Rheology and scattering methods
(SANS and SAXS under flow)

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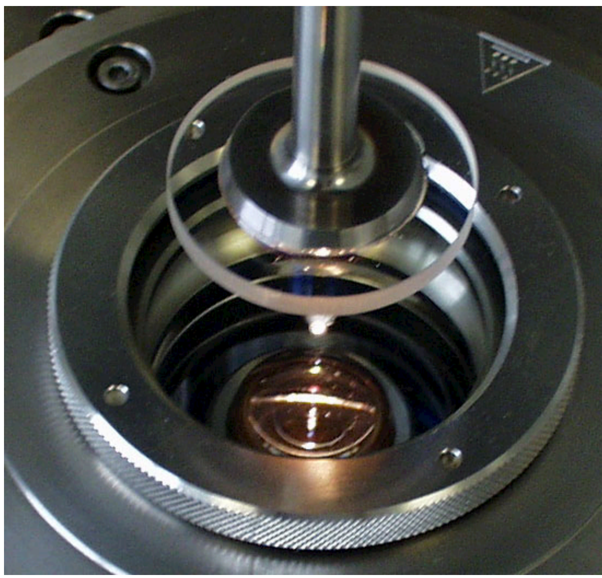
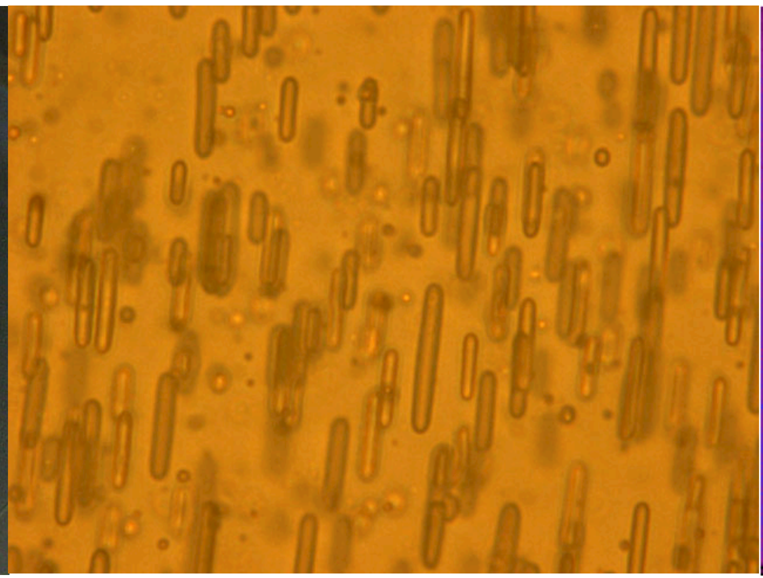
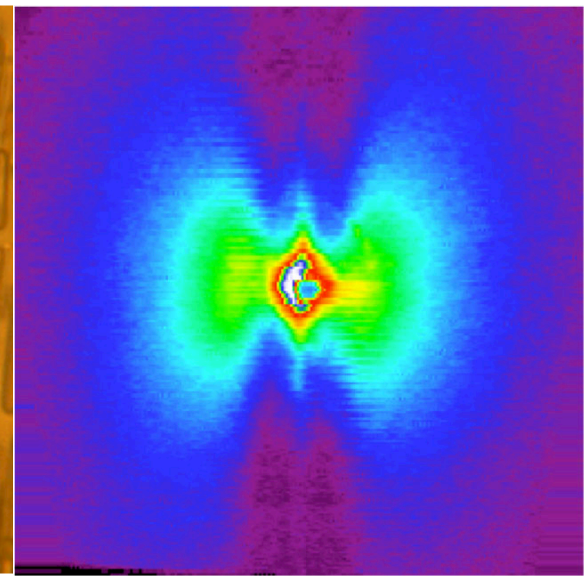
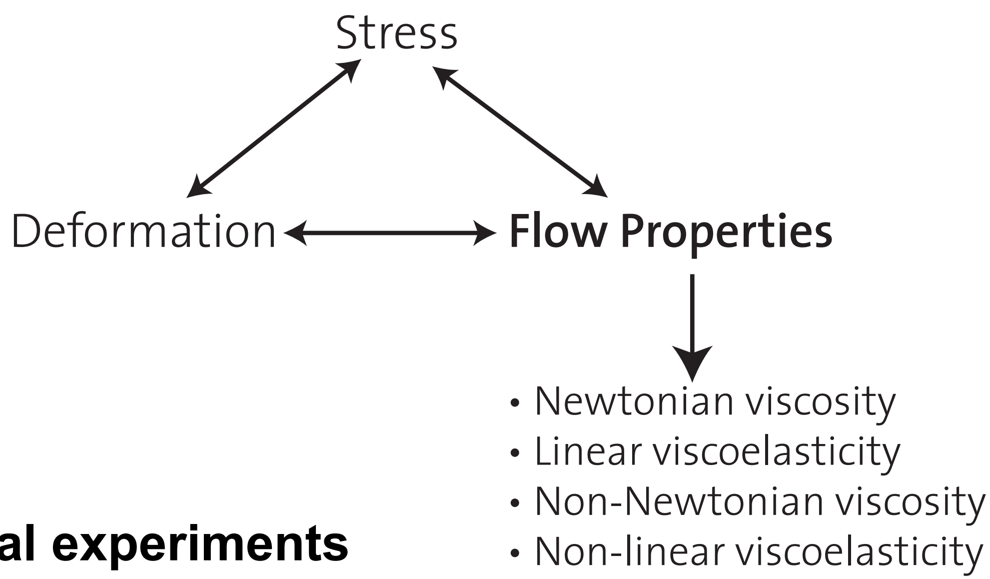




Rheology: Study of deformation and flow of matter[1]

Constitutive Equation:
Stress = Flow Properties • Deformation

παντα ρει – **Everything flow[2]:**
Polymers, colloids, food & pharma, biology, geology, ...



Information obtained from rheological experiments

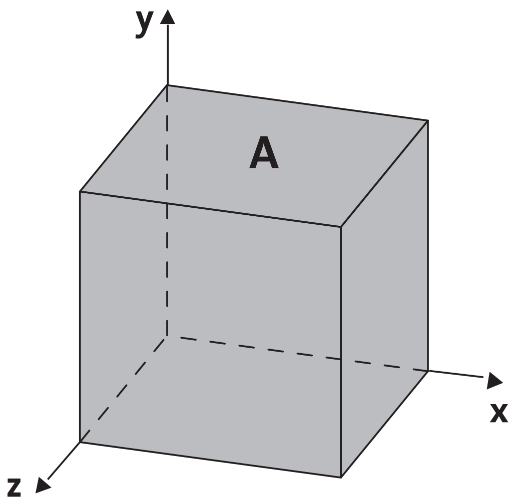
1) Flow properties
Macroscopic properties (viscosity, elasticity, viscoelasticity, ...)

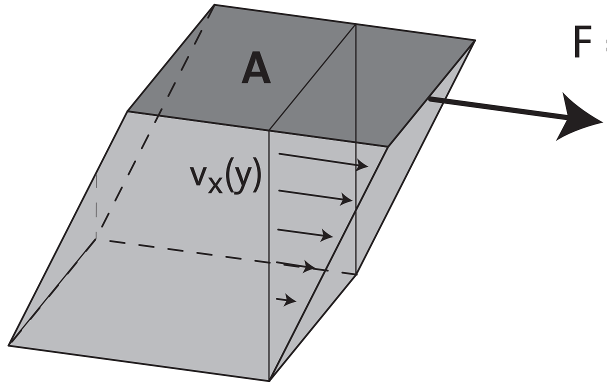
2) Molecular Structure
Flow as fingerprints of morphology, conformation, orientation, ….

3) Link between Structure development, process optimization, …[3]

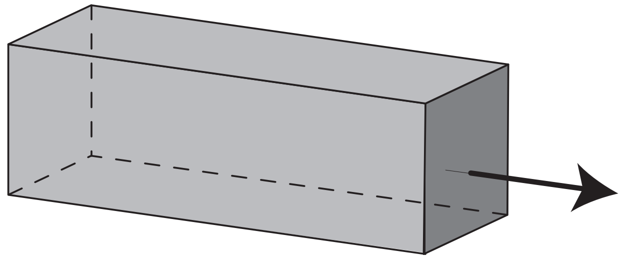
[1] E.C. Bingham & M. Reiner (ca. 1932), [2] Heraklit von Ephesus (550 - 480 B.C.)
[4] Review: P. Fischer, et al.: Comptes Rendus Physique 10 (2009) 740

Rheology: Shear and elongation

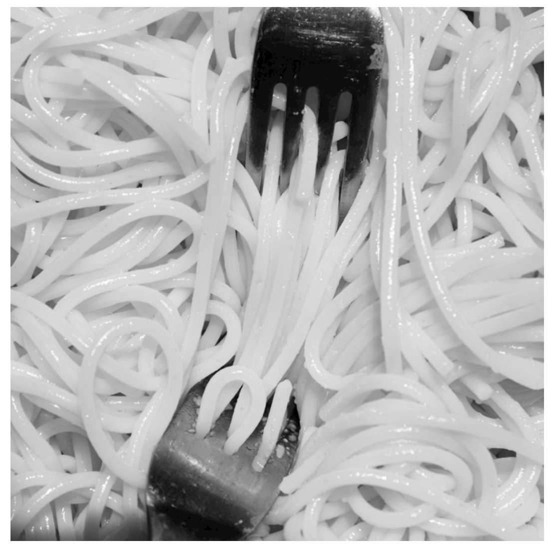




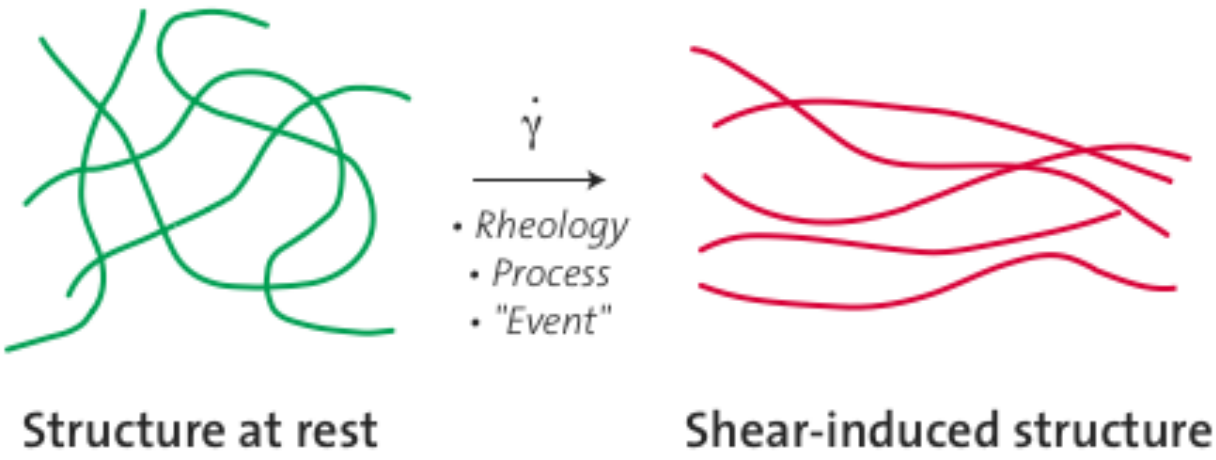
$F = \tau A$



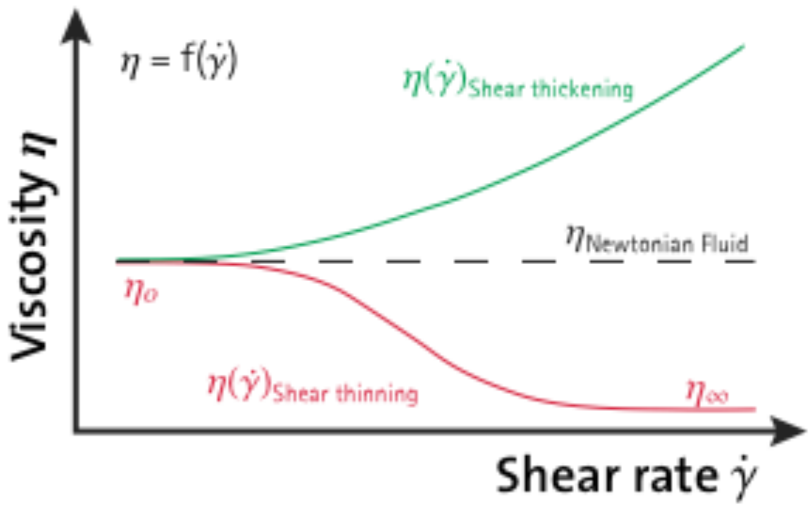
At Rest | **Under Shear Flow** | **Under Elongational Flow**



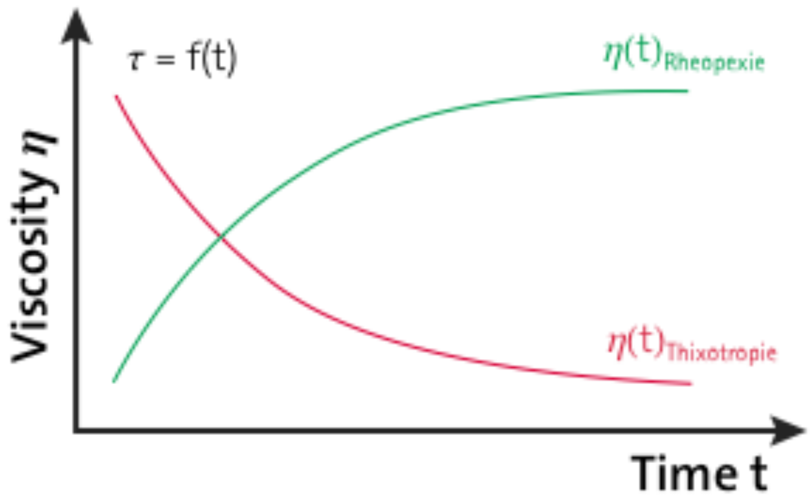
Rheology: Newtonian and non-Newtonian flow



