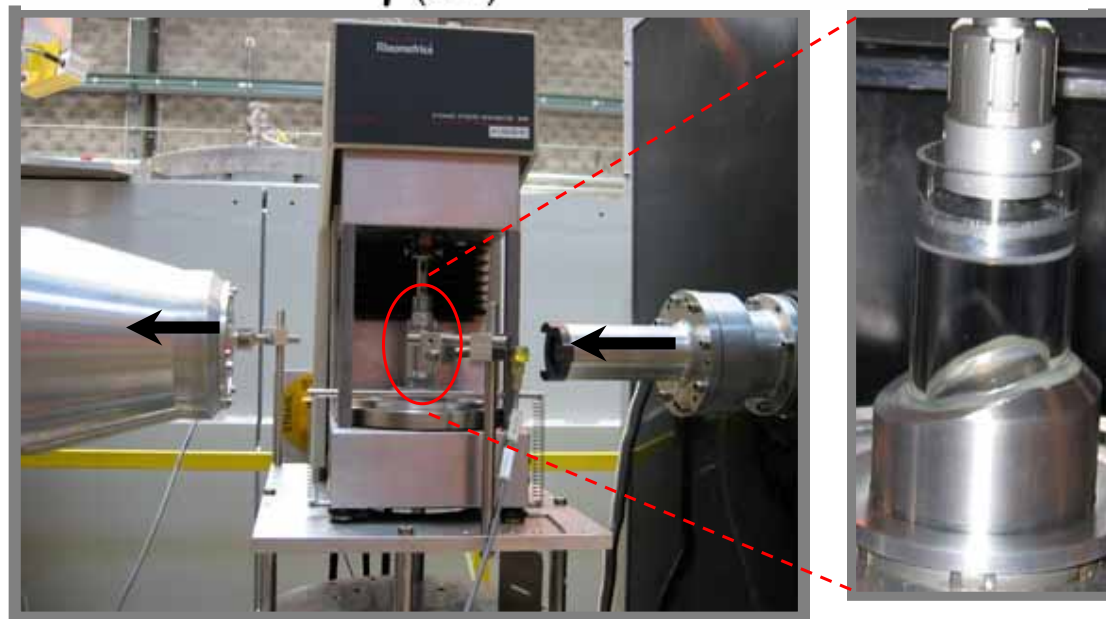
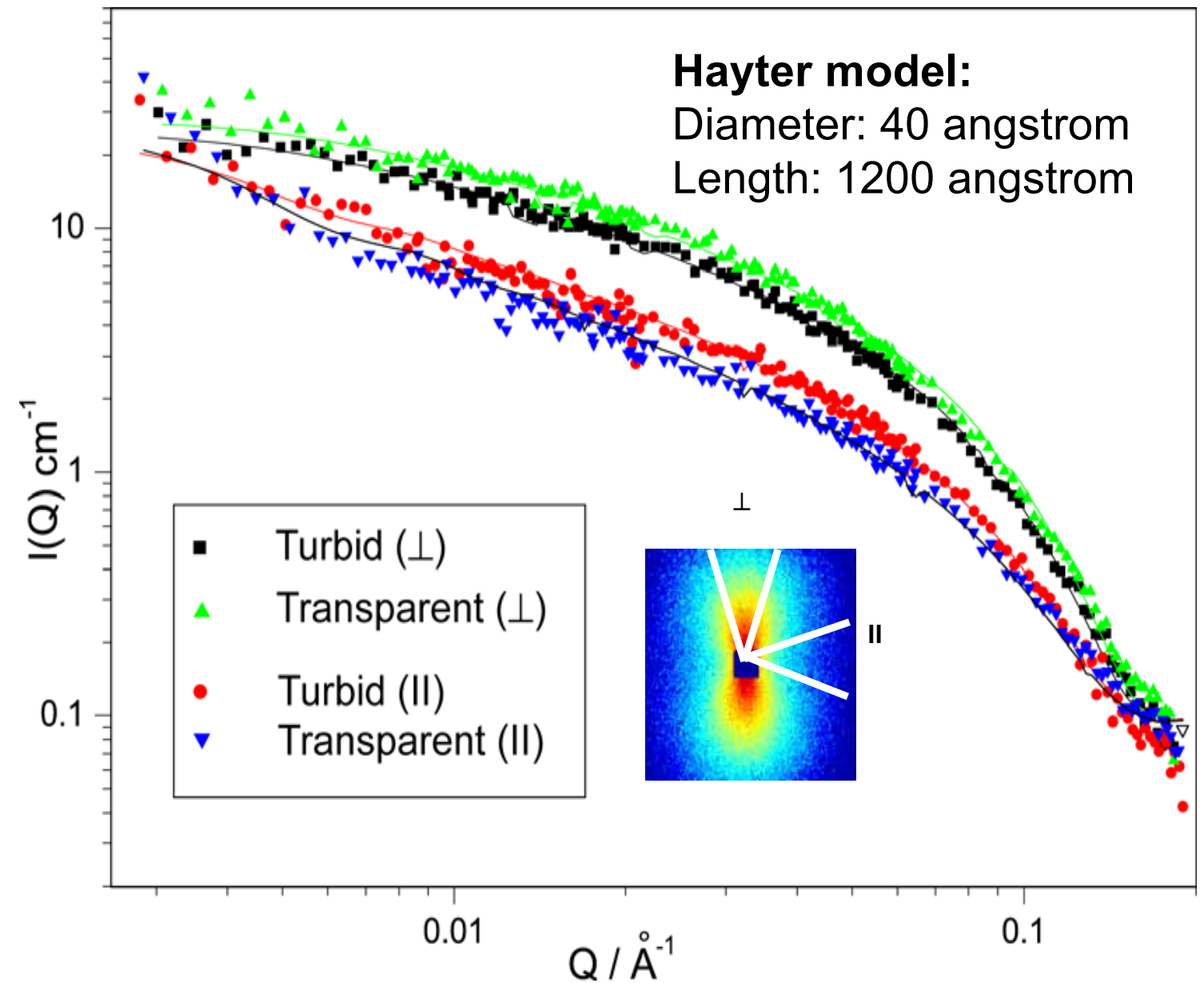
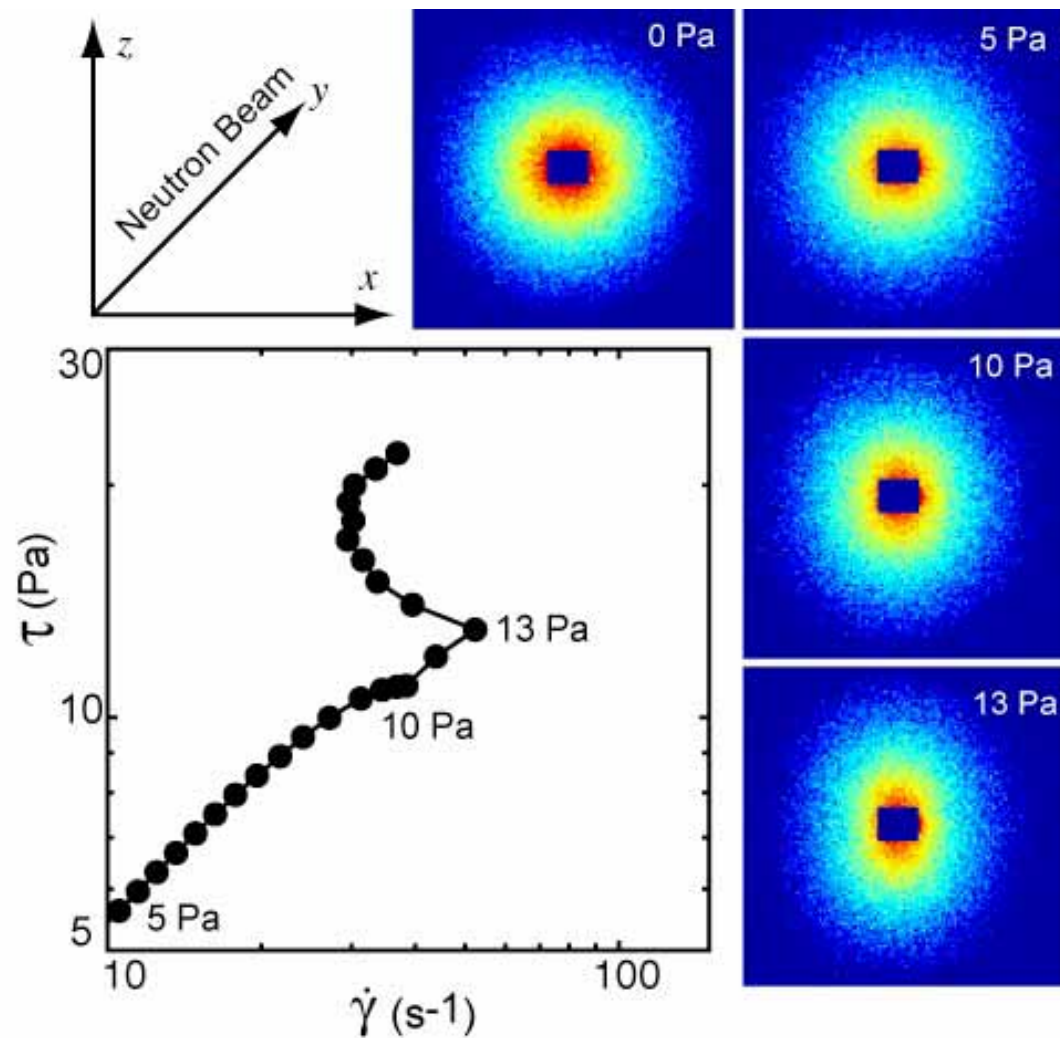
The freaky surfactant solution:
Equimolar solution, e.g.
CPyCl-NaSal, CTAB-NaSal, ...
(20-20 to 60-60 mM)

Example: Shear banding in surfactant solutions III



- Triggered SANS setup:**
- Set a threshold value
 - Trigger the SANS detector
 - Collect the data