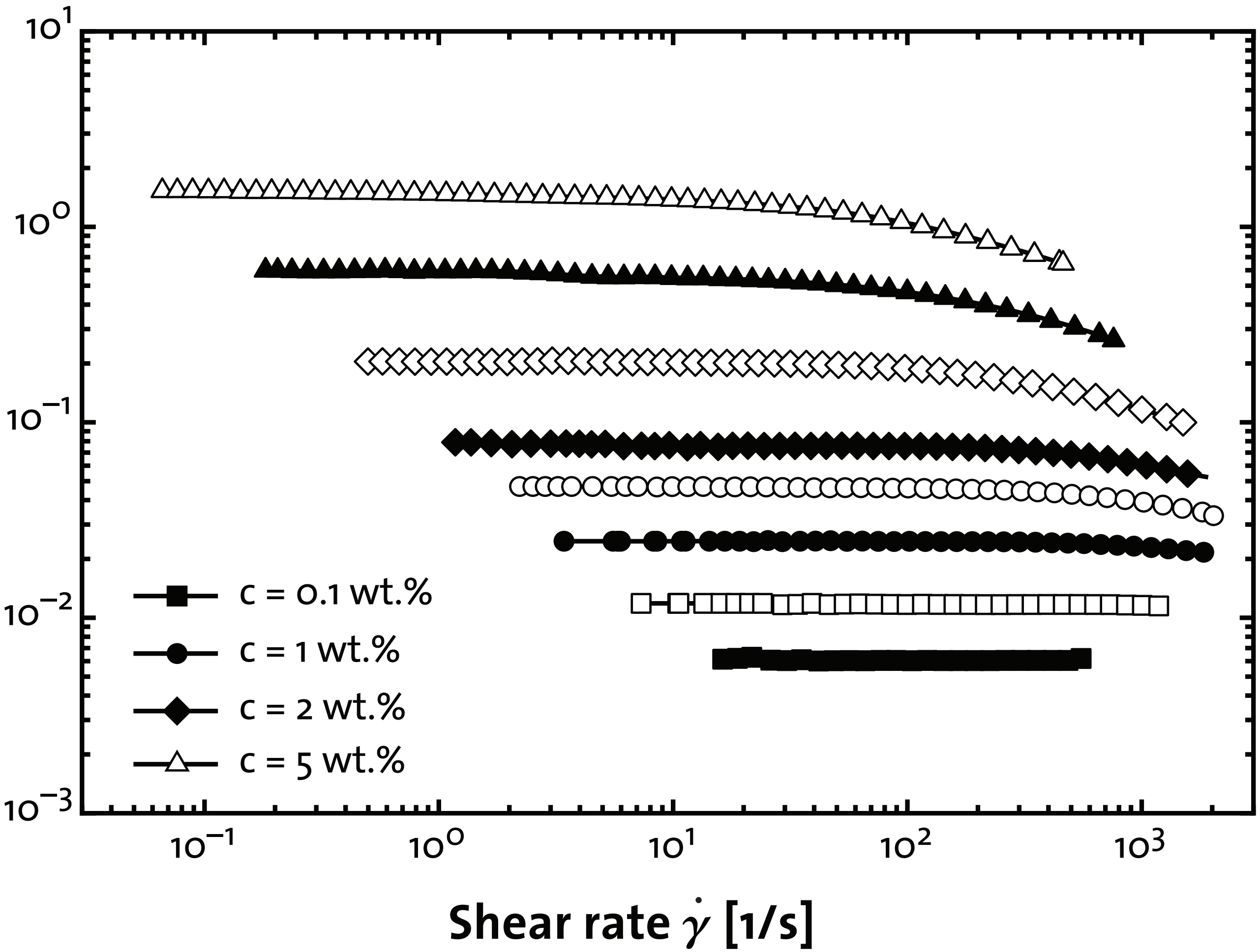
Effect of shear:

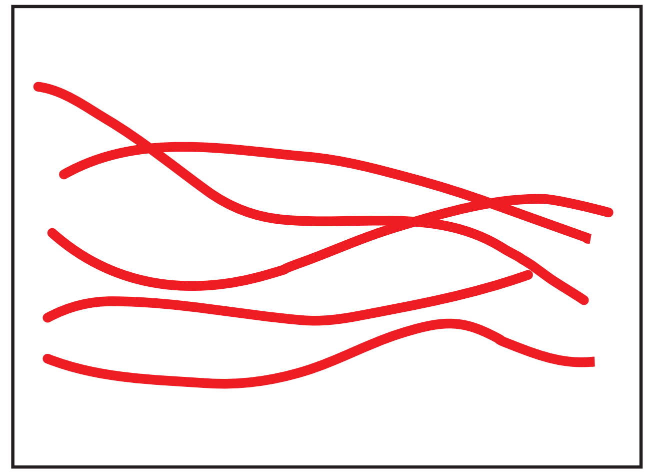


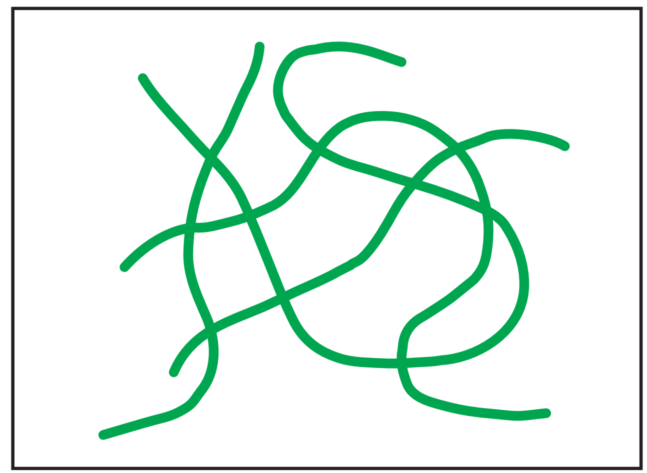
Effect of time:



Rheology: Shear-thinning in polymer solutions

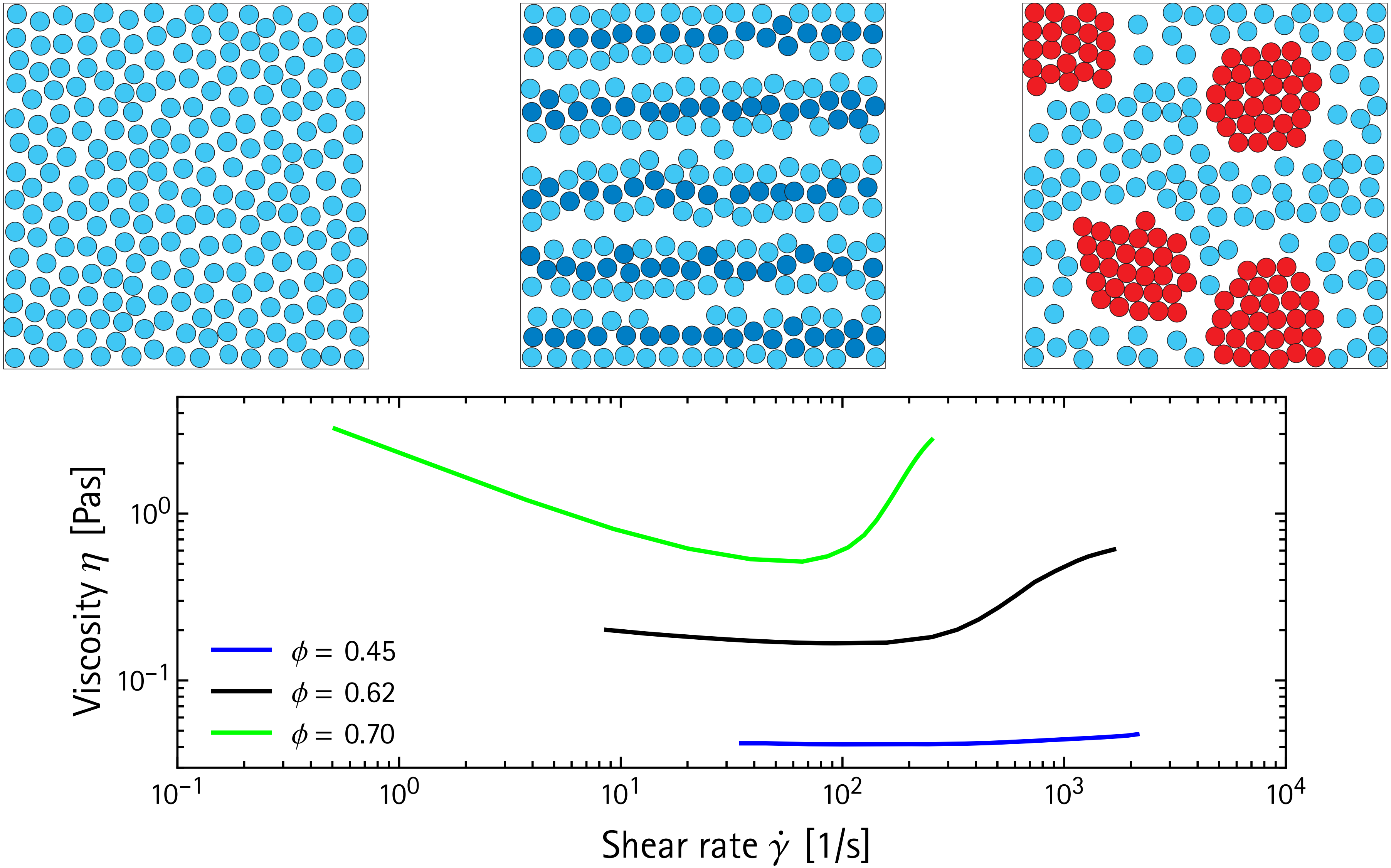






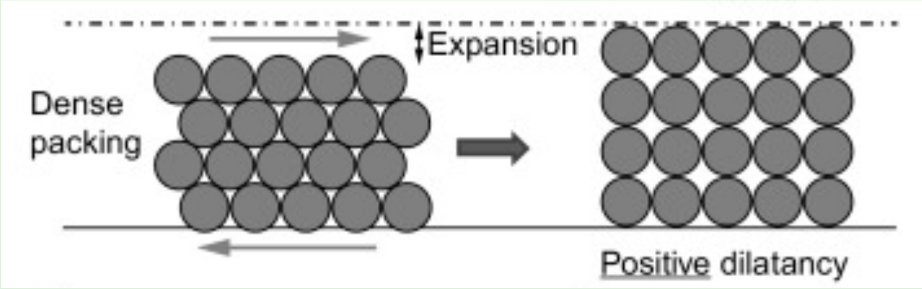
Flow curve of aqueous κ-carrageenan solution (concentration c = 0.5 to 6 wt%). The increase of concentration leads to an increase in viscosity and a shift of the onset of the shear thinning behavior (log-log plots are commonly used).

Rheology: Shear-thickening & dilatancy in suspensions



Rheo-Disaster: Dilatancy at the beach

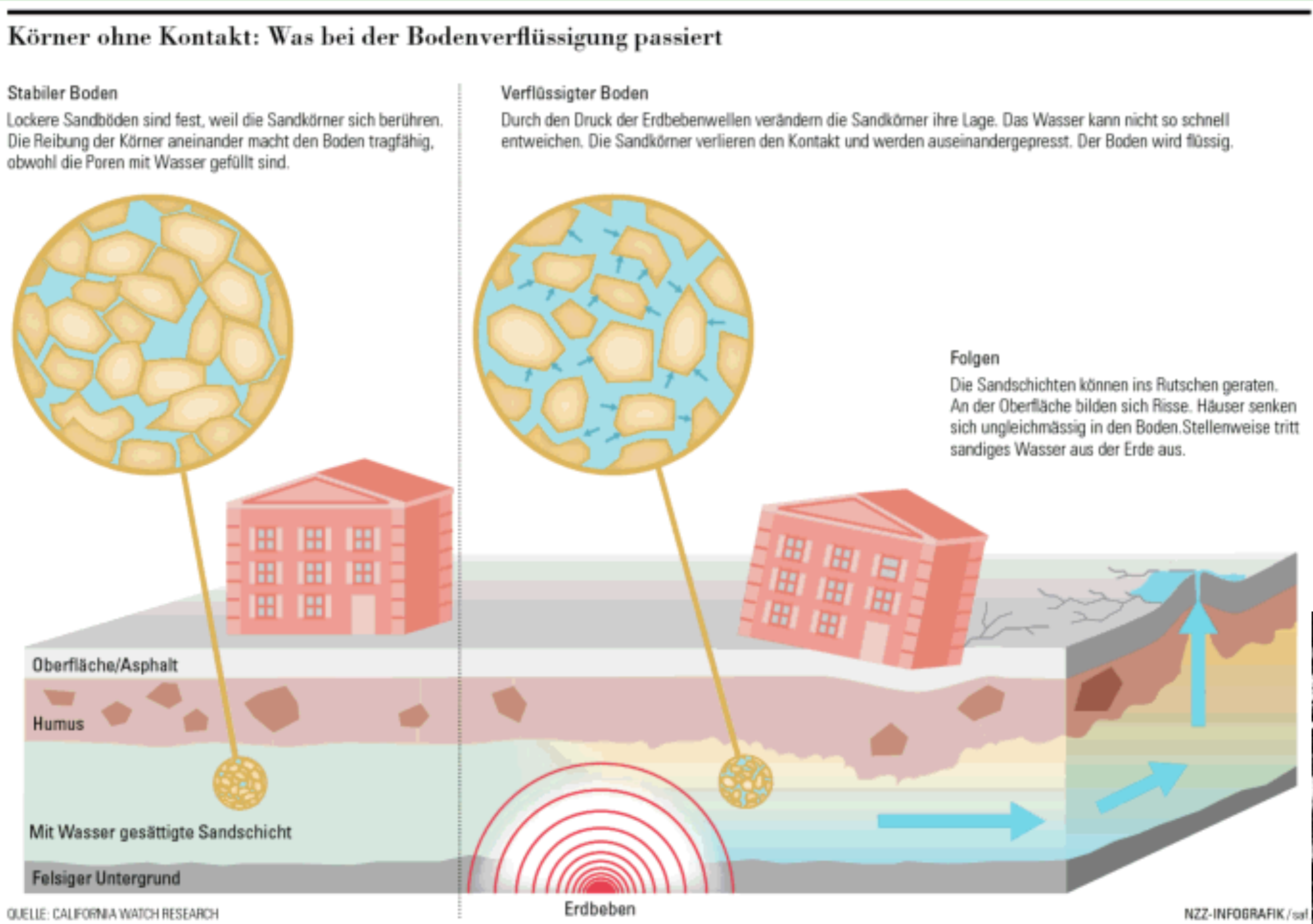
Structure at rest: Sand fully saturated with water.



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

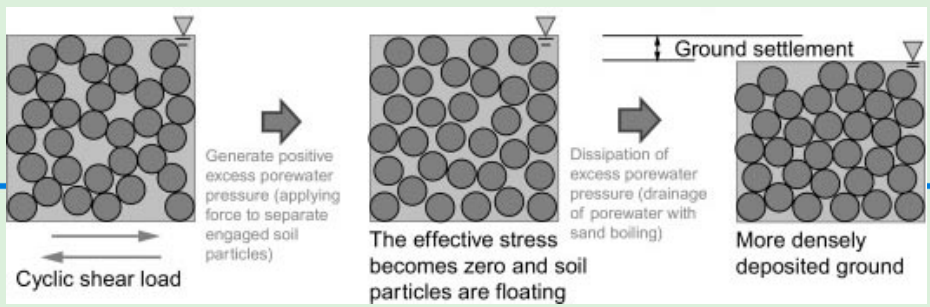
http://mpegmedia.abc.net.au/science/articles/mp4/sand_experiment.mp4

Rheo-Disaster: Dilatancy during earthquakes



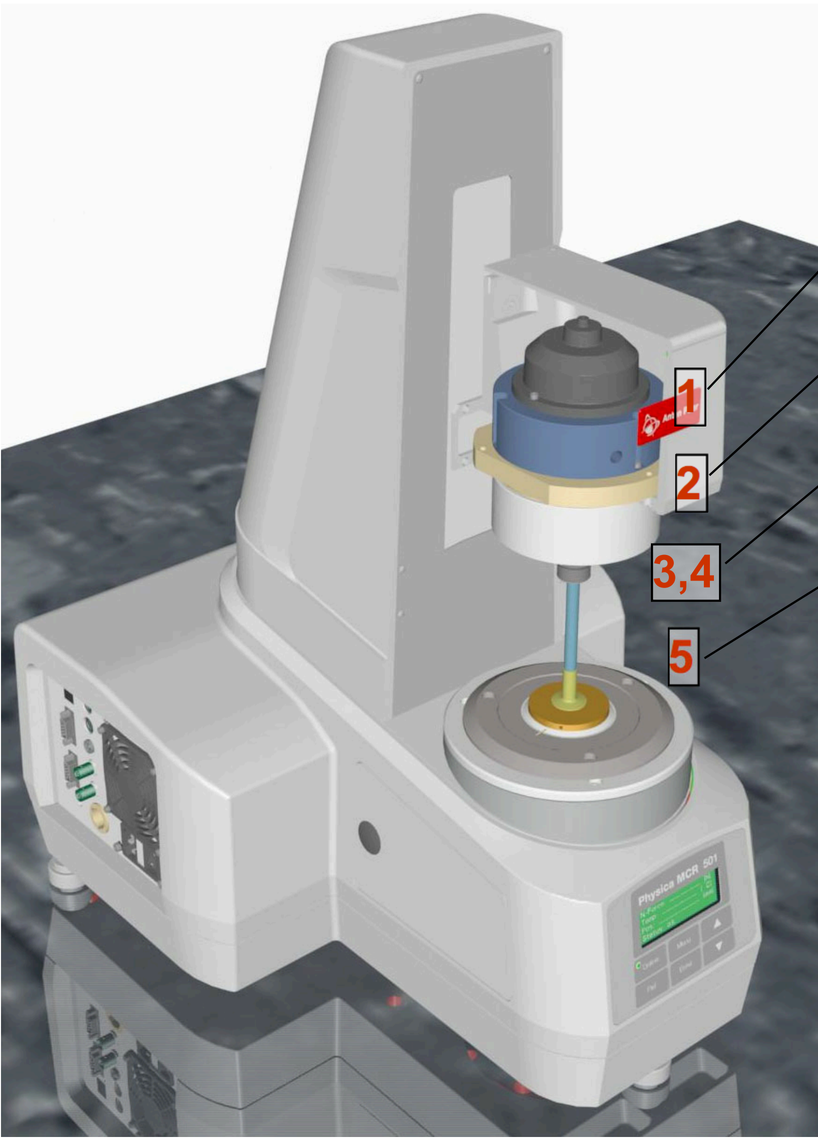
Christchurch/New Zealand

Niigata/Japan



Standard rotational rheometers

Design of a rotational rheometer



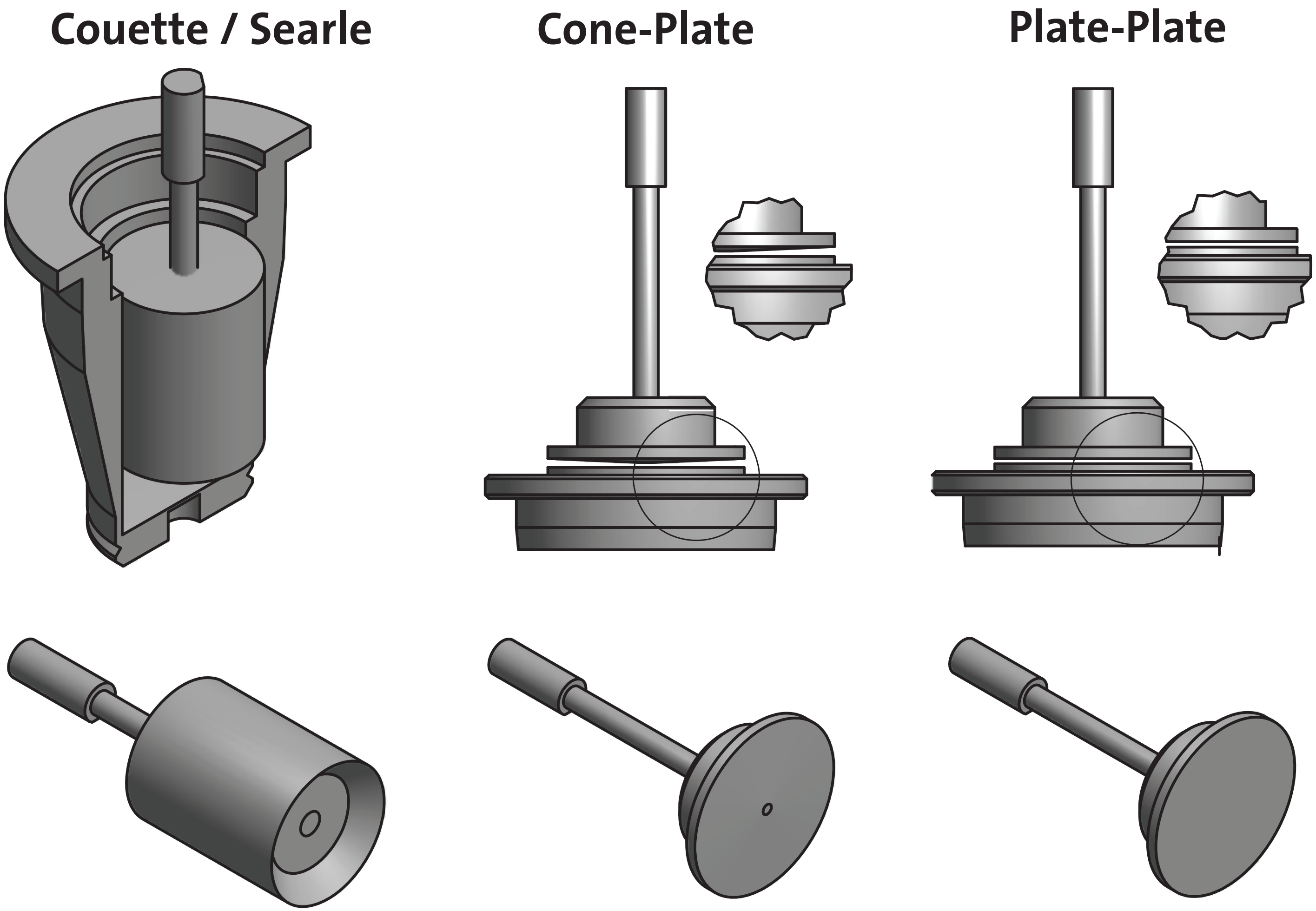
Optical Encoder

Motor (drag cup, EC)

Air Bearing & Normal Force Sensor

Measuring geometry

Standard measuring geometries

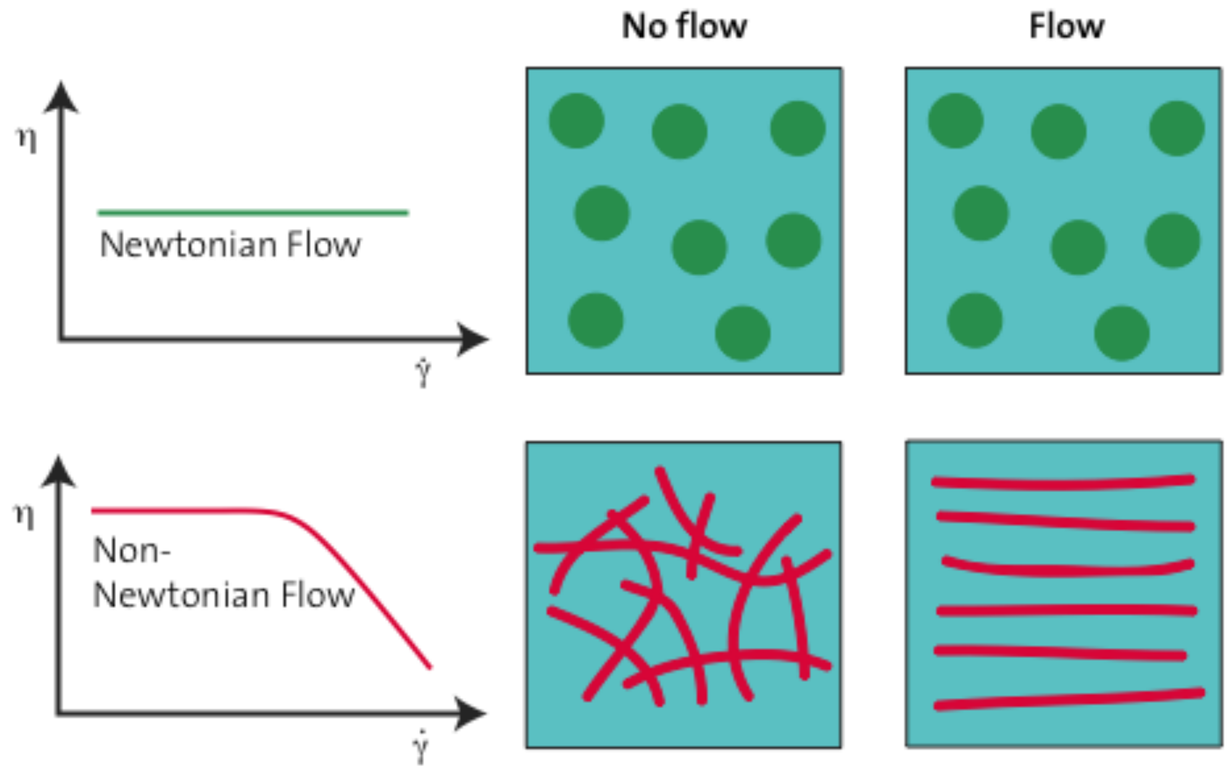


Raw data such as torque, normal torque, angular velocity, and angular displacement are transferred into rheological data via geometry factors

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:

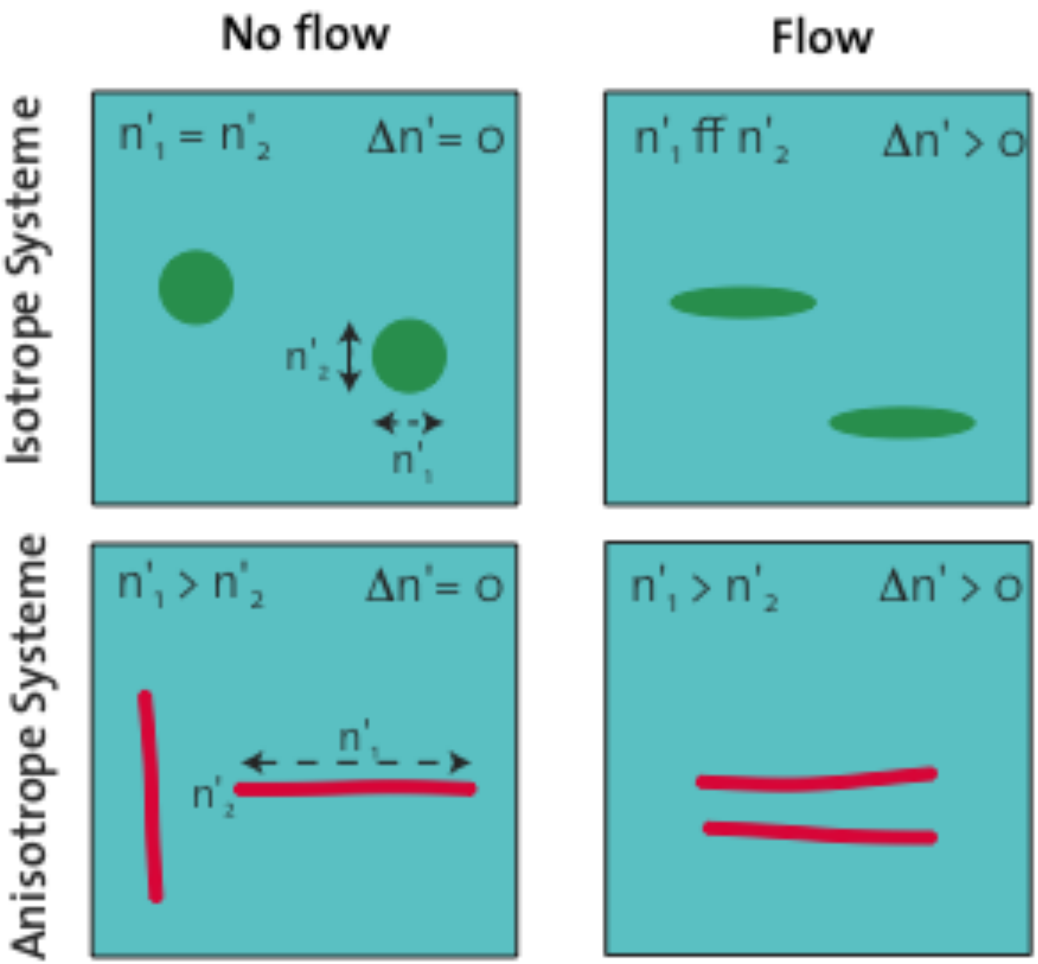
Superposition of rheology and an external field