Example: Shear banding in surfactant solutions IV



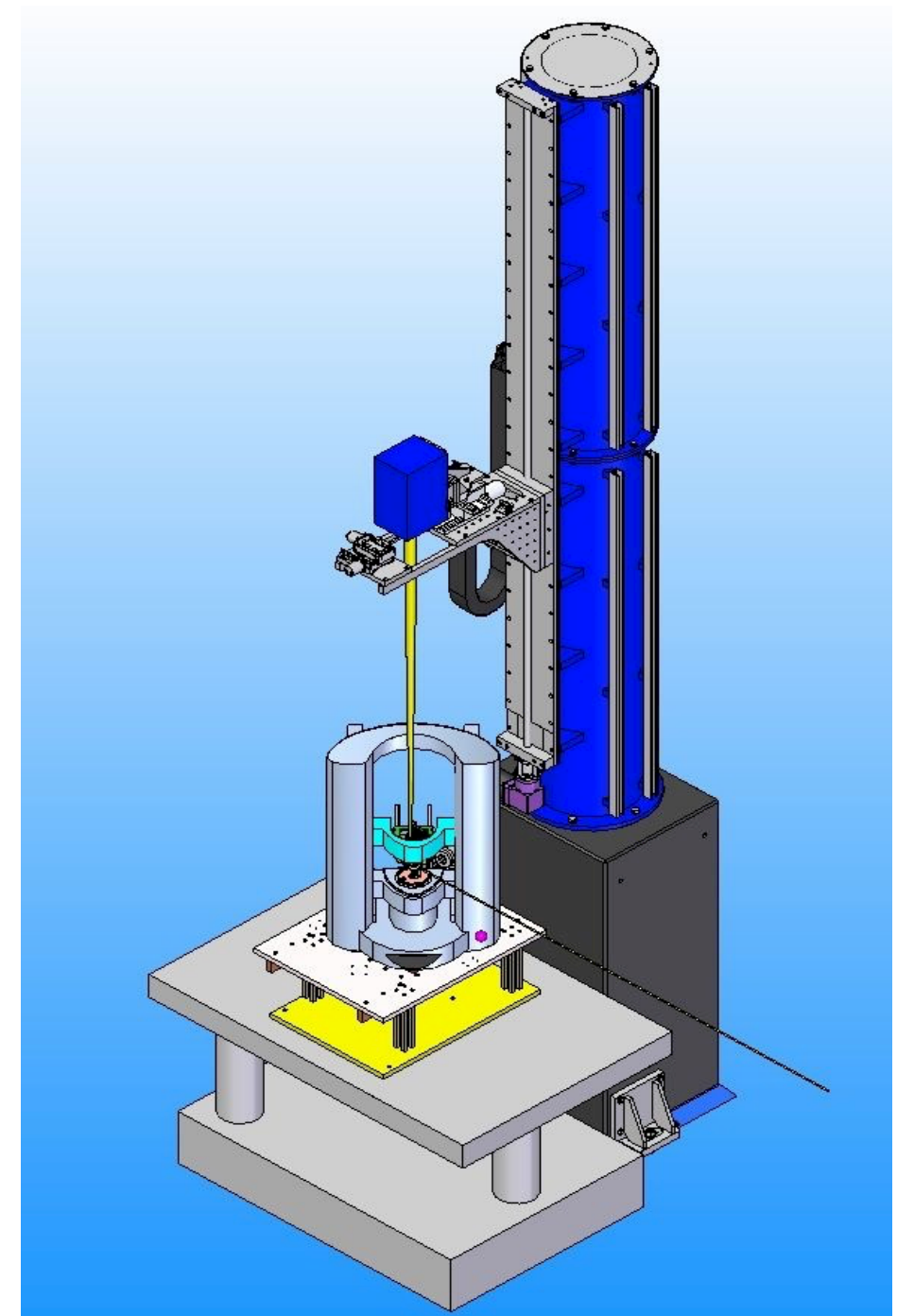
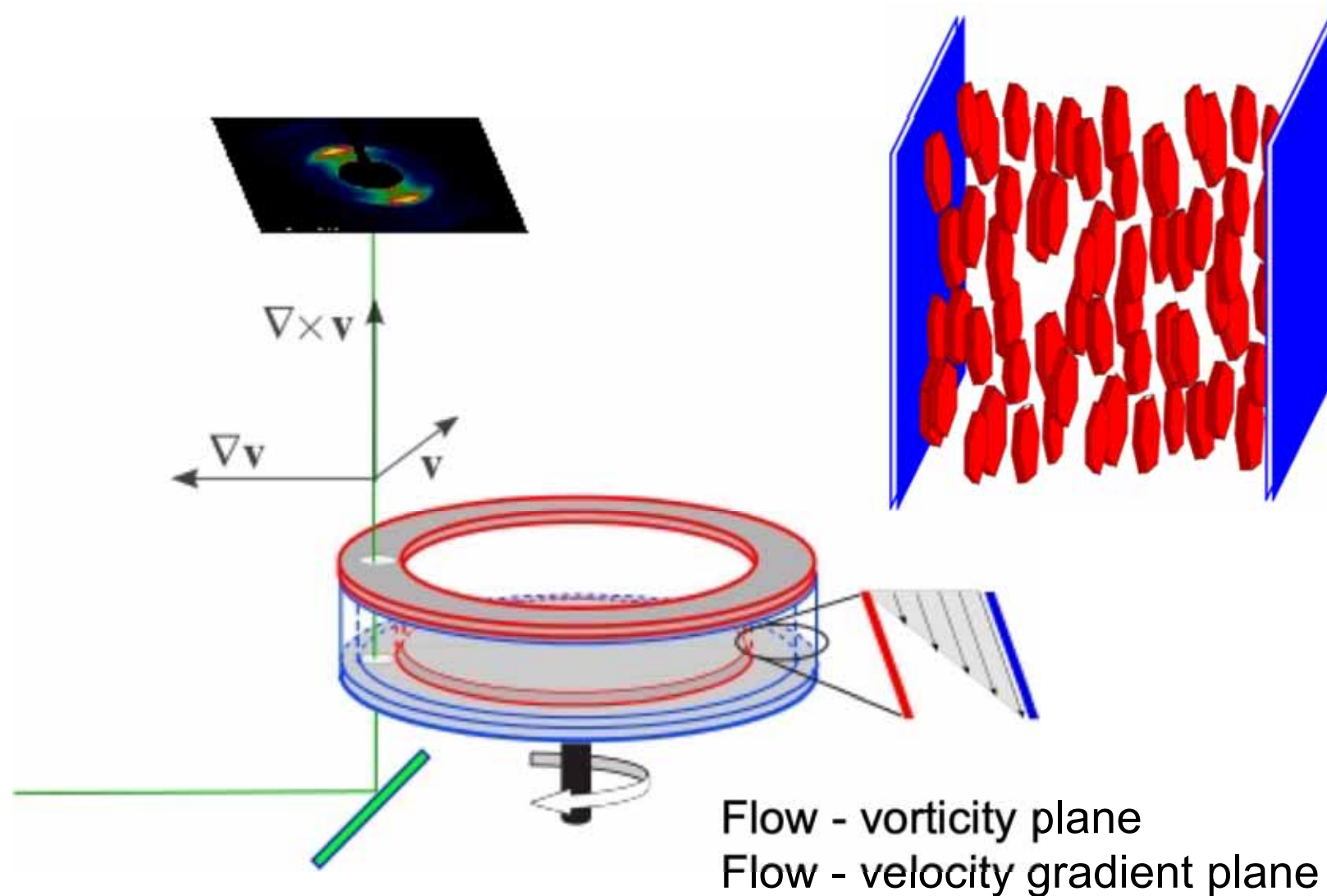
Data analysis:

Pattern analysis (flow mapping, orientation)

Modeling: (Structure and form factor, size, contrast, ...)