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



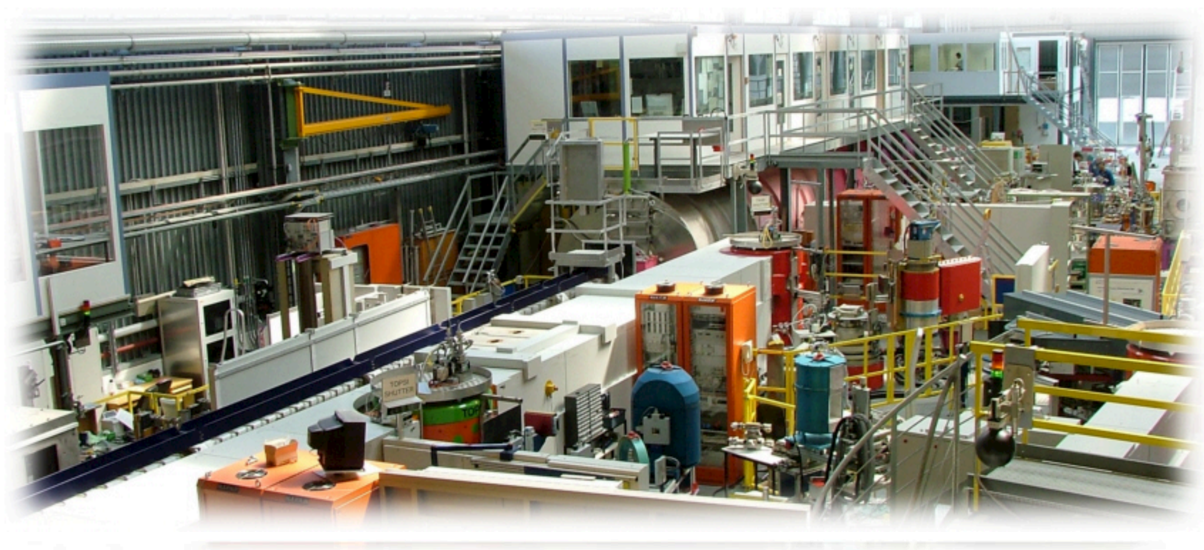
Changes in form or changes in alignment are used to investigate orientation effects in flow fields

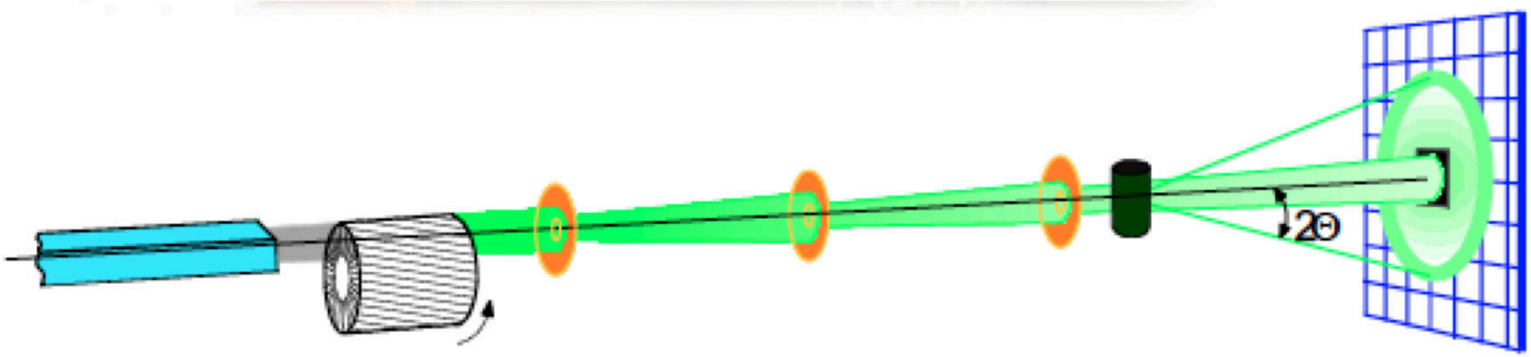
• Deformable object like droplets or bubbles align and deform under flow. The optical properties change in line with the deformation.

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

Rheo-Scattering methods (SALS, SANS, SAXS)

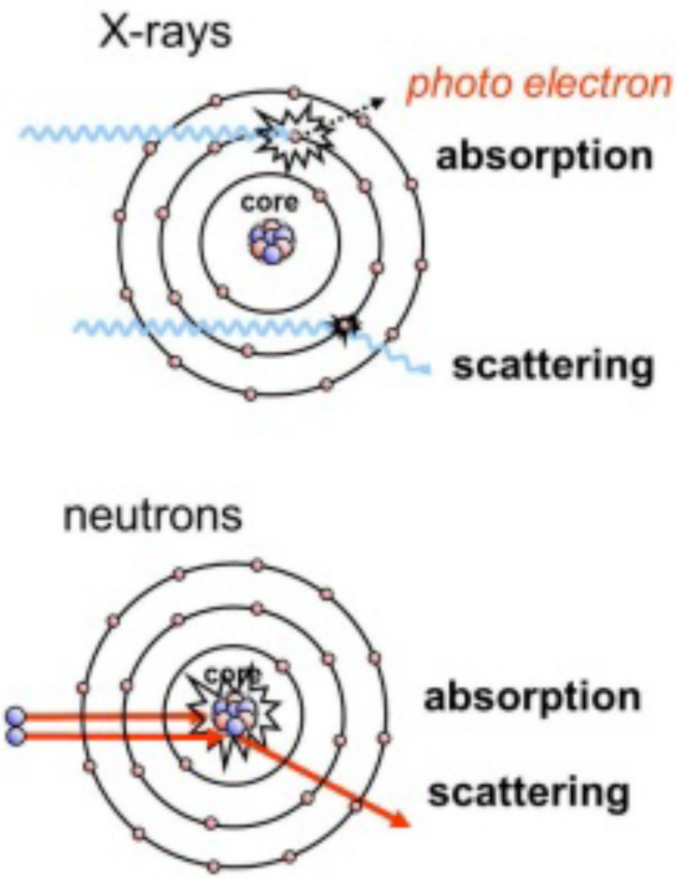
Small Angle Neutron Scattering (SANS)
Small Angle X-Ray Scattering (SAXS)
Small Angle Light Scattering (SALS)

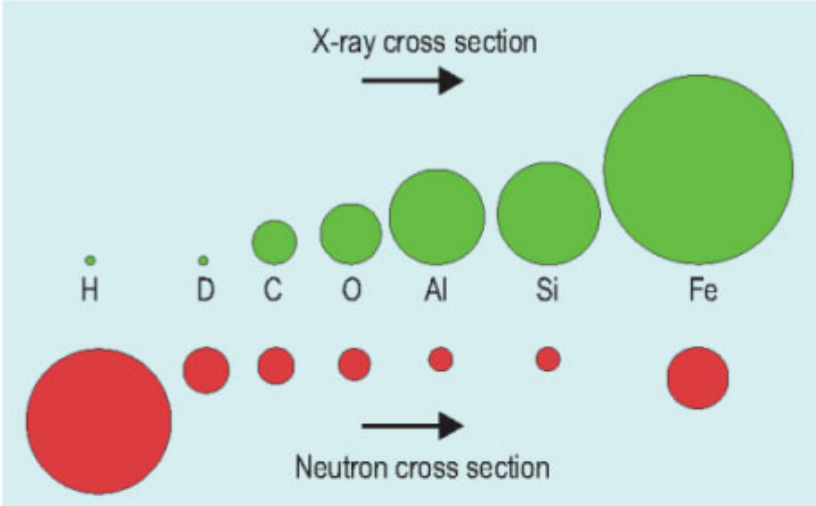




Neutron and X-ray scattering

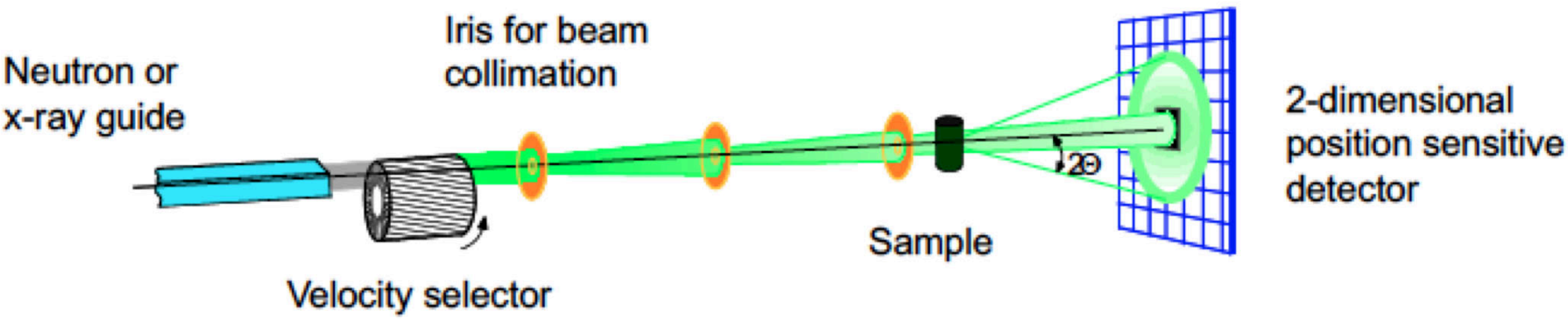
Interactions with matter:
- X-rays: electron density
- Neutrons: nucleus (isotope contrast)

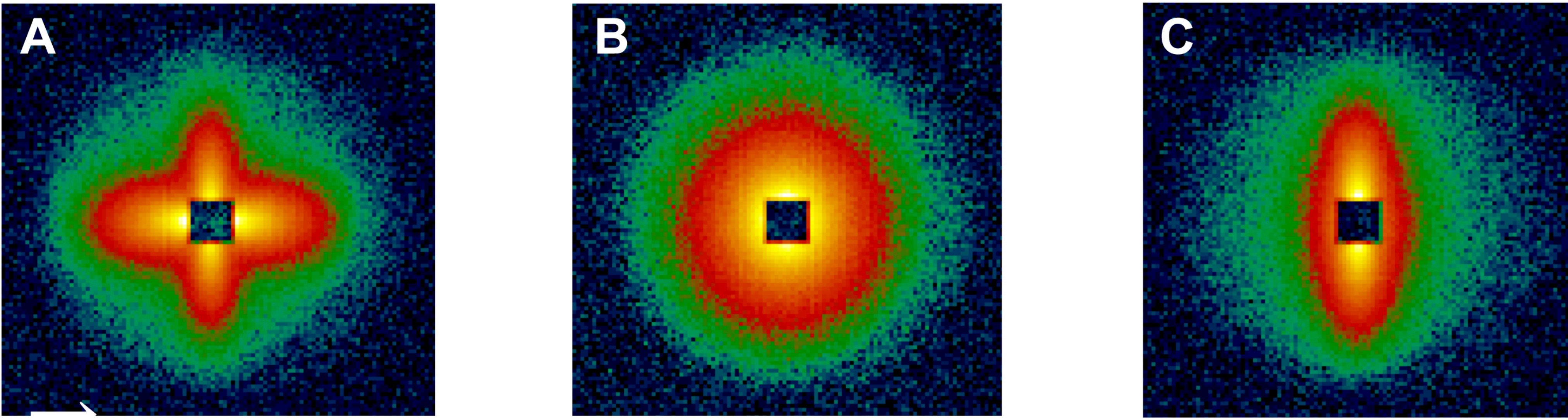




Neutron imaging

Principle setup and the obtained data

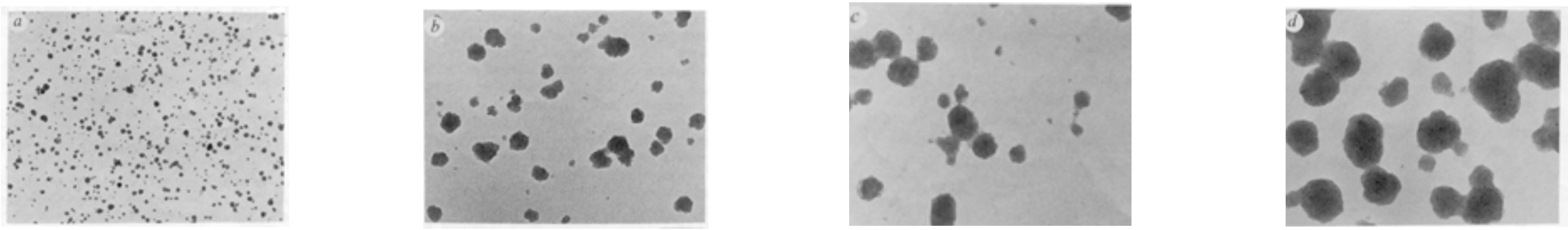




Color code correspond to scattering intensity, i.e. amount of neutrons or photons detected per unit area (yellow- high intensity, blue – low intensity)

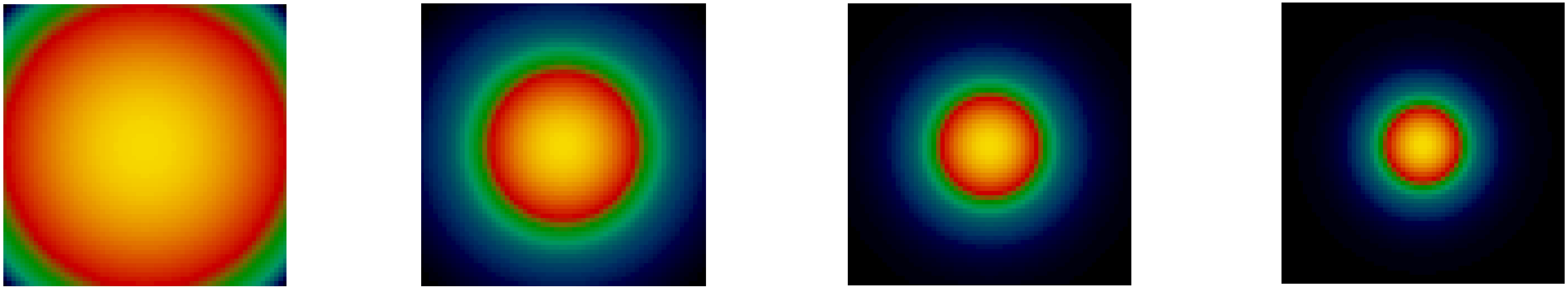
Real h(r) and reciprocal space $I(q)$ I

Dependency of SAS intensity on particle size:



larger particle sizes

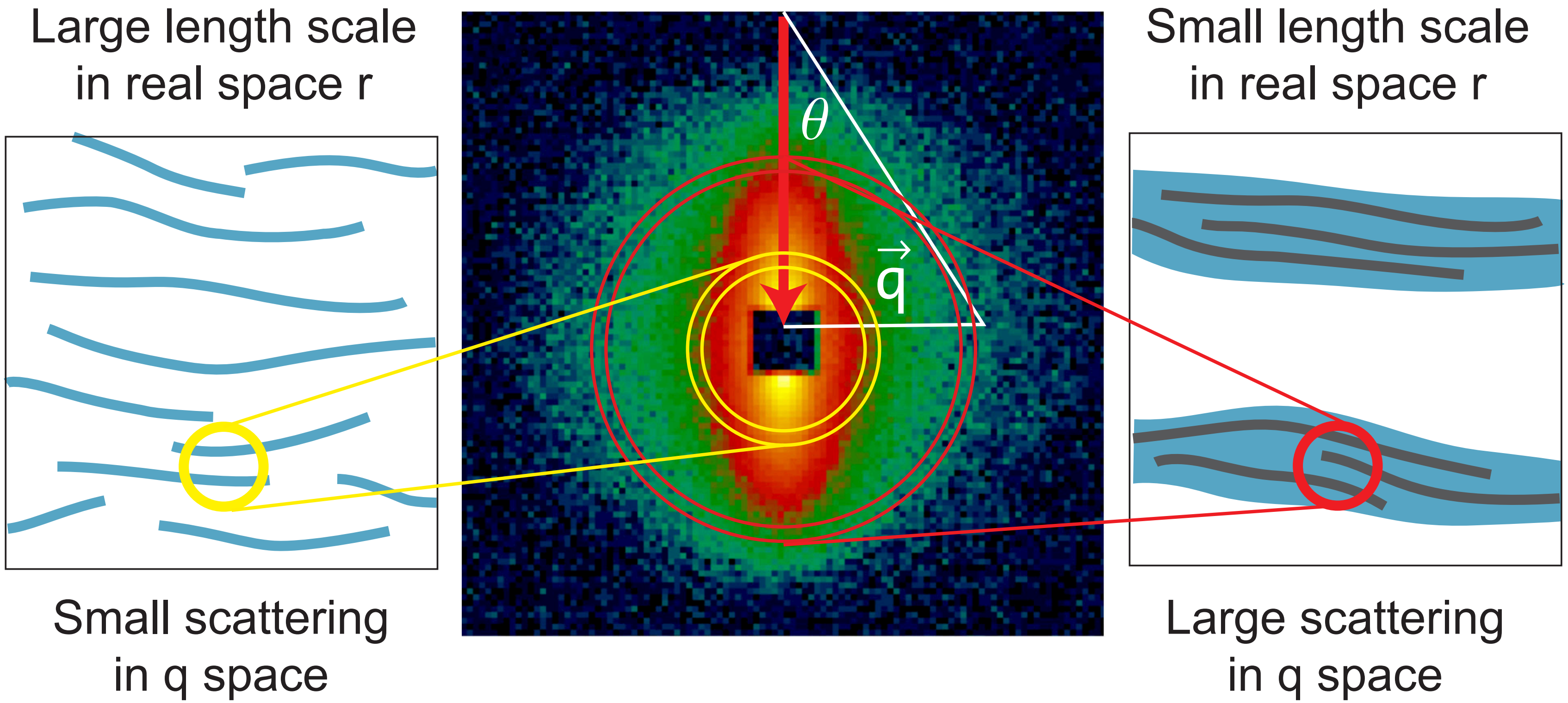
scatter at smaller angles



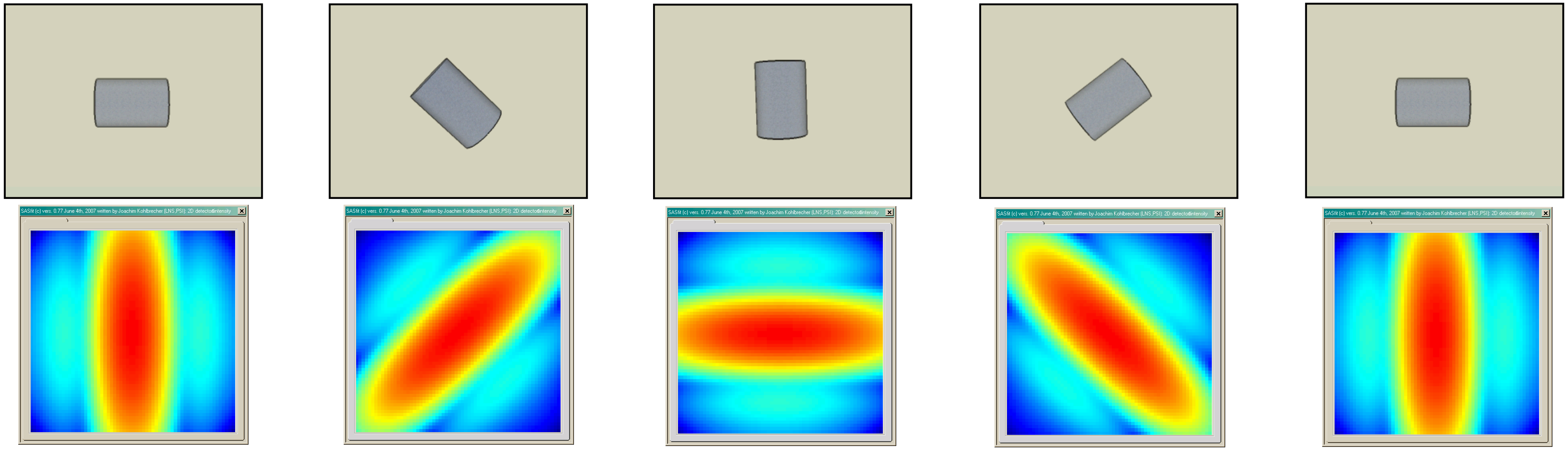
Real h(*r*) and reciprocal space *I*(*q*) II

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:

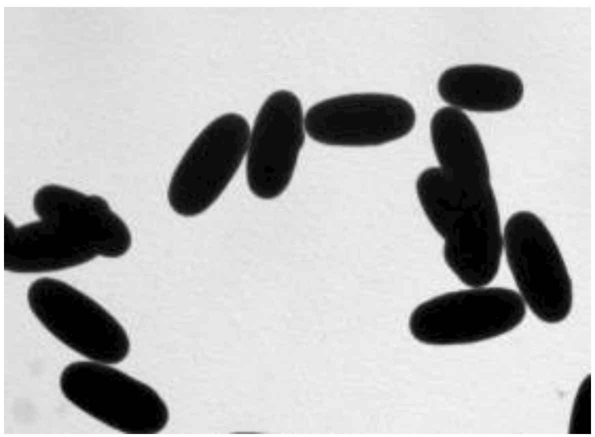
- Large structures lead to small scattering angles (small scattering vectors)
- Small structures lead to large scattering angles (large scattering vectors)
- Object shape is tilted by 90° in the scattered image