Example: LAOS and scattering I

Rheo-structural response of nematic colloidal platelets in LAOS

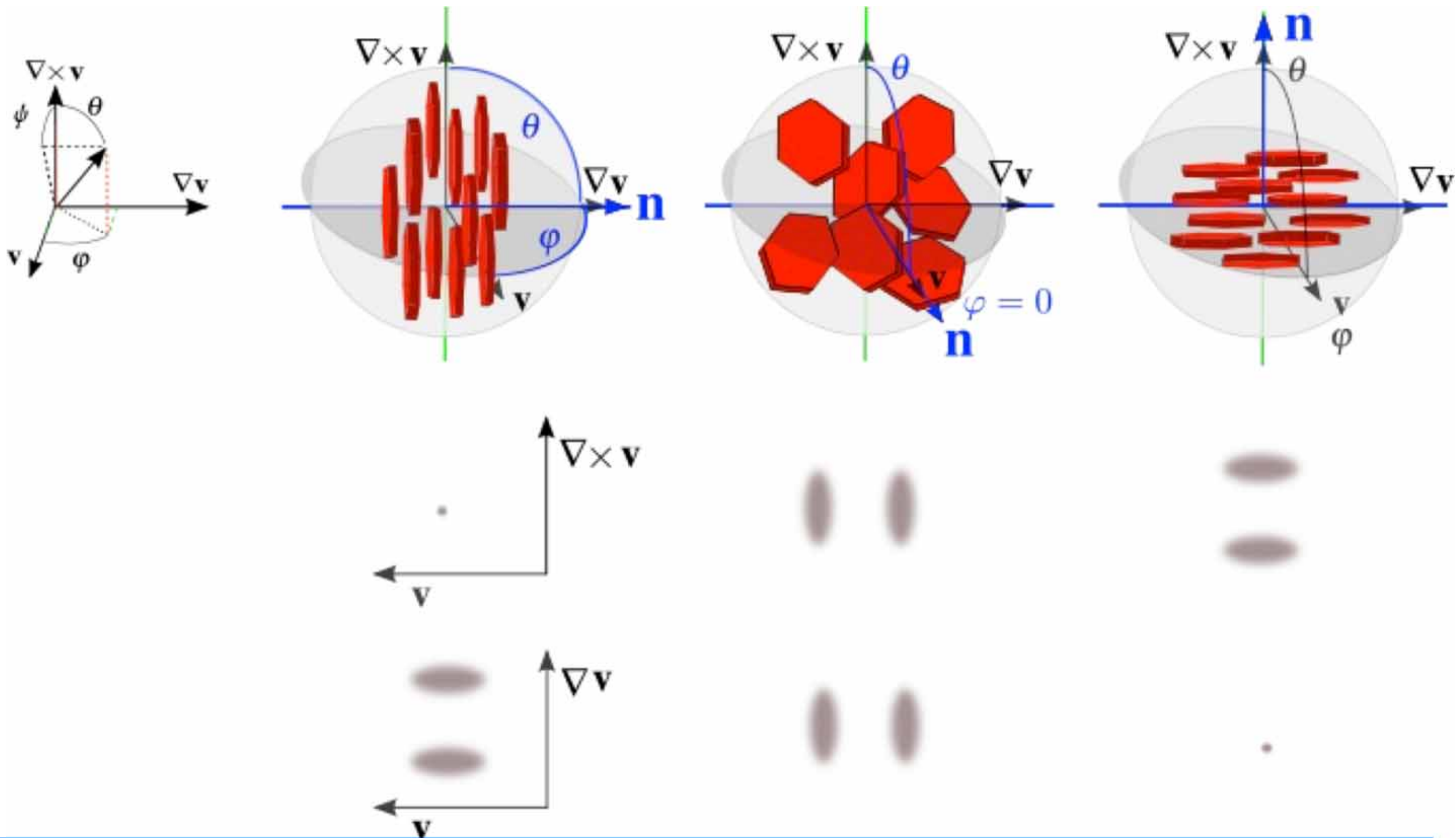


Gibbsite platelets (AlOOH)

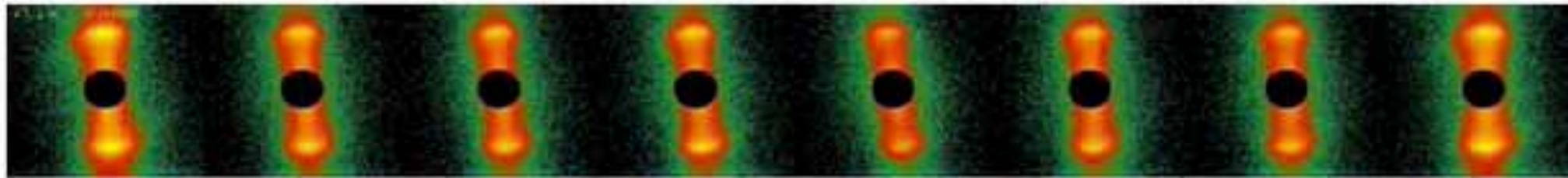
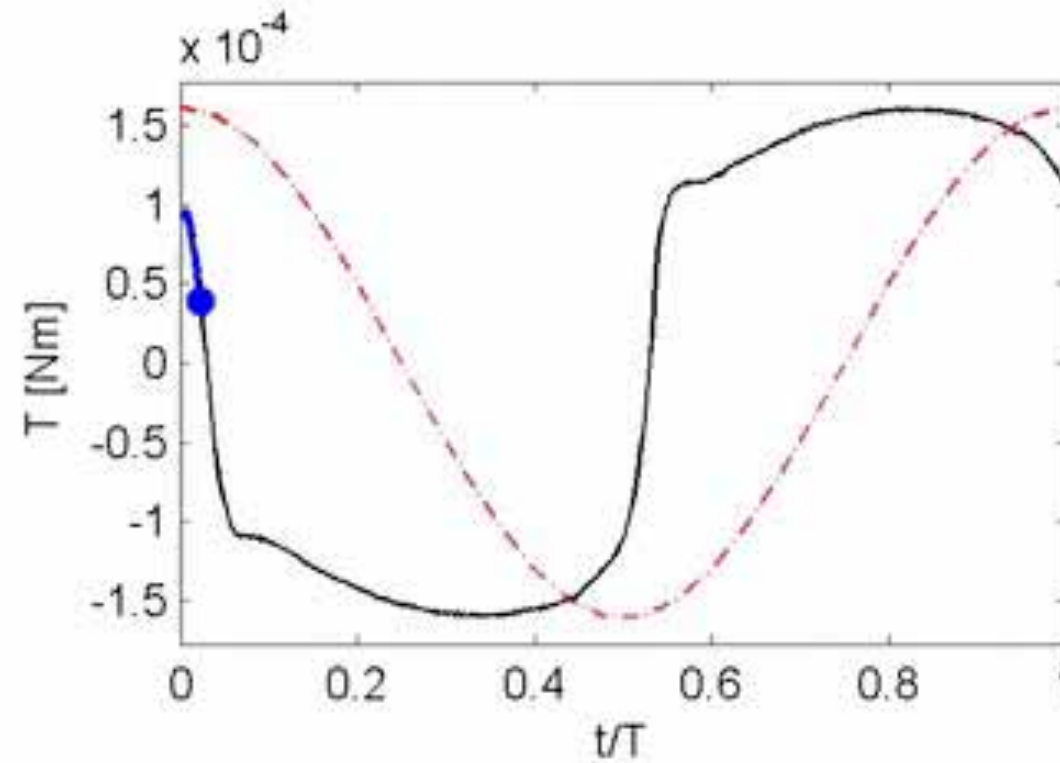
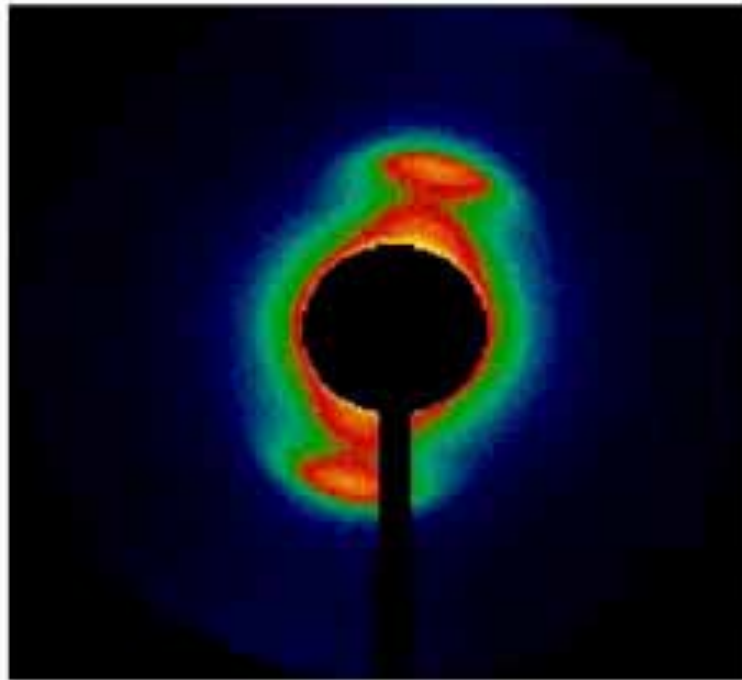
- Homogeneous positive charge
- Relatively thick ($d \sim 250$ nm, $h \sim 11$ nm)
- Relatively mono-disperse ($\sim 13\%$)
- Dispersed in glycerol at 12.4 vol%

Example: LAOS and scattering II

Rheo-structural response of nematic colloidal platelets in LAOS

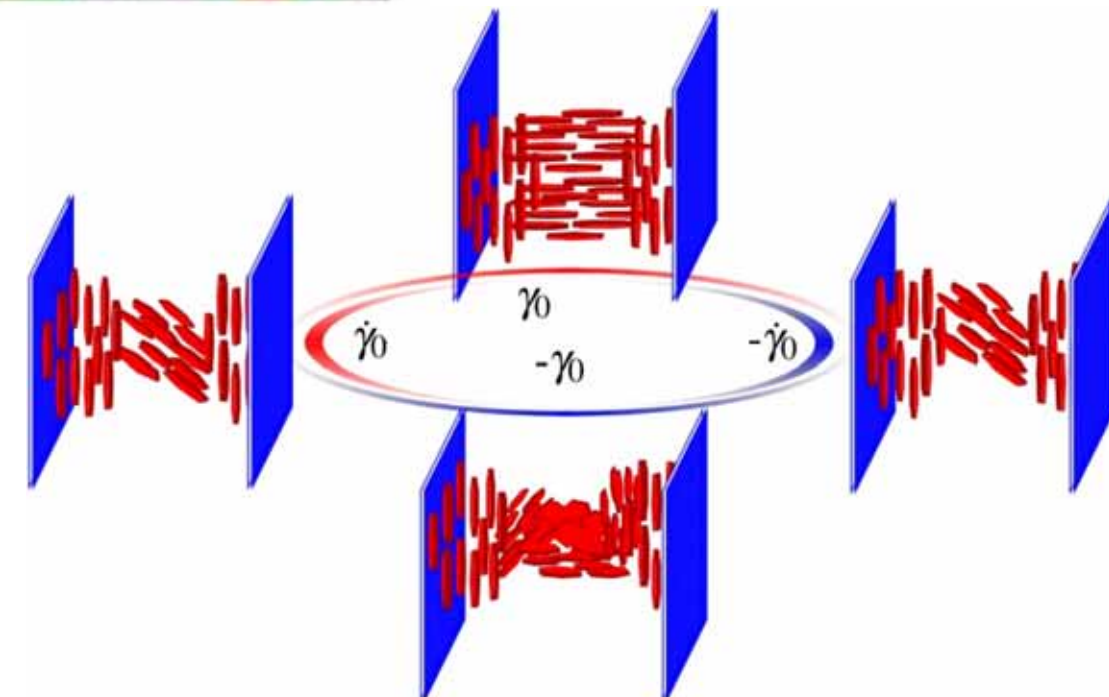


Example: LAOS and scattering III



Transient stress signal and flipping SAXS patterns indicate:

- Disorder in gap
- Huge effect of wall anchoring



Nanostructure surveys of macroscopic specimens by small-angle scattering tensor tomography

Marianne Liebi¹, Marios Georgiadis², Andreas Menzel¹, Philipp Schneider³, Joachim Kohlbrecher¹, Oliver Bunk¹ & Manuel Guizar-Sicairos¹