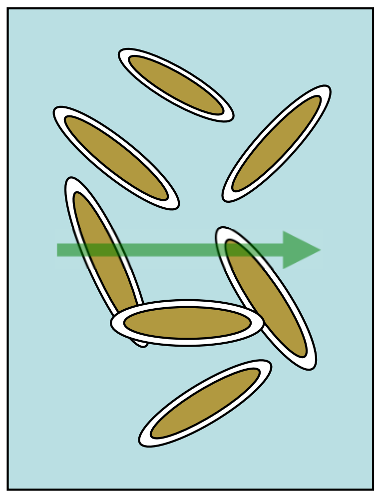


Scattering of anisotropic particles I

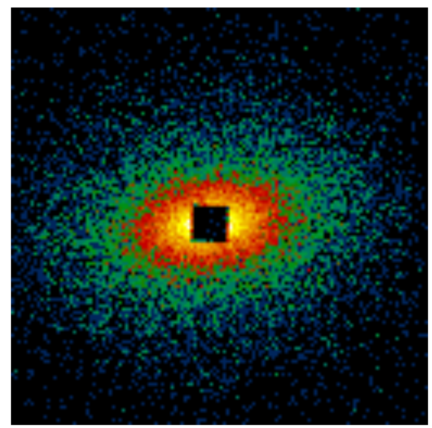


Silica coatings on α-Fe_2O_3 particles

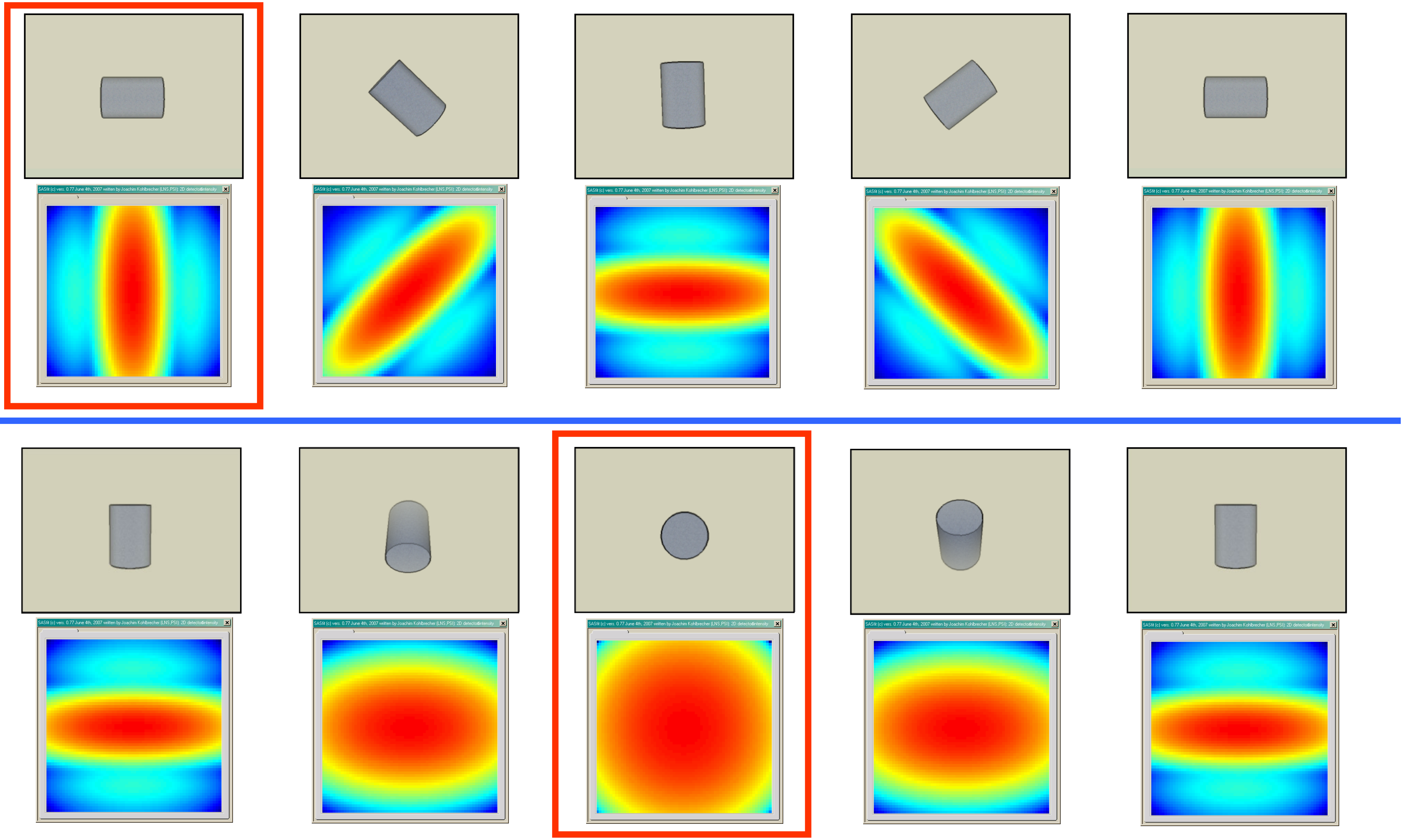




f=10Hz   B=5mT



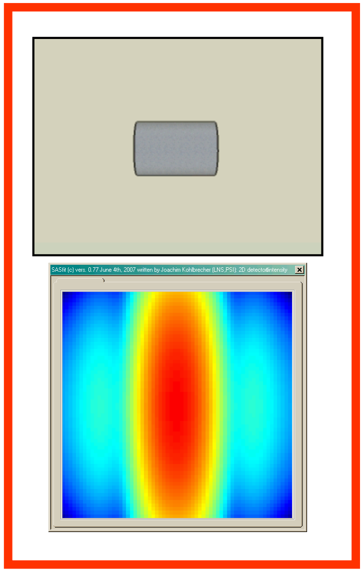
Scattering of anisotropic particles II

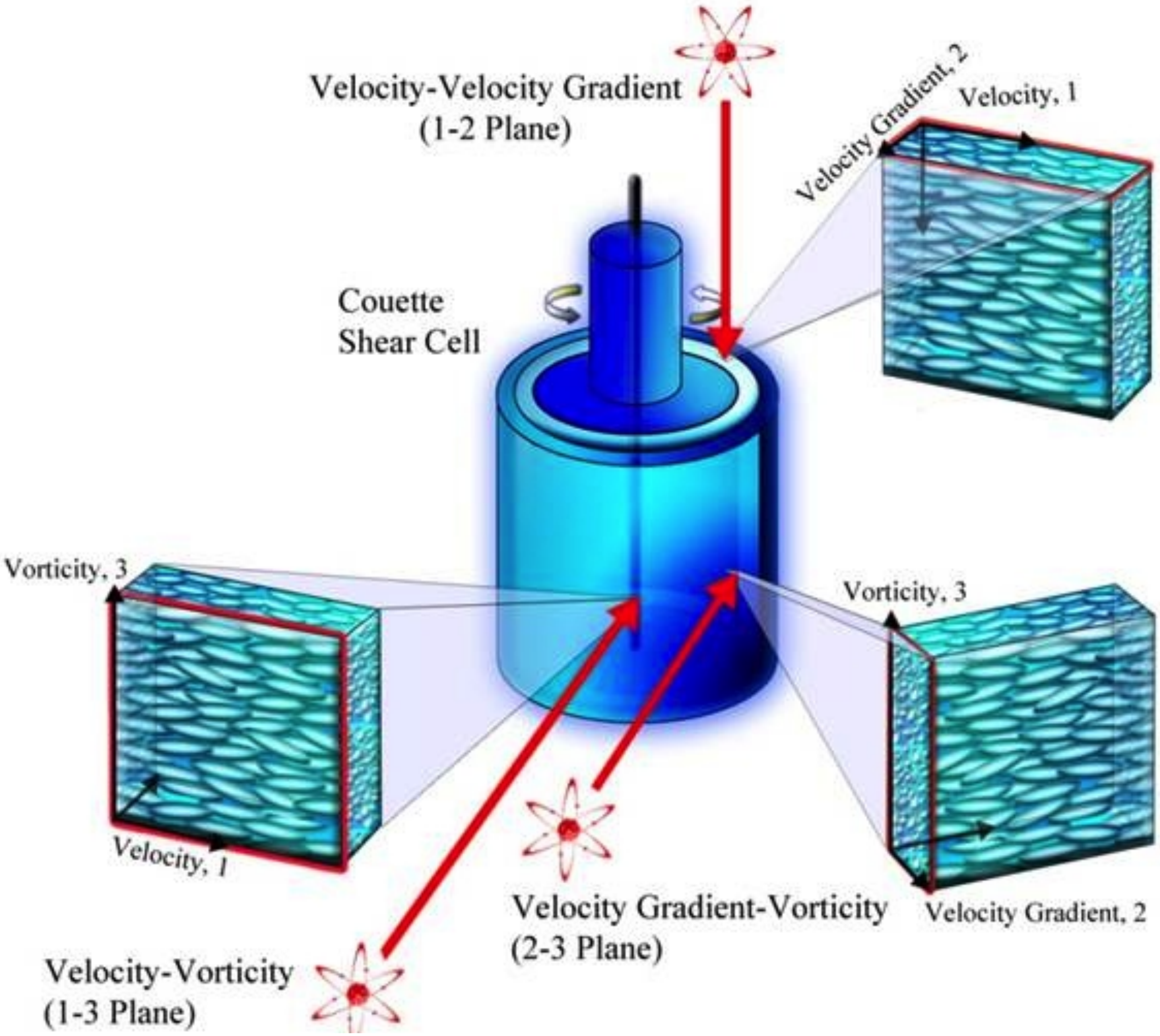


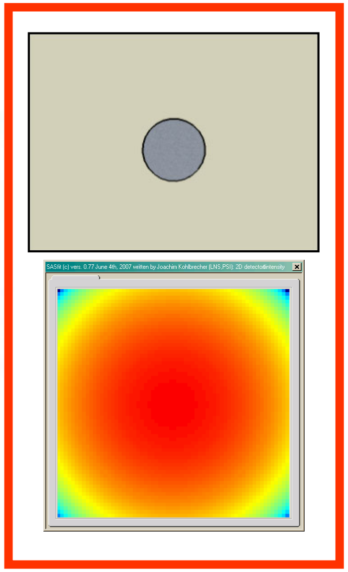
http://www.lookingatnothing.com/index.php/archives/349

Scattering of anisotropic particles III

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







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Swiss Federal Institute of Technology Zurich

PAUL SCHERRER INSTITUT

Slide by Norm Wagner, University of Delaware

Rheometer and flow cells I

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

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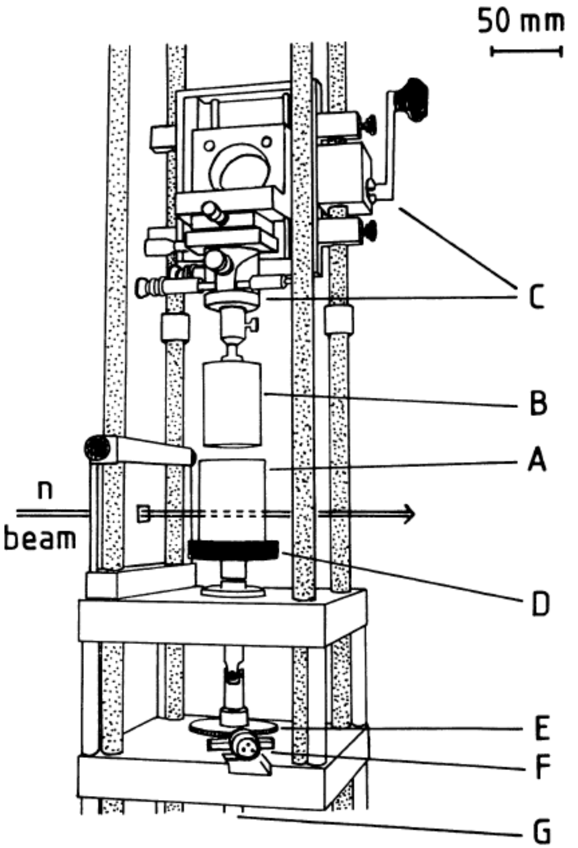

Fig. 2. — Schematic view of the central part of the apparatus. A : quartz-glass rotor, B : stator, C : support for adjustment, D : fixation with screw crap on turn-table, E : rotating cog, F : magnetic detector, G : connection to motor drive (not shown).

In situ rheometric shearing apparatus at the NIST Center for Neutron Research[1]

G.C. Straty[a], C.D. Muzny[a,*], B.D. Butler[a], M.Y. Lin[b], T.M. Slawecki[b], C.J. Glinka[b], H.J.M. Hanley[a]

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

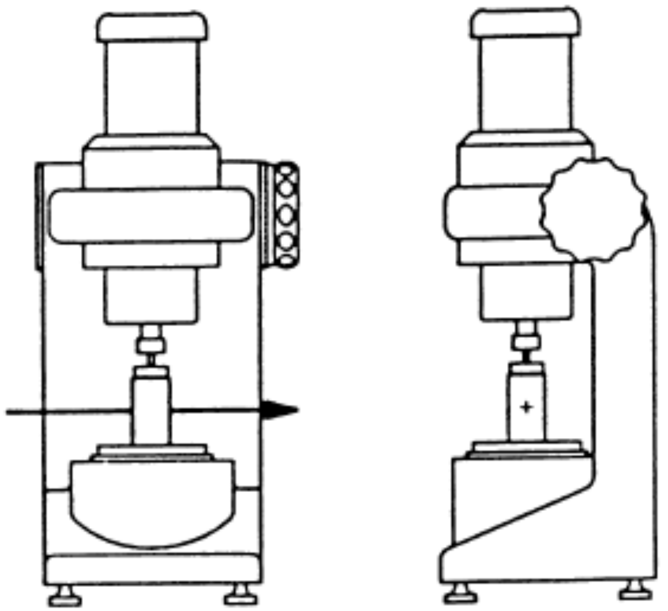

Fig. 1. Rheometer showing position of cell and beam direction.

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, Padulaan 8, 3584 CH Utrecht, The Netherlands

R. P. May
Institut Laue-Langevin, Grenoble, France

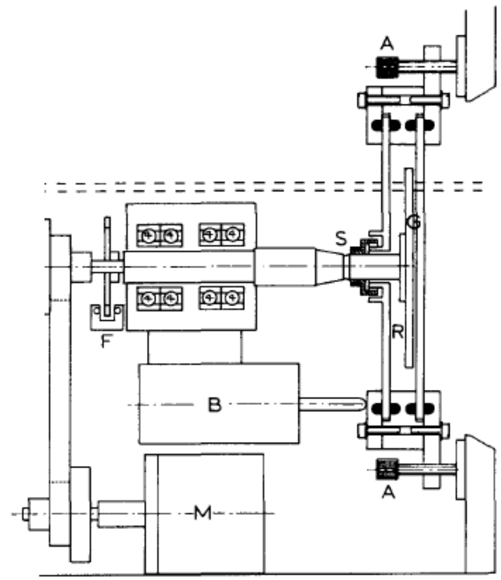

FIG. 1. Schematic diagram of the vertically mounted, parallel-plate flow cell: A, micrometer adjustment screws; B, micrometer distance sensor; C, position of incident neutron beam; F, encoder disk for angular velocity measurement; G, gap containing the sample; M, dc motor; R, rotating quartz disc; and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

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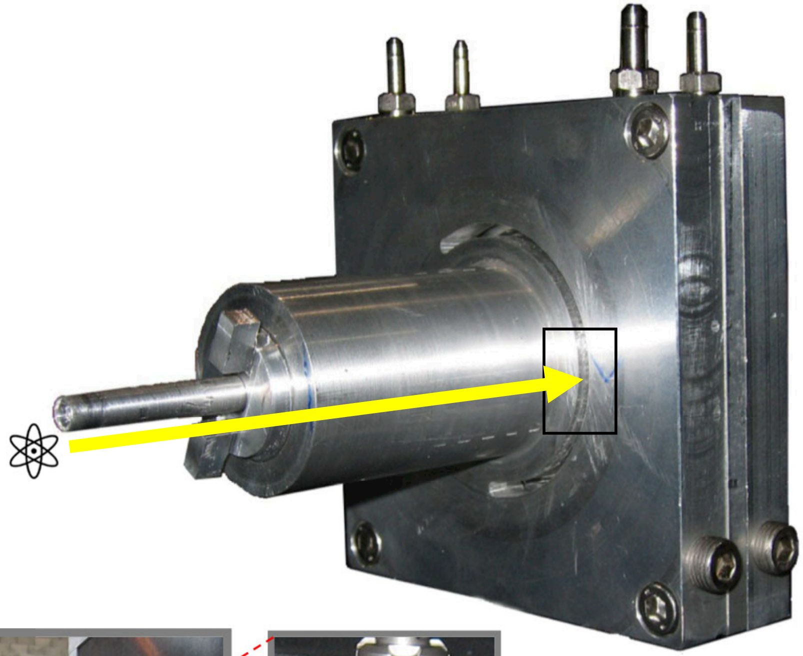
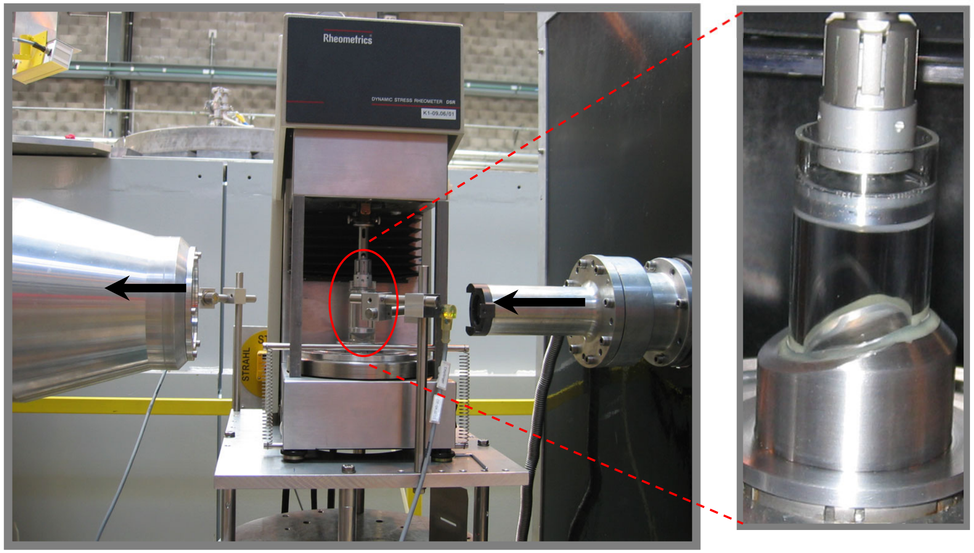
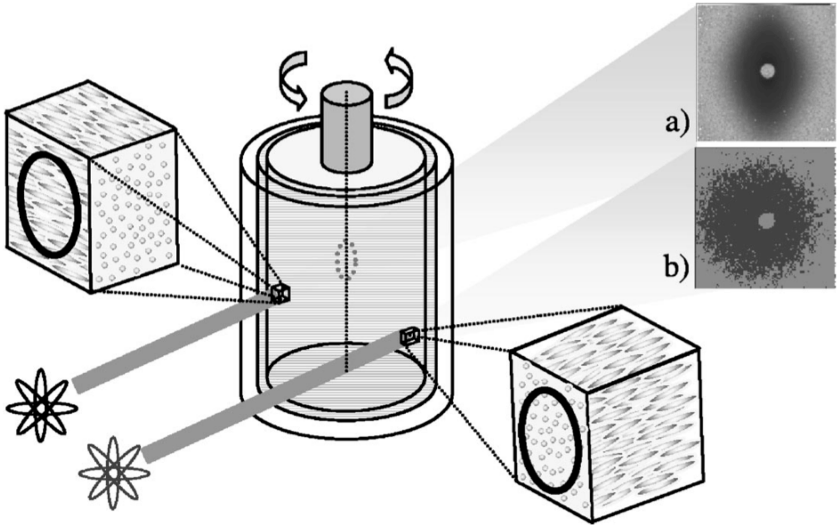
Rheometer and flow cells II

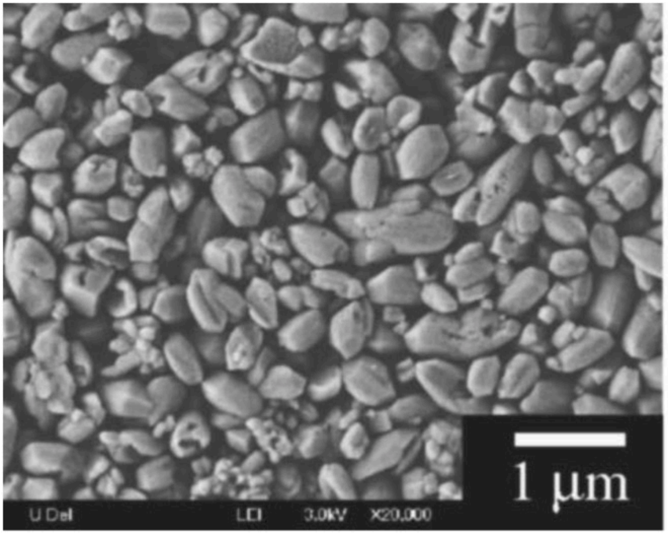




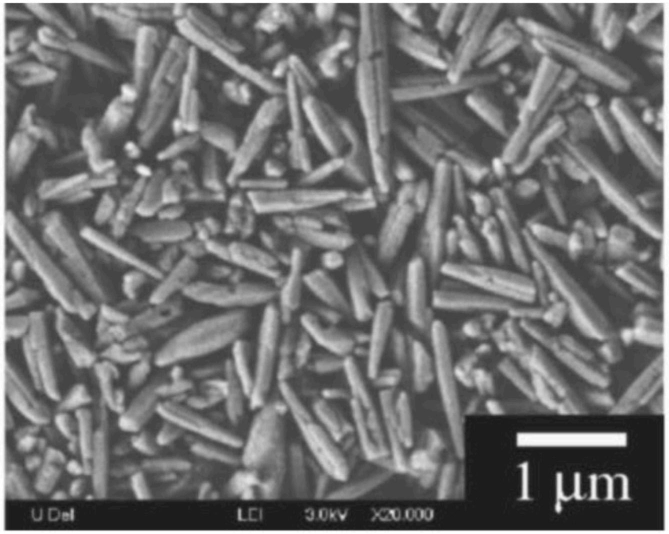
Example: Shear induced structure in suspensions I