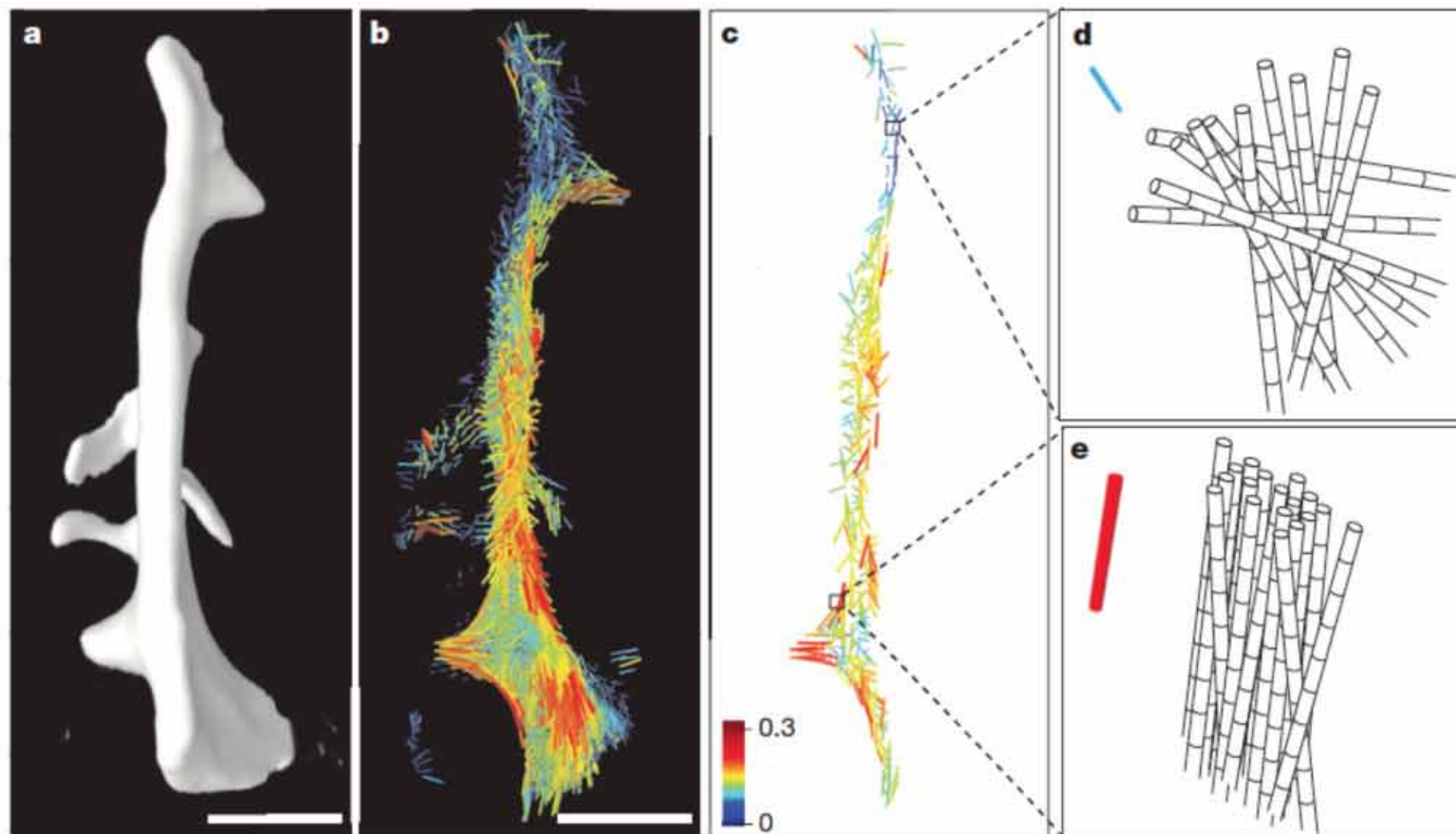


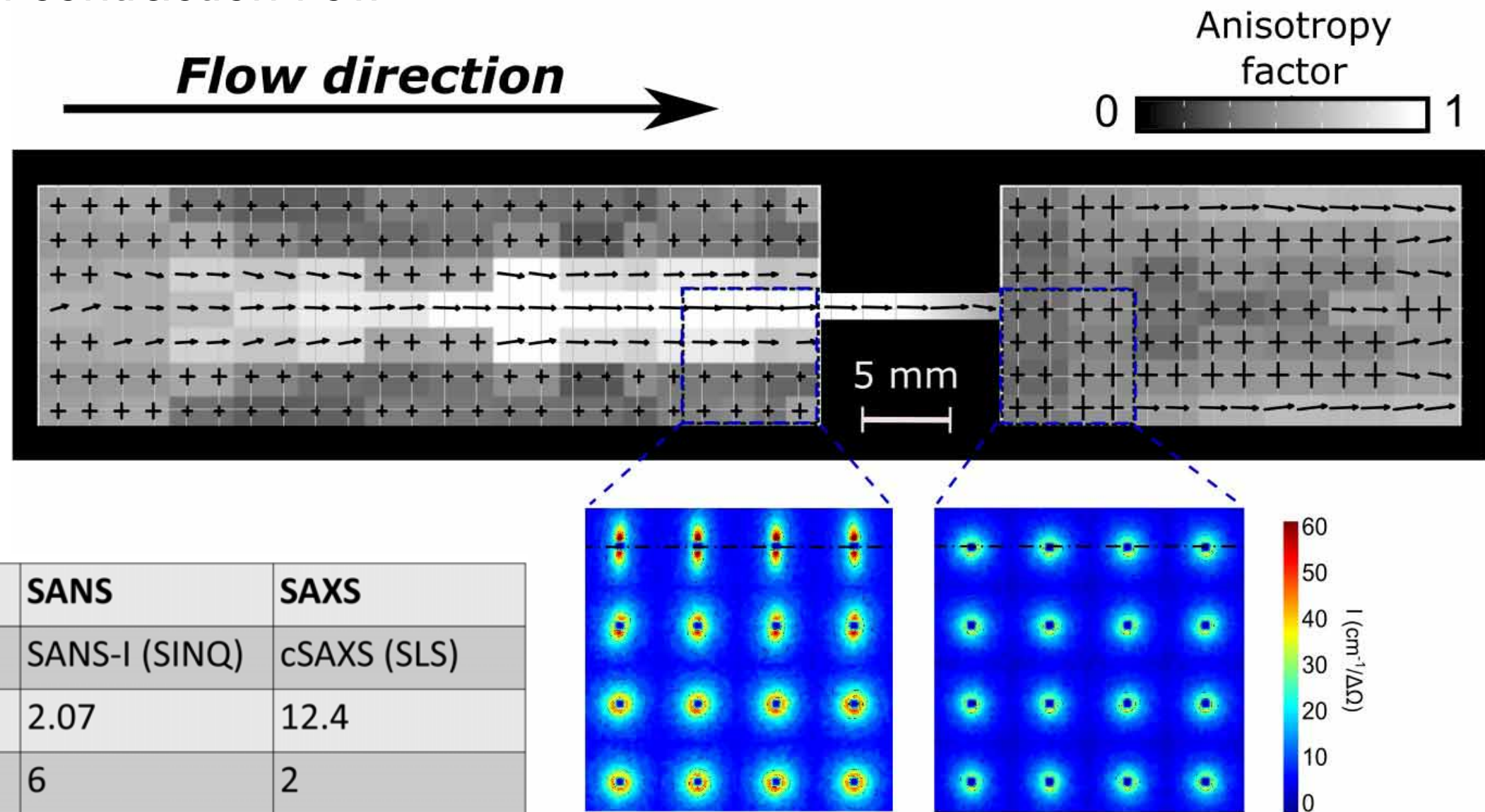
Figure 3 | Orientation of collagen fibrils within a human trabecular bone sample. a, Computed-tomography reconstruction obtained from the transmitted intensity using standard filtered backprojection. b, Orientation of bone ultrastructure as determined using SAS tensor tomography (see also Supplementary Video 1). c, One tomographic slice of the reconstruction shown in b. The cylinder orientations represent the main orientation of collagen fibrils in the corresponding voxel as

schematically depicted in d and e. The degree of orientation is represented by both the colour (indicating the ratio of anisotropic scattering to total scattering) and the length of the cylinders, where a low degree of orientation (blue) means a low degree of alignment of the collagen fibrils (d), and a high degree of orientation (red) means the collagen fibrils are well aligned with respect to each other (e). Scale bars in a and b correspond to 0.5 mm.