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

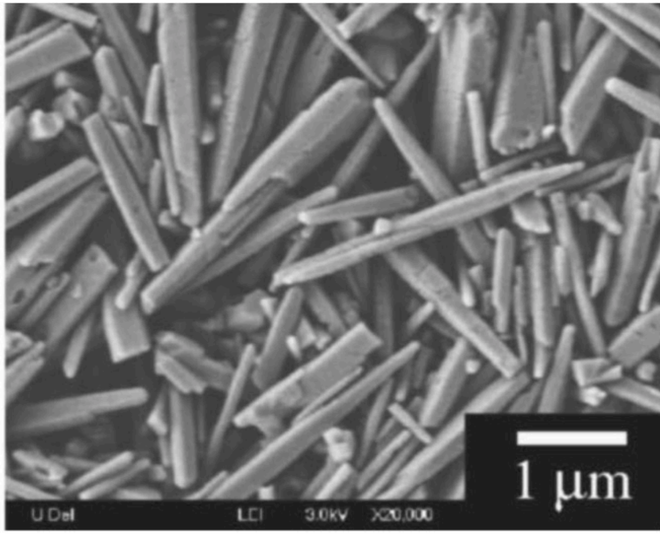




L/D: 2



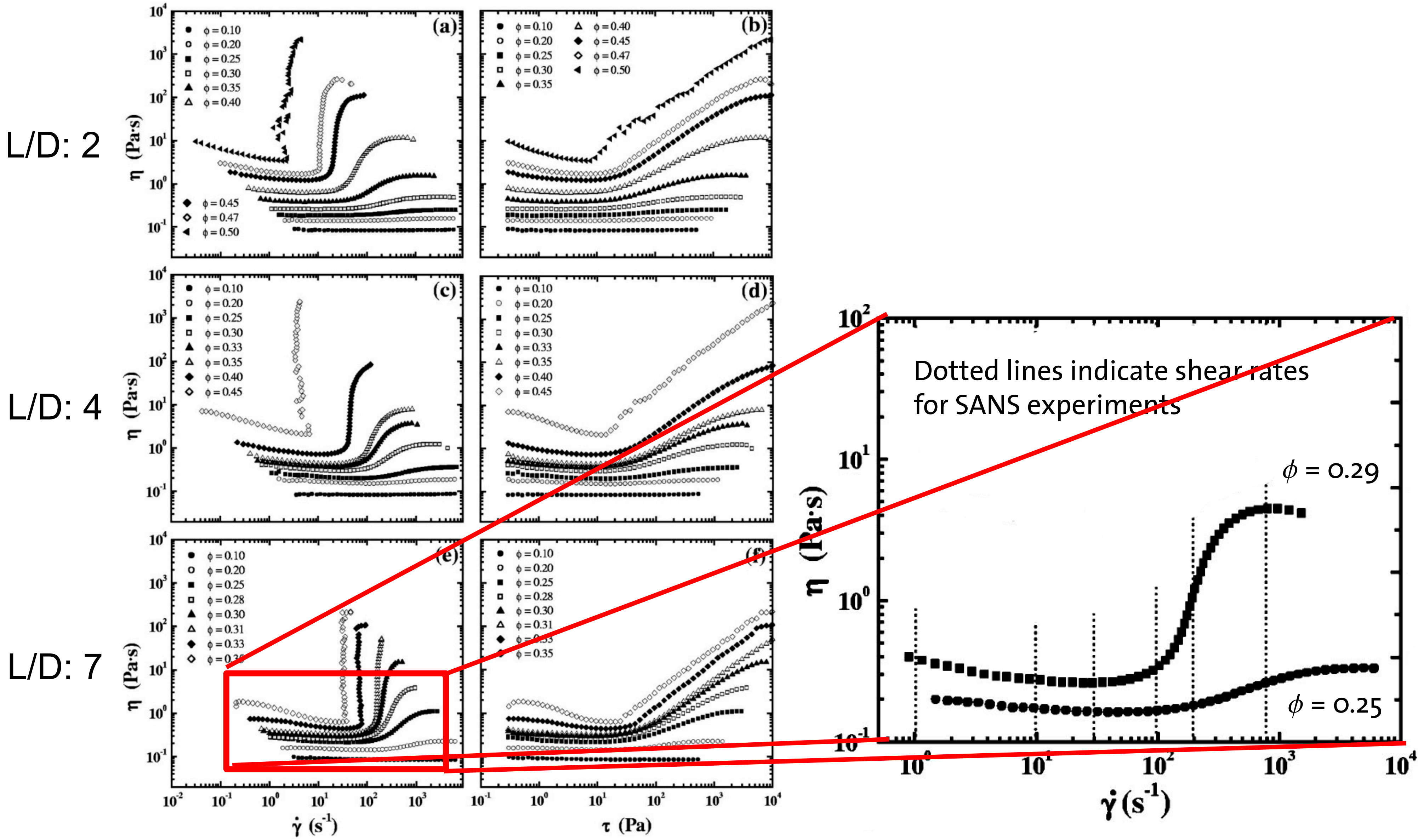
L/D: 4



L/D: 7

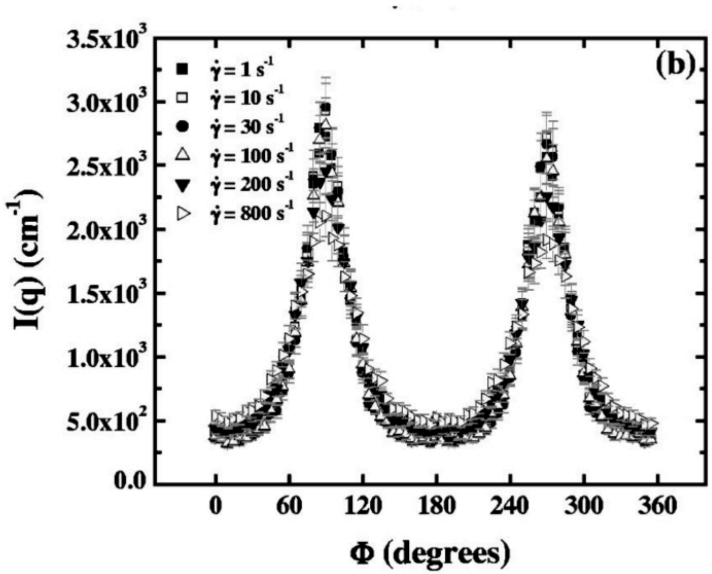
Egres RG, Wagner NJ: J. Rheol. 49 (2005) 719

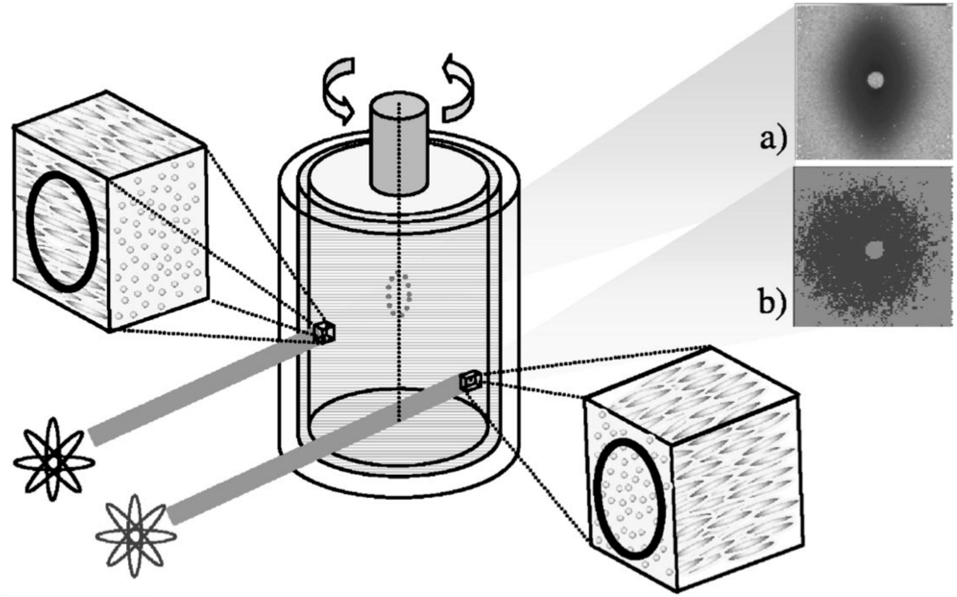
Example: Shear induced structure in suspensions II



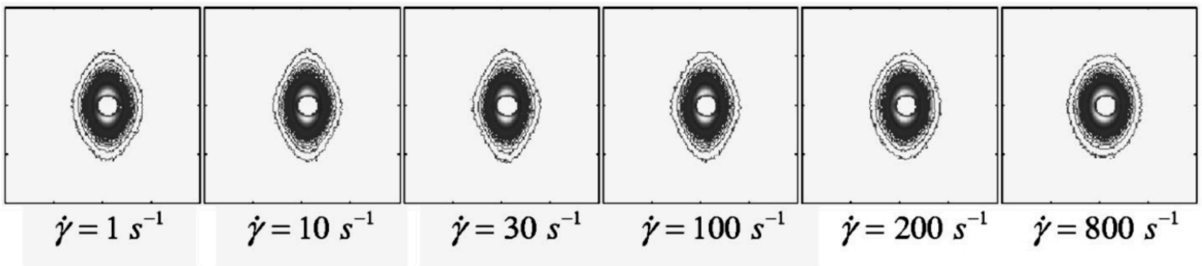
Egres RG, Wagner NJ: J. Rheol. 49 (2005) 719

Example: Shear induced structure in suspensions III

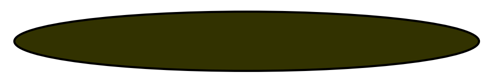




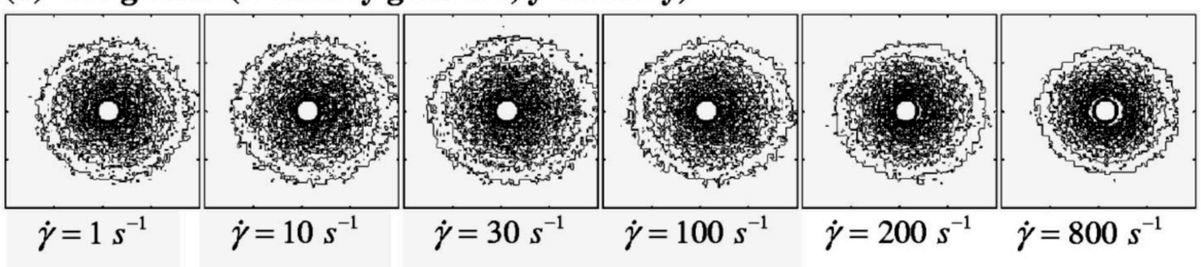
(c) Radial (x-velocity, y-vorticity)



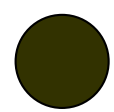
Orientation of rods (radial view)



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



Orientation of rods (tangential view)



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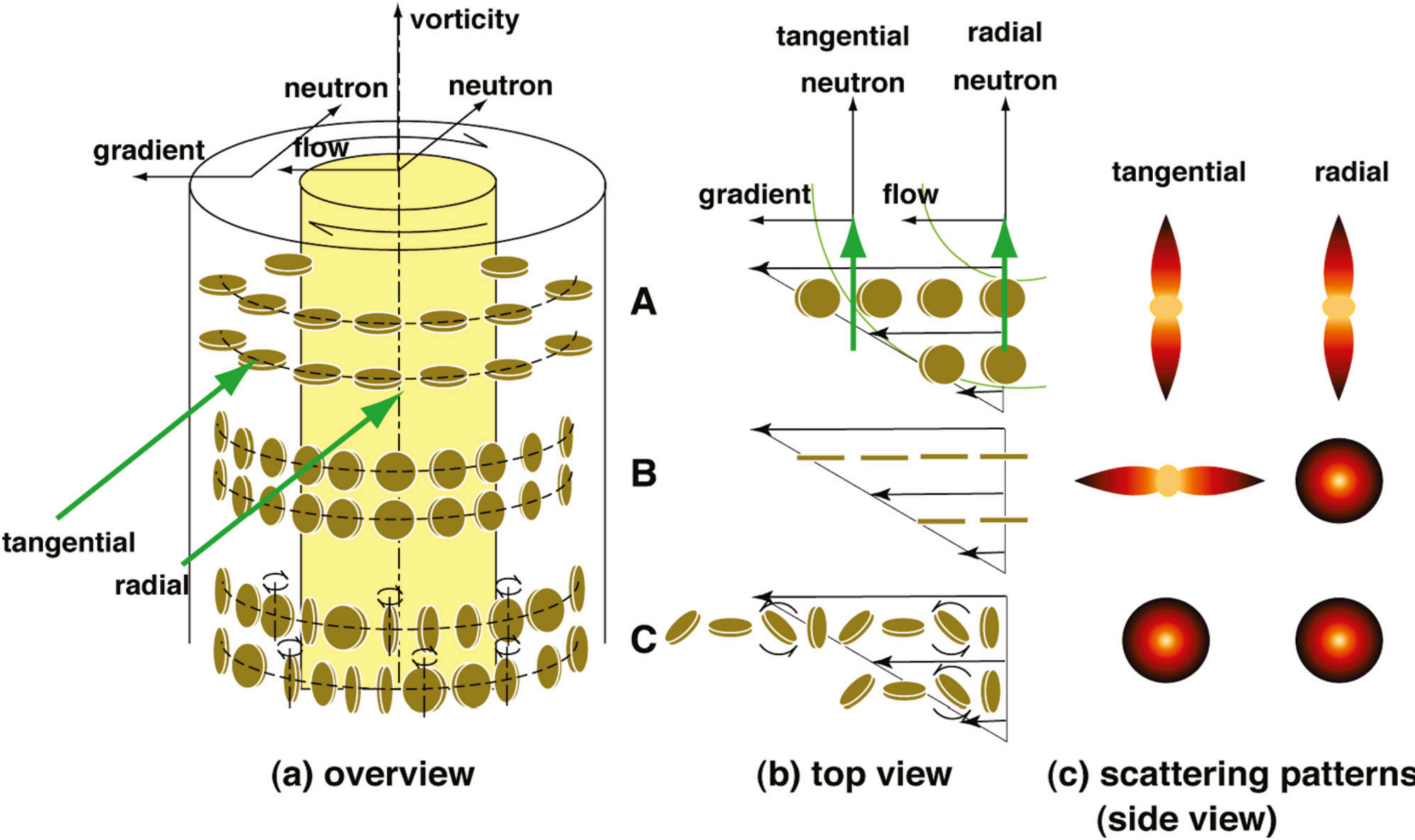
Summary: Probing different shear planes