Scanning SANS: Mapping complex fluids under flow I

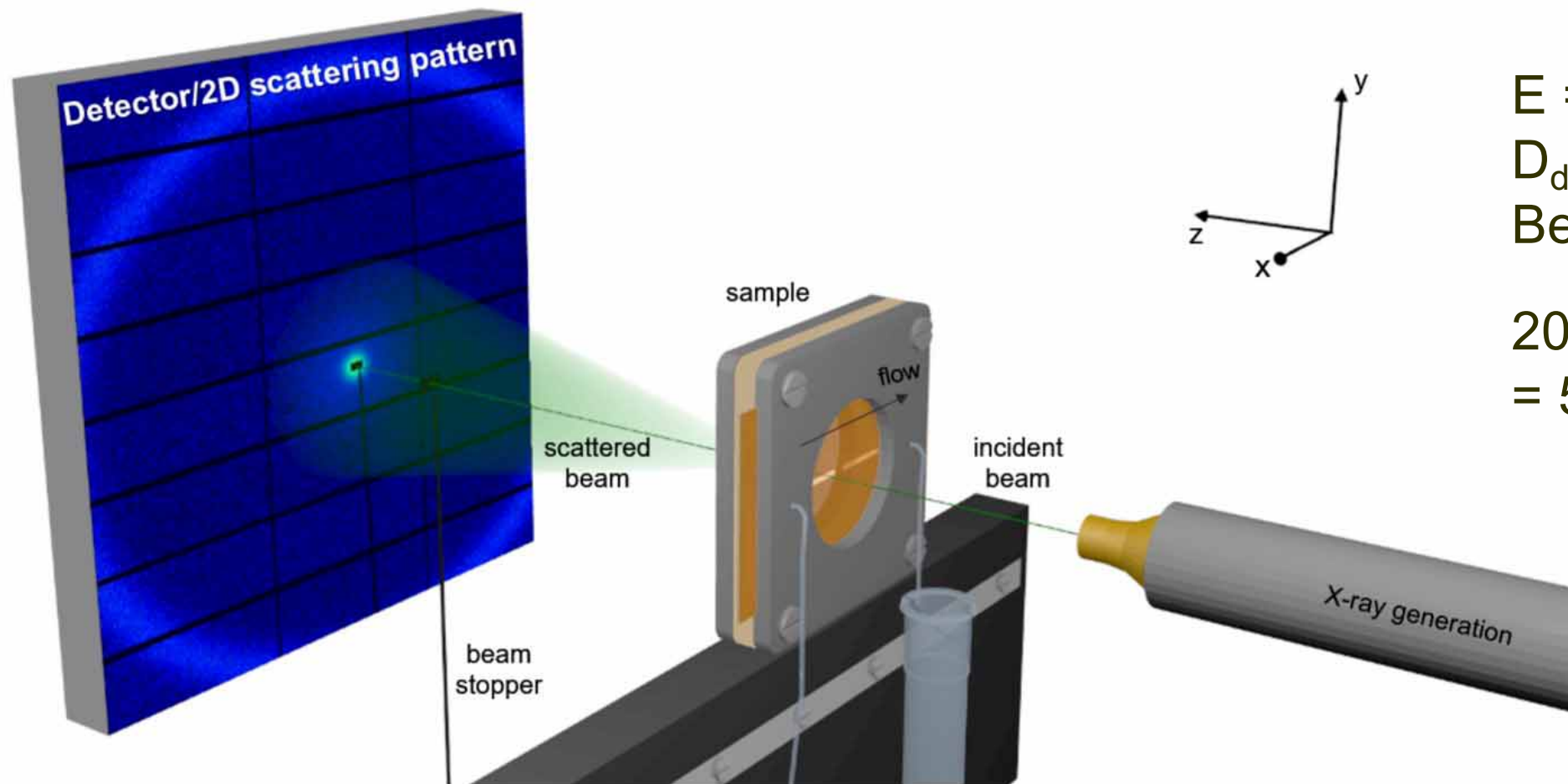
Worm-like micelle in contraction flow



Technique	SANS	SAXS
Beamline	SANS-I (SINQ)	cSAXS (SLS)
Energy (keV)	2.07	12.4
Detector distance (m)	6	2
Beam size (μm^2)	3.1×10^6	1.6×10^3
Acquisition time (s)	≈ 720	0.1
Scattering volume (μm^3)	3.1×10^9	0.16×10^6
Number of scanning points	275	6030
Total measurement time (h)	≈ 55	≈ 0.2

Scanning SAXS: Mapping complex fluids under flow II

Experimental setup Scanning SAXS (cSAXS at PSI)

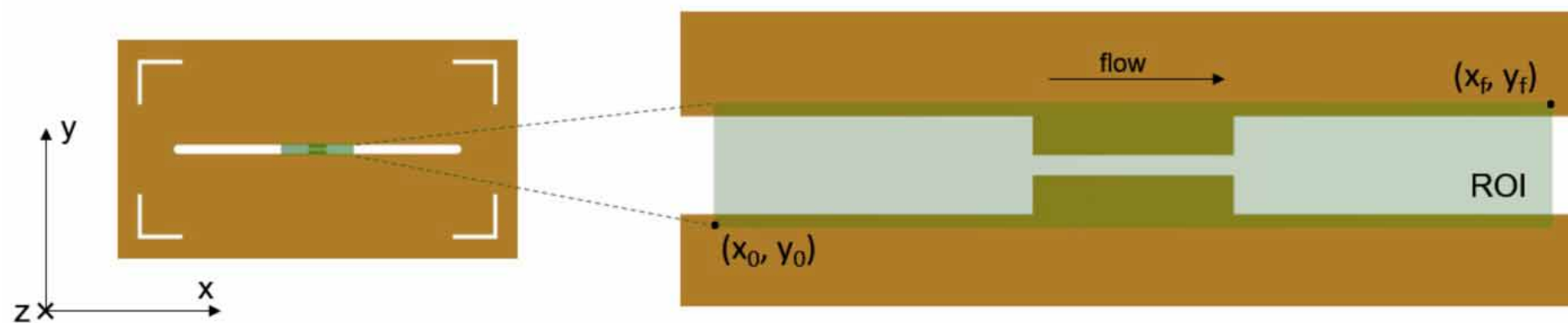


$E = 12.4 \text{ keV}$

$D_{\text{dist}} = 7 \text{ or } 2 \text{ m}$

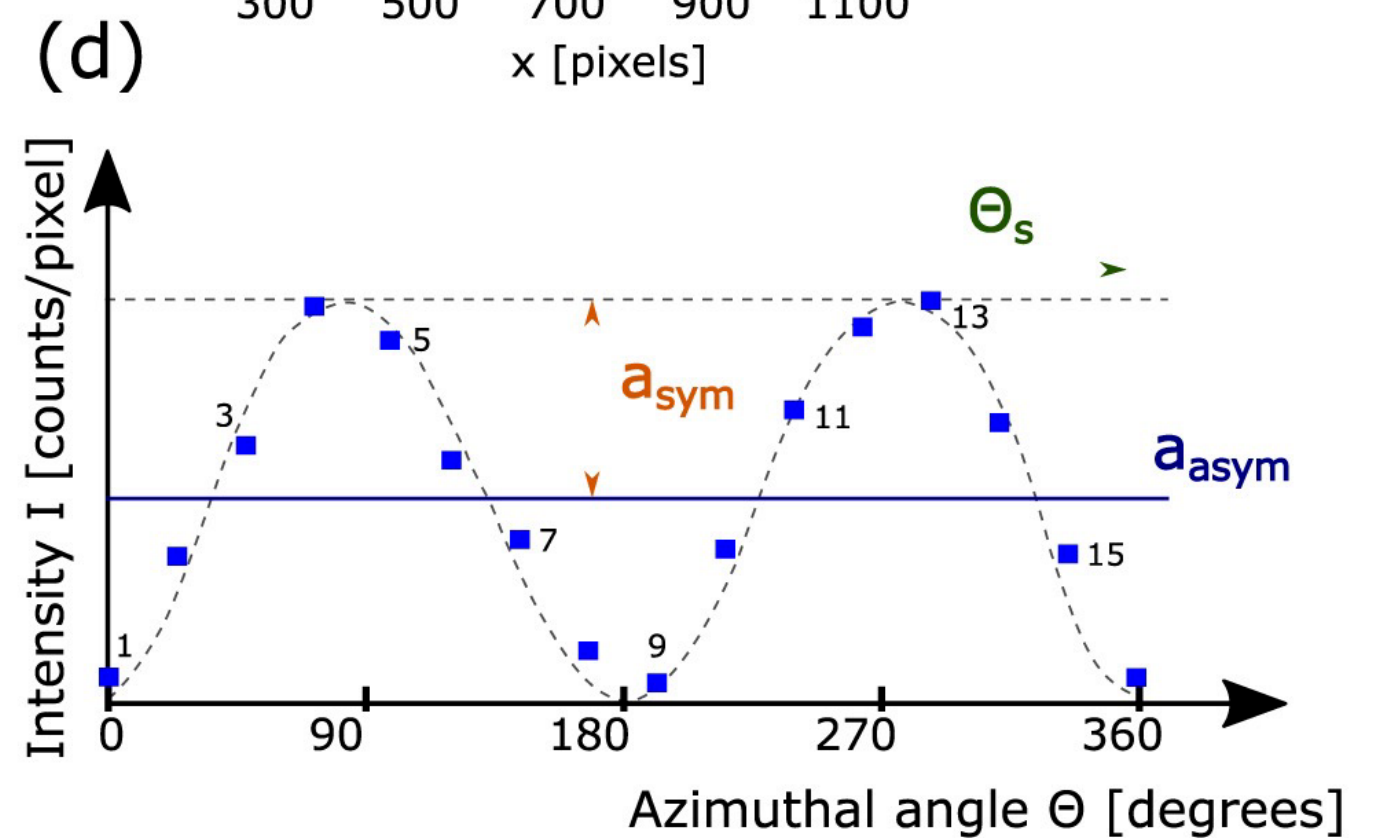
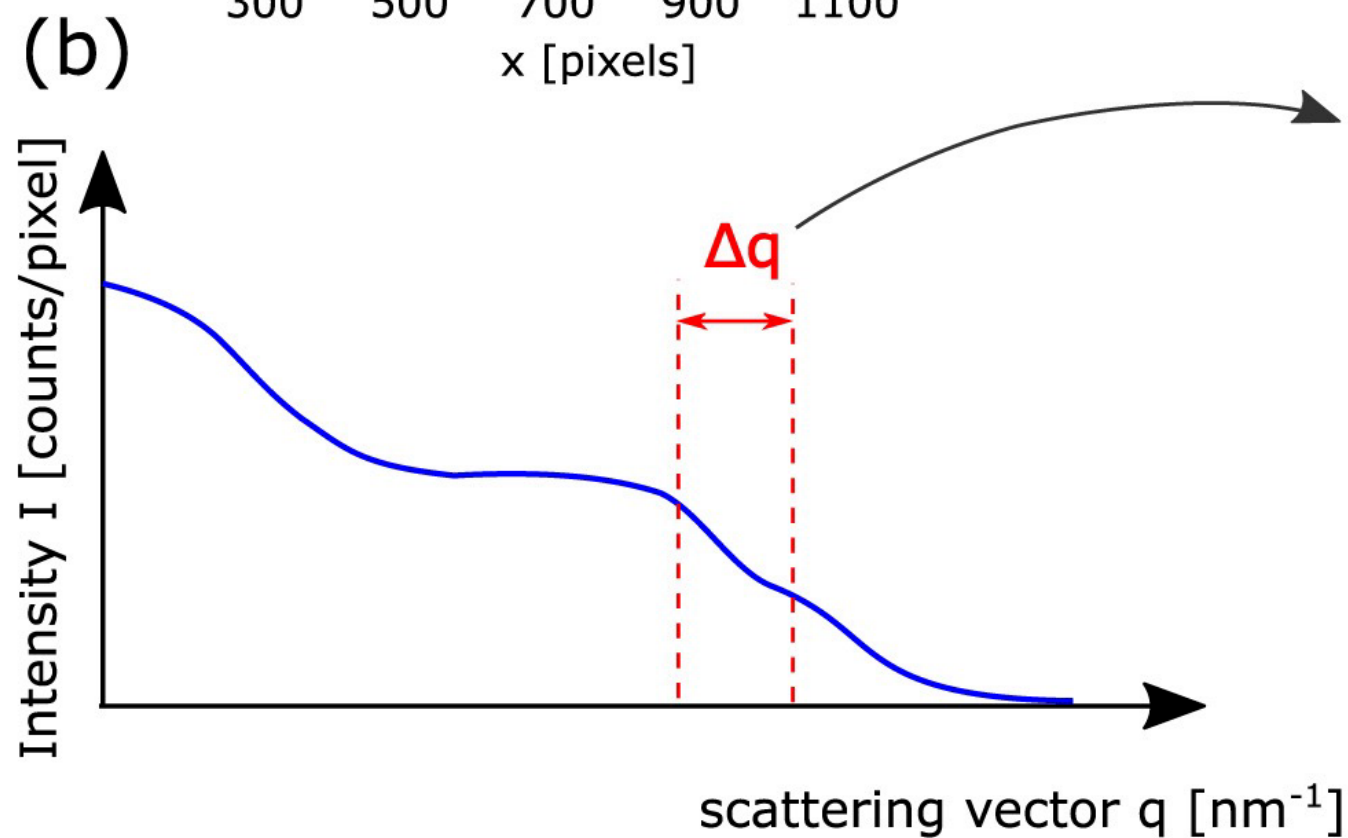
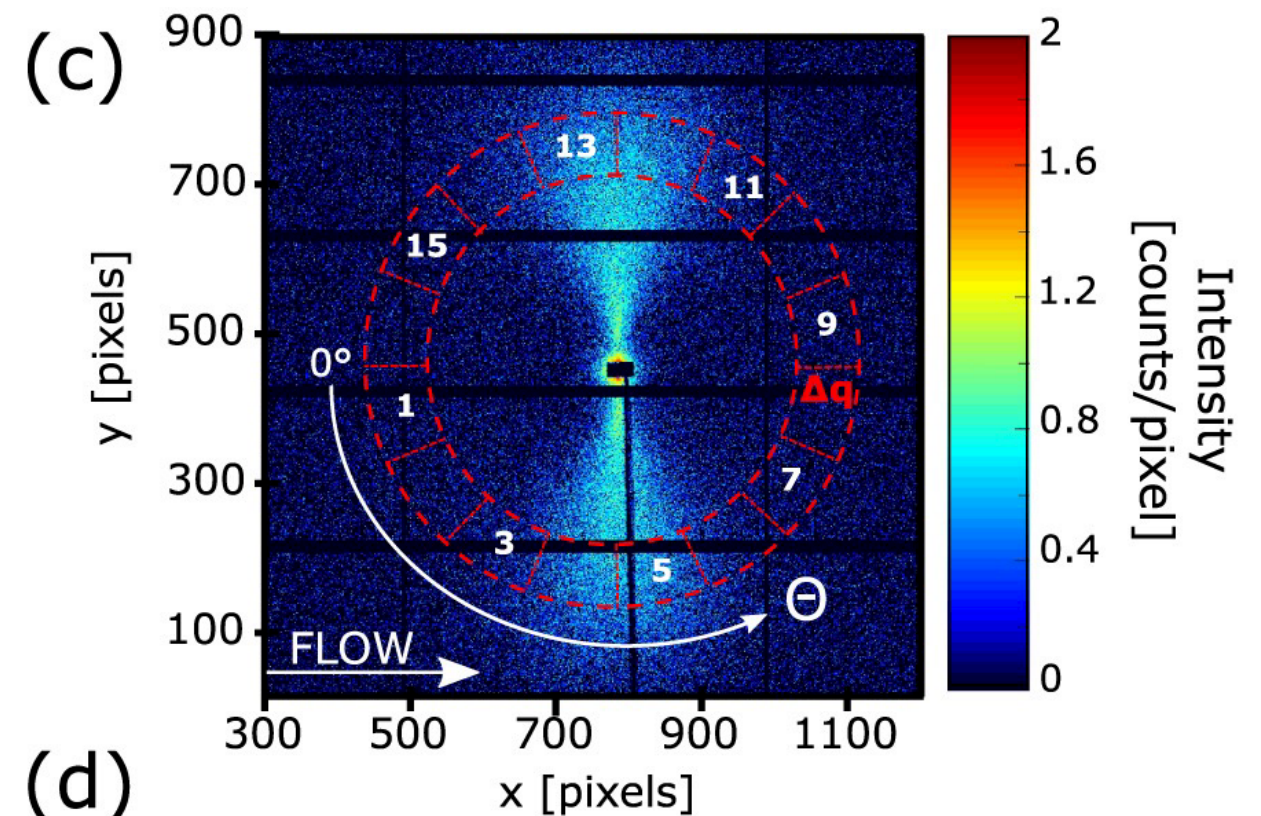
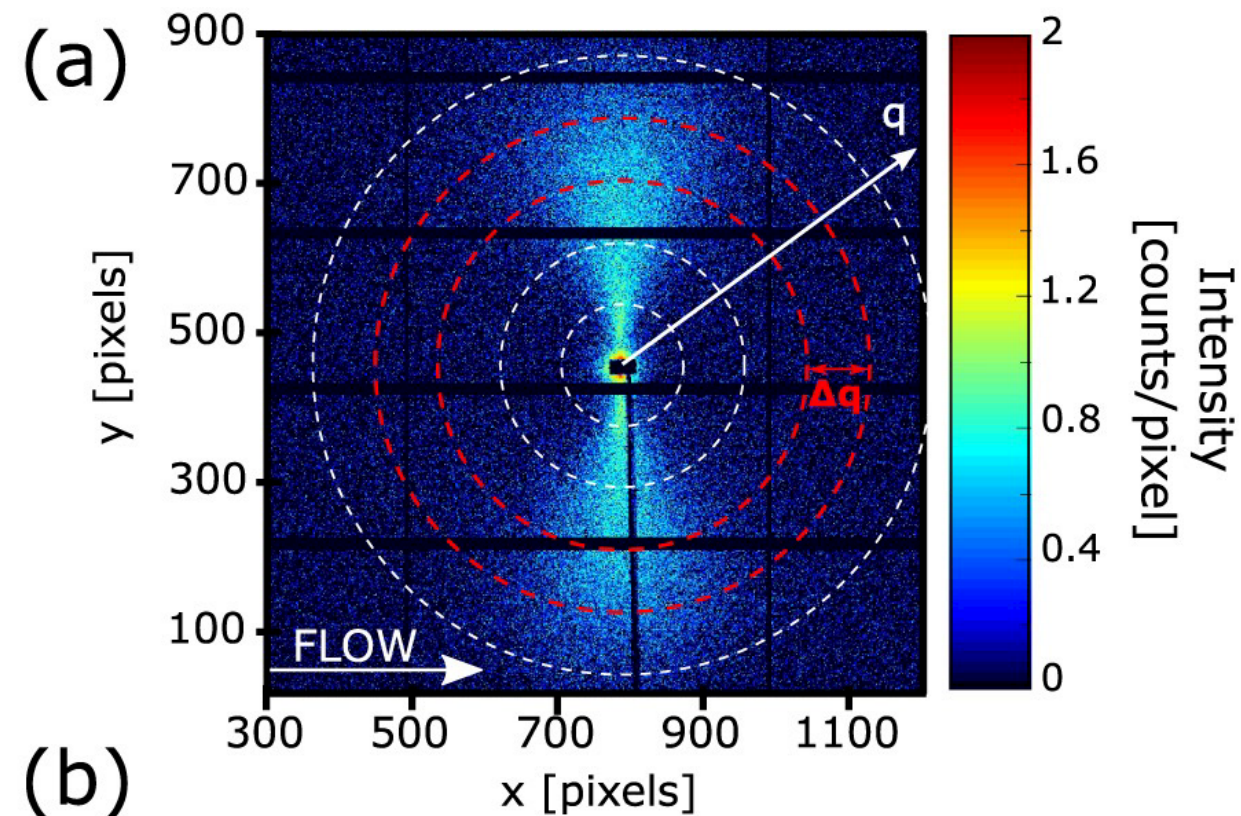
Beam size = $40 \times 40 \mu\text{m}^2$

200 x 25 scattering patterns
= 5000 2D images to process!



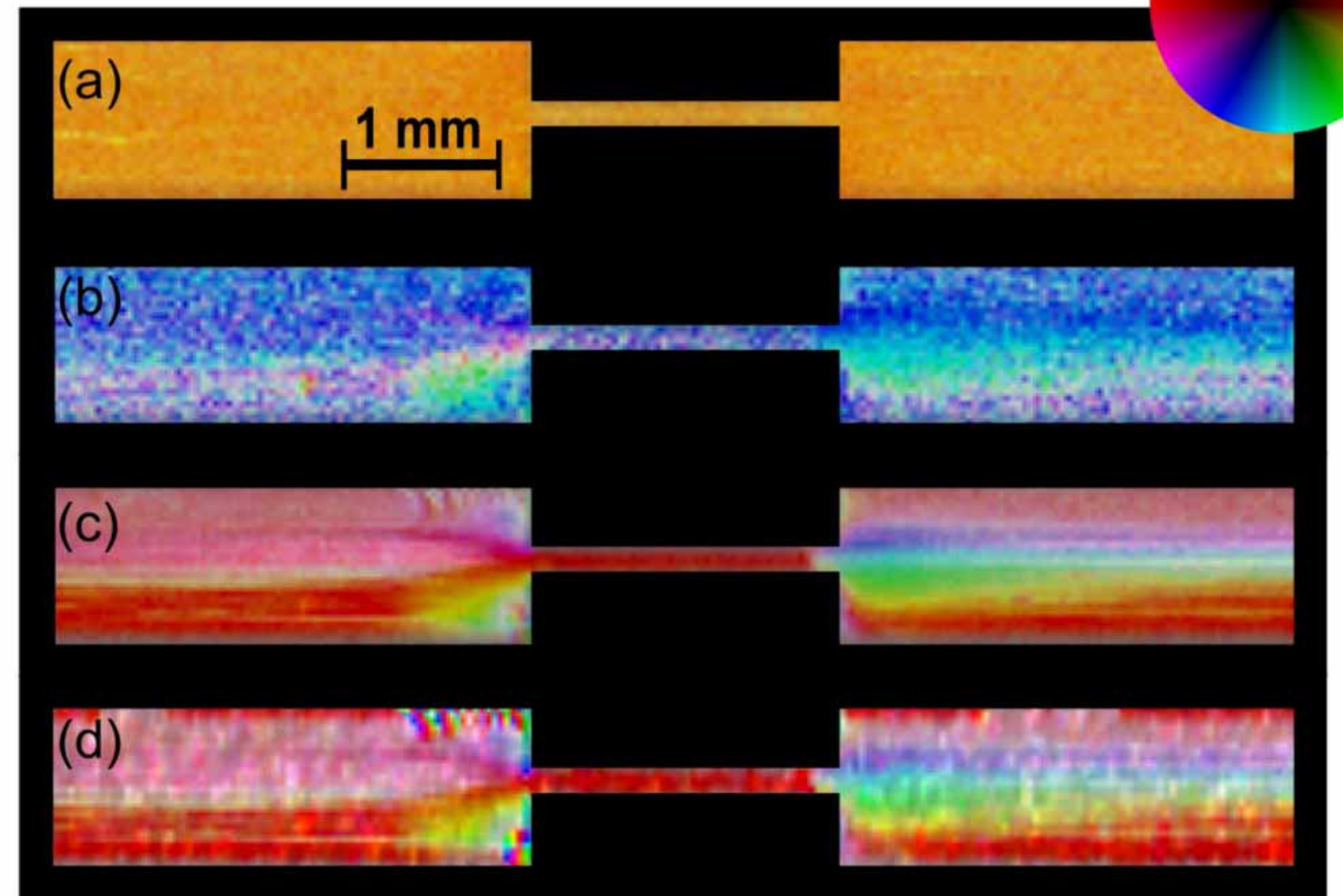
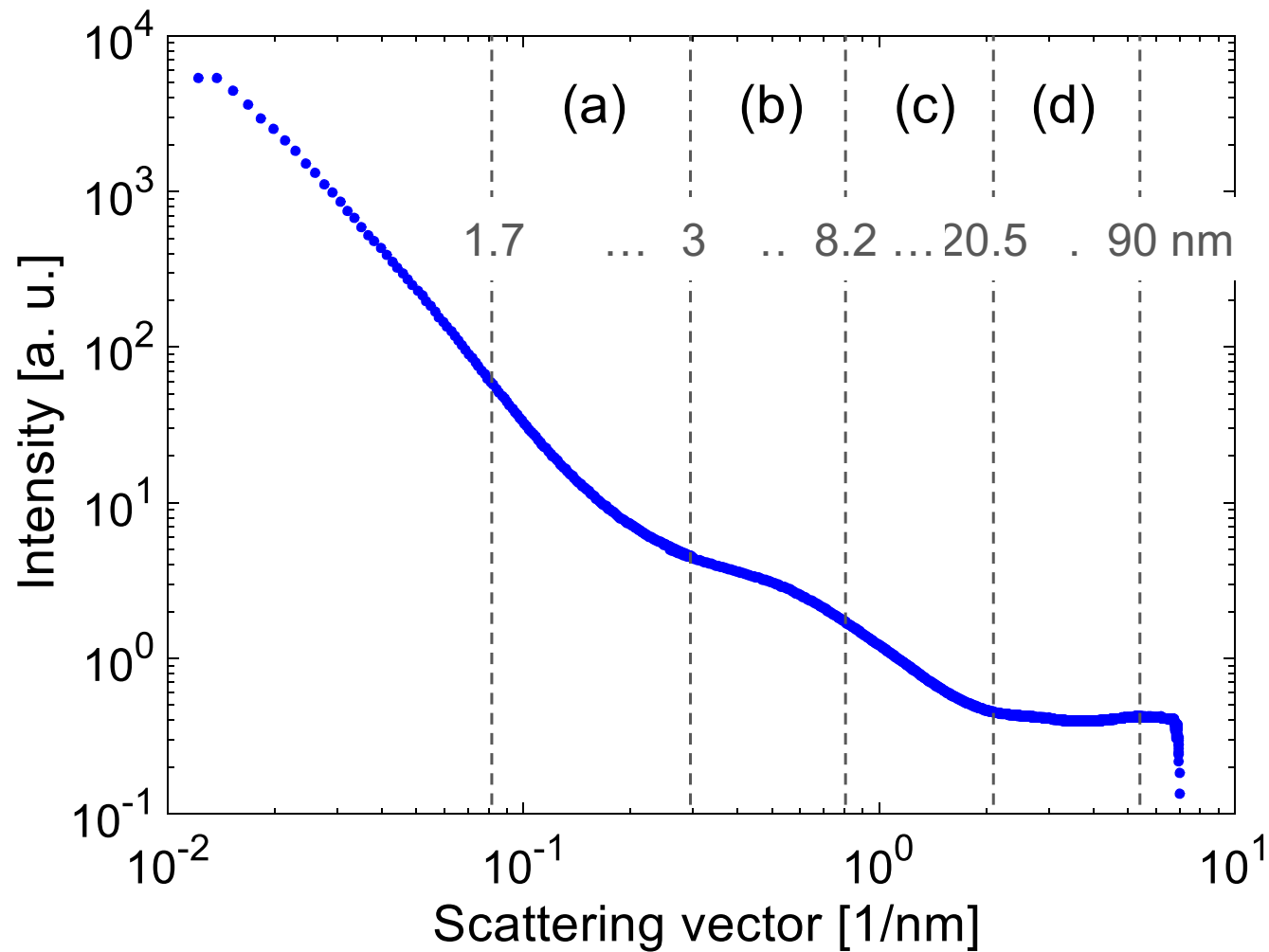
Scanning SAXS: Mapping complex fluids under flow IV

A few Tb of data ... and now? - **Color coding** for anisotropy in each scattering pattern

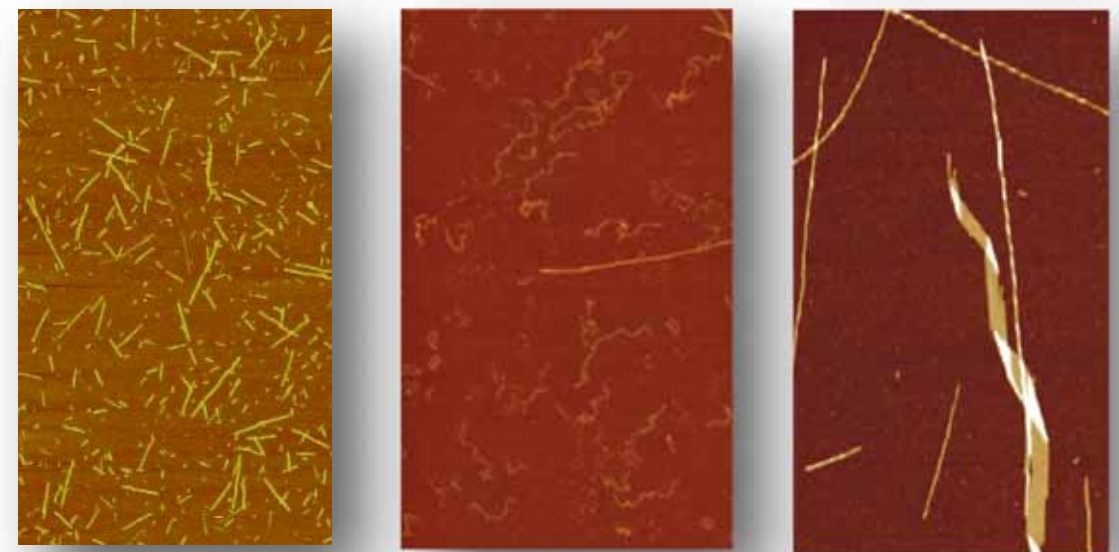


Scanning SAXS: Mapping complex fluids under flow V

Amyloid fiber under flow: Estimate of polydispersity

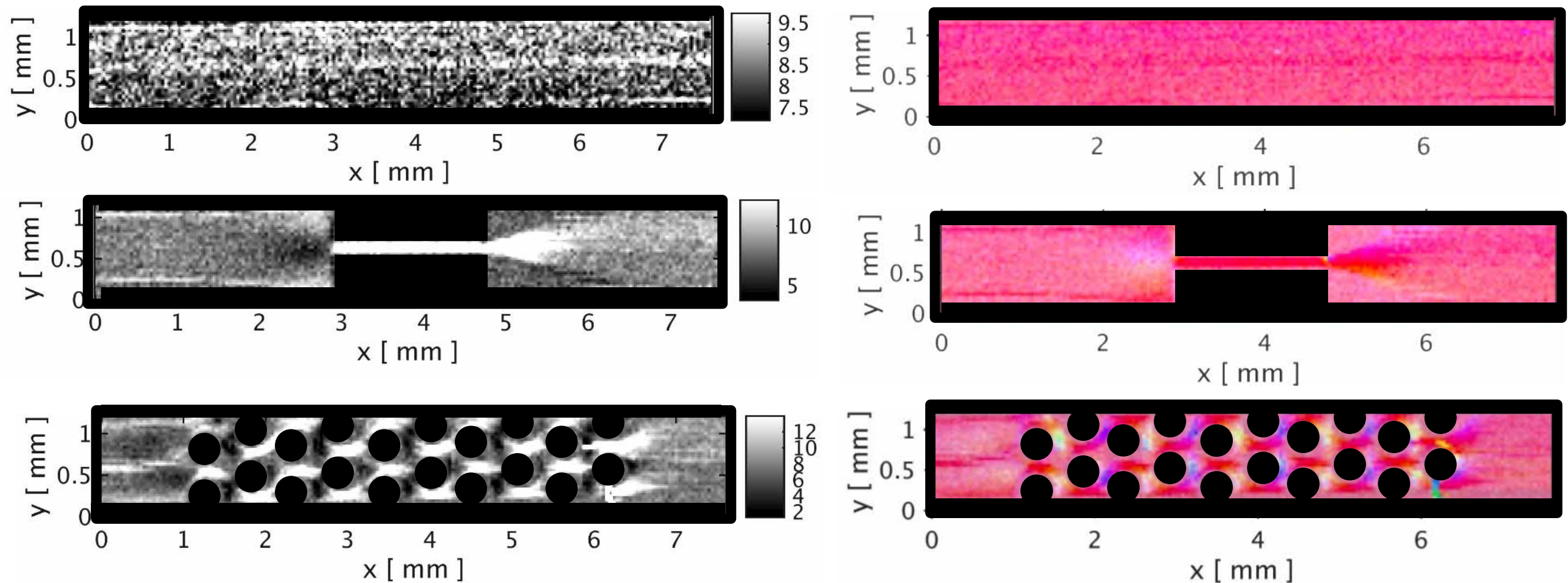


Probing of different dimensions of the fibers from same measurement



Scanning SAXS: Mapping complex fluids under flow VI

Alignment of worm-like micelles (100 mM CTAB – 30 mM NaSal) in a microfluidic channel (thickness 100 μm)





Changes in microstructure and alignment is expressed by the color coding of the anisotropy of the individual scattering patterns (6030 patterns per channel and flow condition)

Microfluidics and scattering: Review papers

 molecules Molecules 27 (2022) 4602 

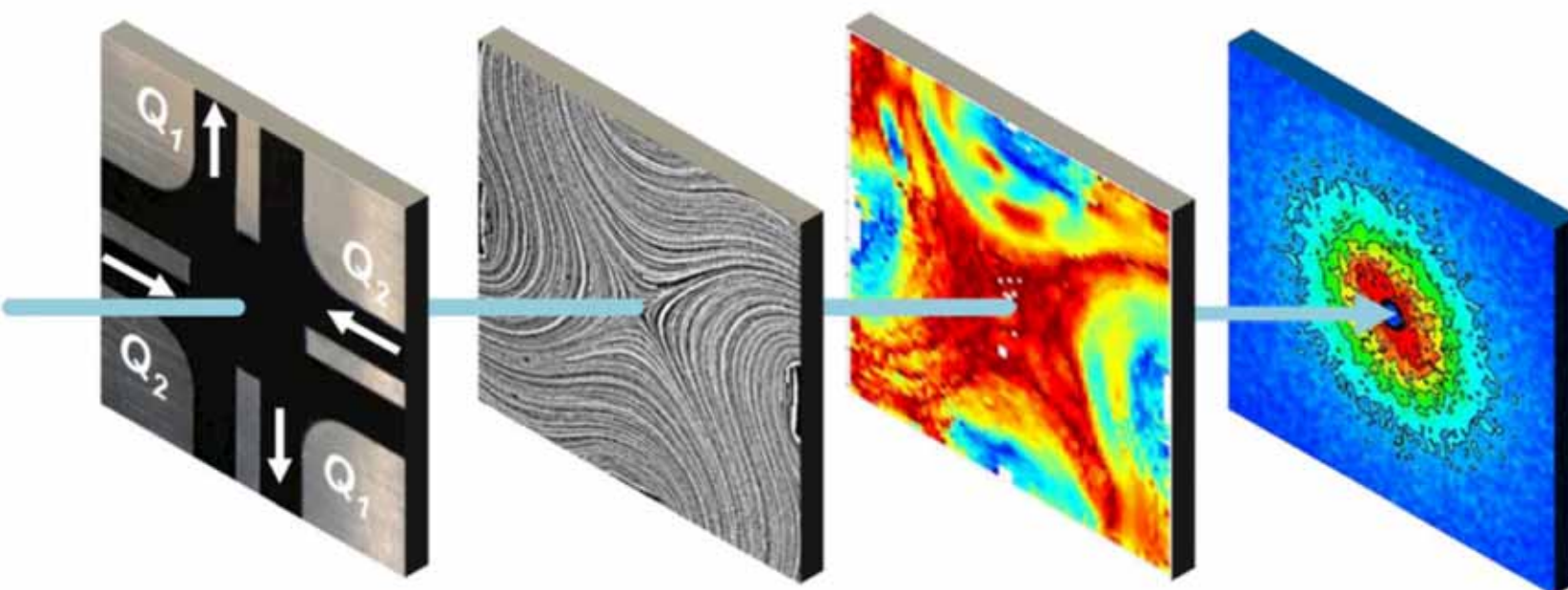
Review
Microfluidic Nanomaterial Synthesis and In Situ SAXS, WAXS, or SANS Characterization: Manipulation of Size Characteristics and Online Elucidation of Dynamic Structural Transitions

Anan Yaghmur^{1,*} and Islam Hamad²

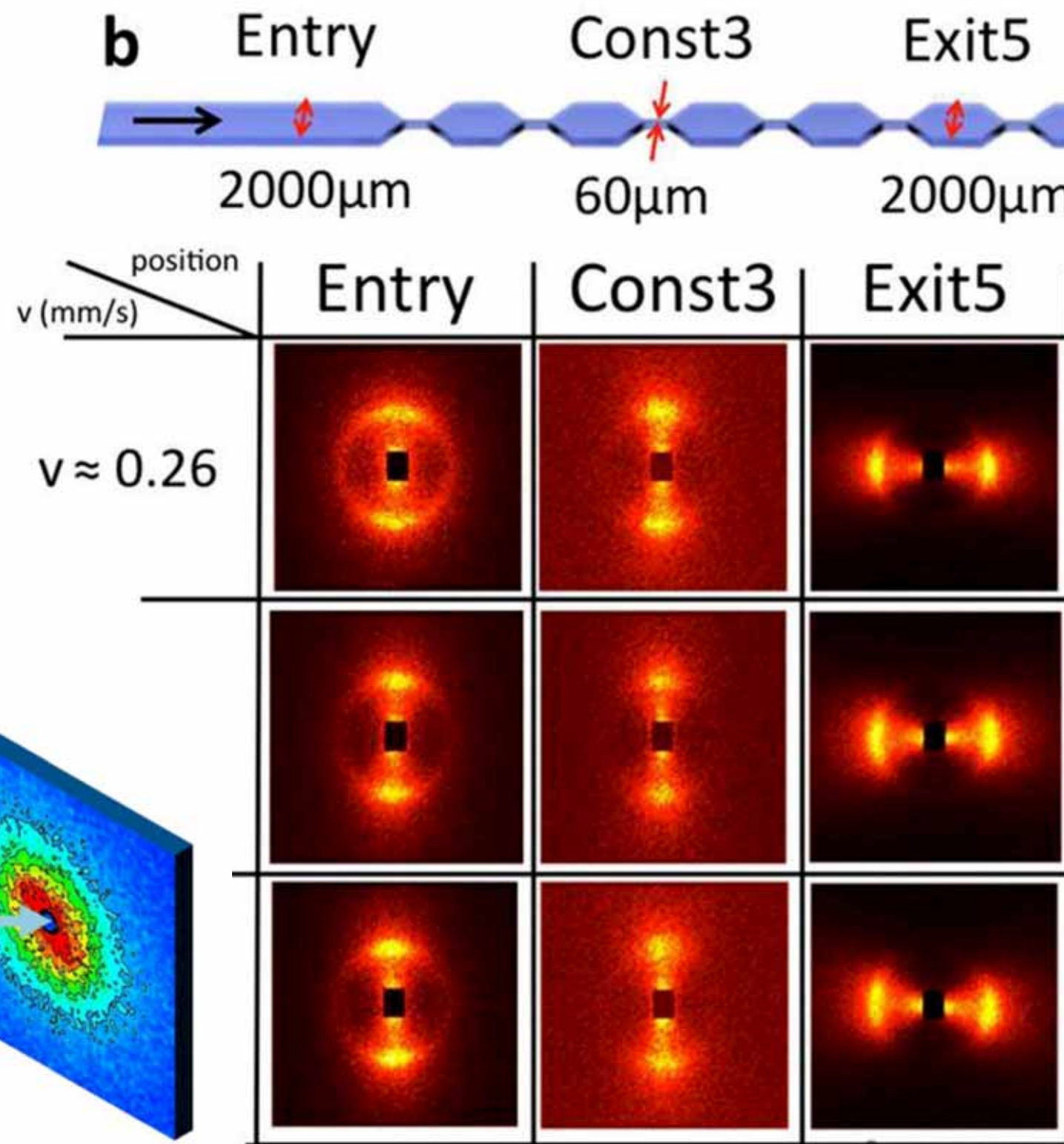
 micromachines Micromachines 13 (2022) 167 

Review
A Review of Microfluidic Devices for Rheological Characterisation

Francesco Del Giudice



Corona et al.: Sci. Rep. 8 (2018) 15559



Lopez et al.: Sci Rep. 5 (2015) 7727

Closing remark on the use of scattering techniques



Choose your problem and attack strategy wisely:

Only go for Rheo-SANS and Rheo-SANS, when you have a very, very **clear question** and attack strategy. Otherwise it is waste of time and resources.

Experiments should focus on one aspect with a clear set of parameters.

Always discuss with your beam-line scientist.

Your sample and rheometer should work super smooth prior you go to the beam-line.

Have plan B (even better plan B to plan M) ready.

Have fun with rheo-scattering!