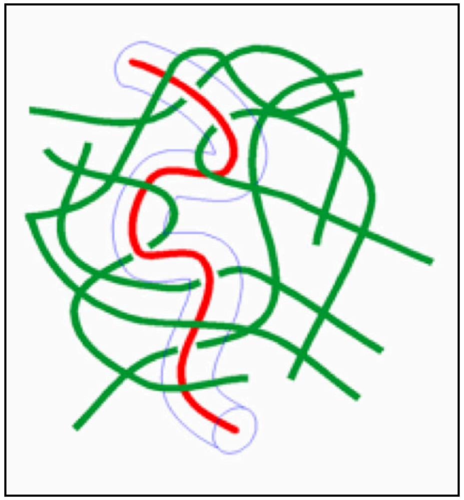


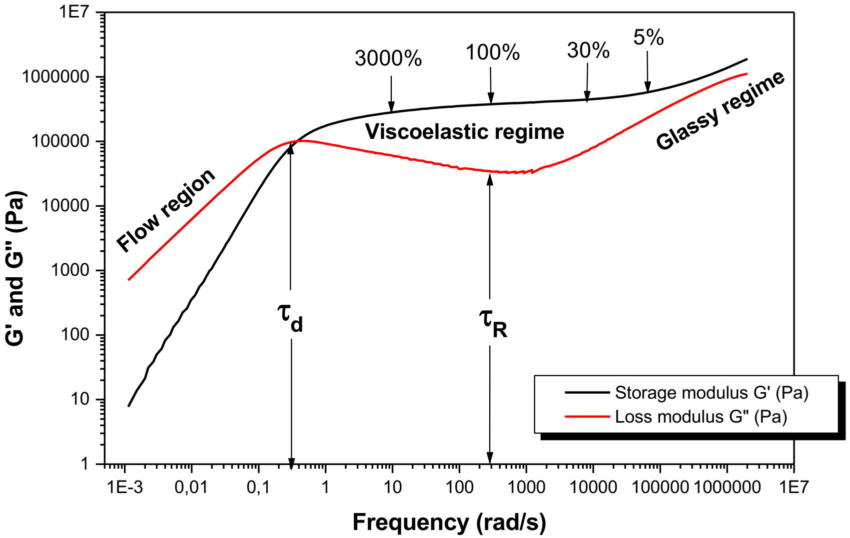
Matsunaga et al.: Macromolecules 43 (2010) 5075

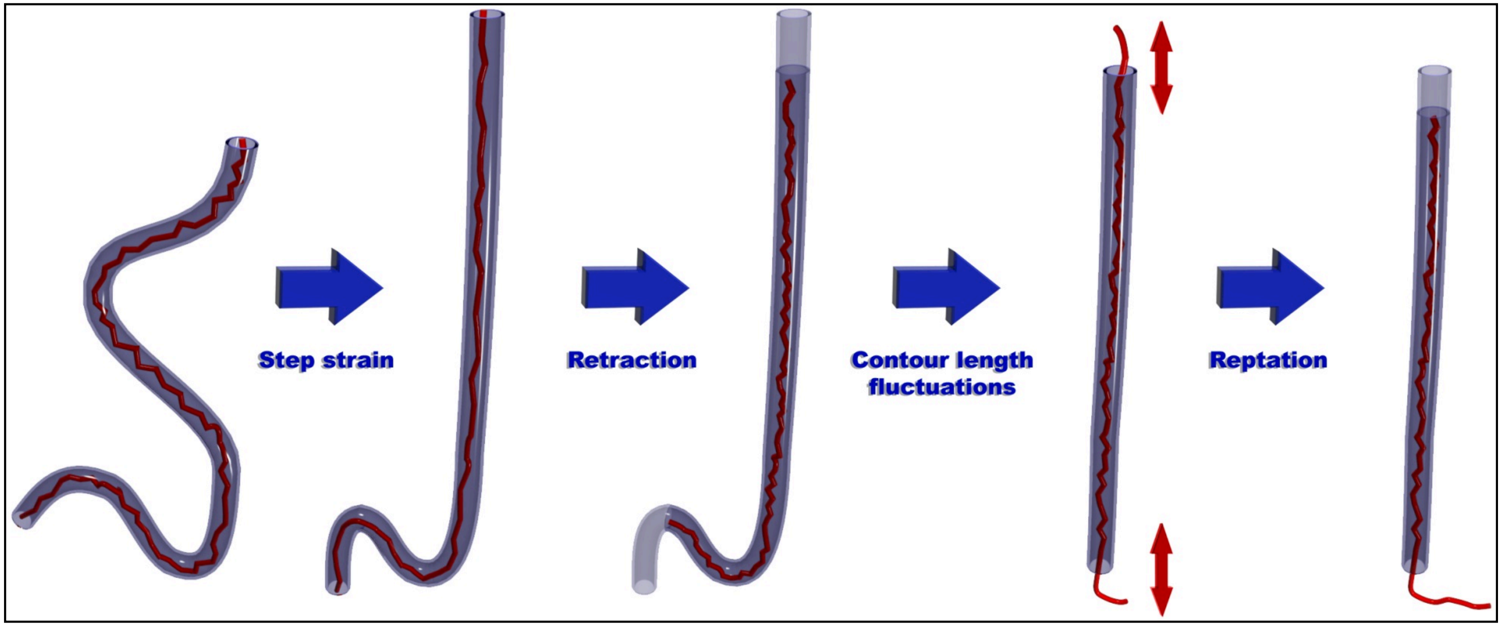
Example: Polymer relaxation (Anisotropic form factor) I

Linear polyisoprene melt:

- R_g ~ 175 Å
- t_d = 21 s
- t_R = 0.02 s
- G_0 = 410000 Pa

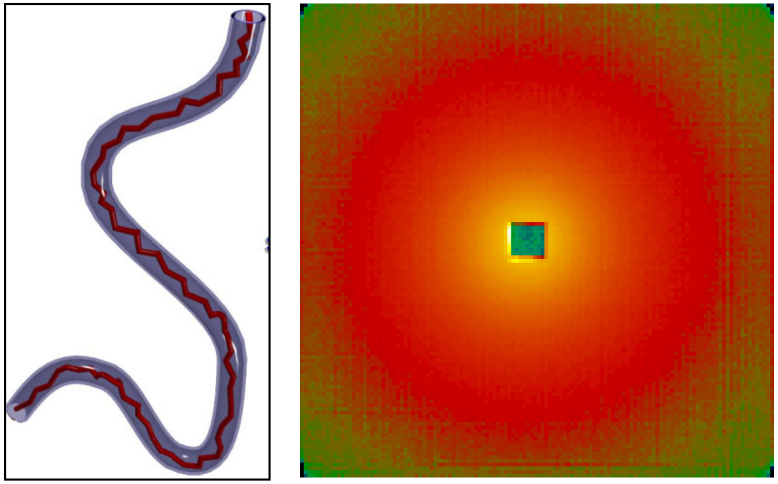




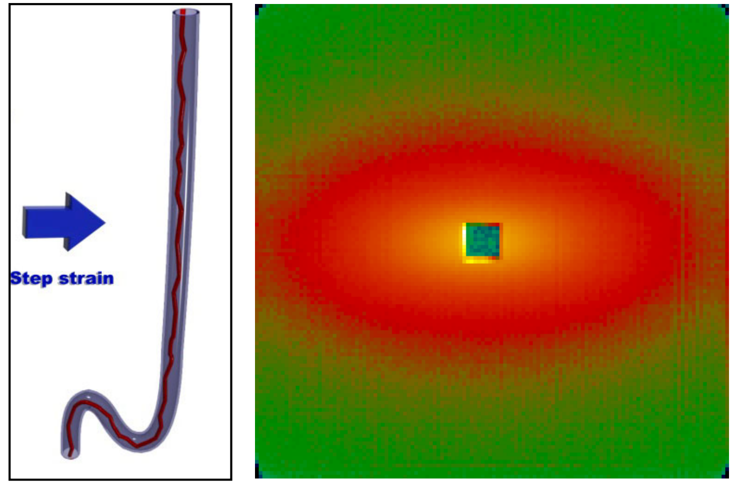


Blanchard A et al.: PRL 95 (2005) 166001

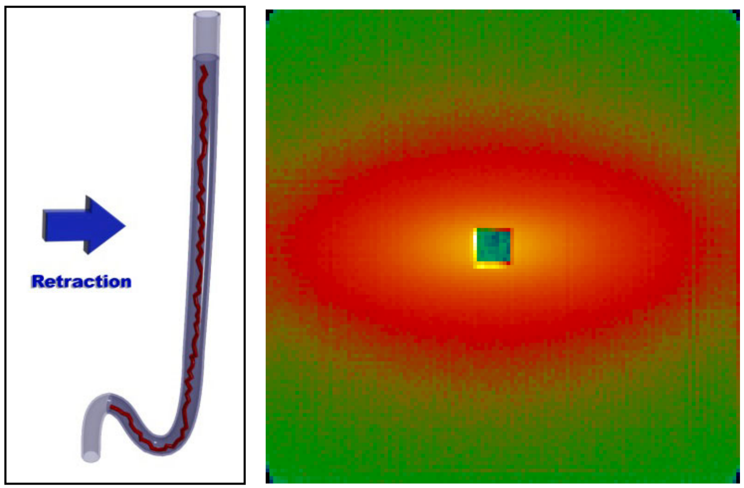
Example: Polymer relaxation (Anisotropic form factor) II



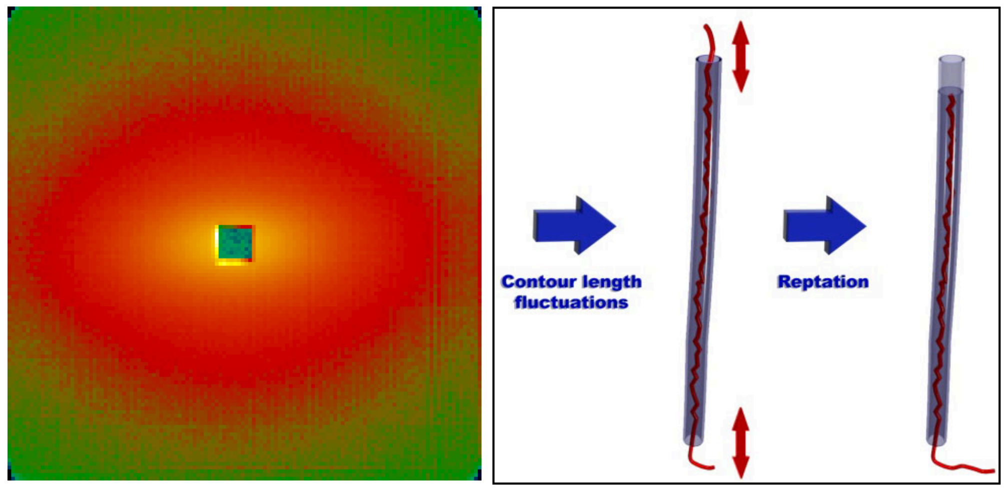
Isotrope



~ 0% of τ_R



~ 100% of τ_R

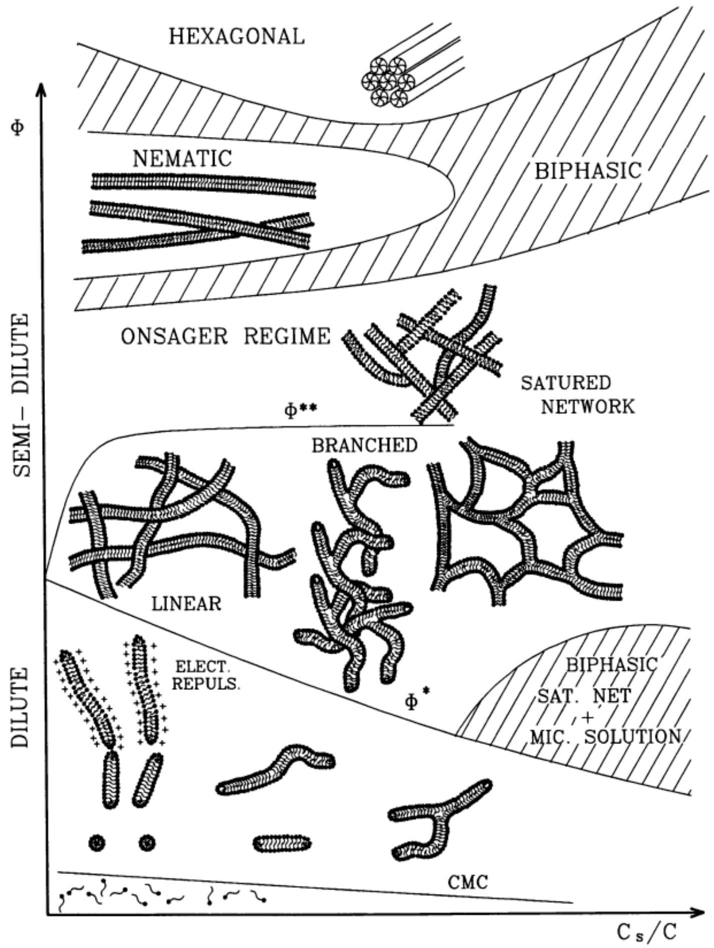


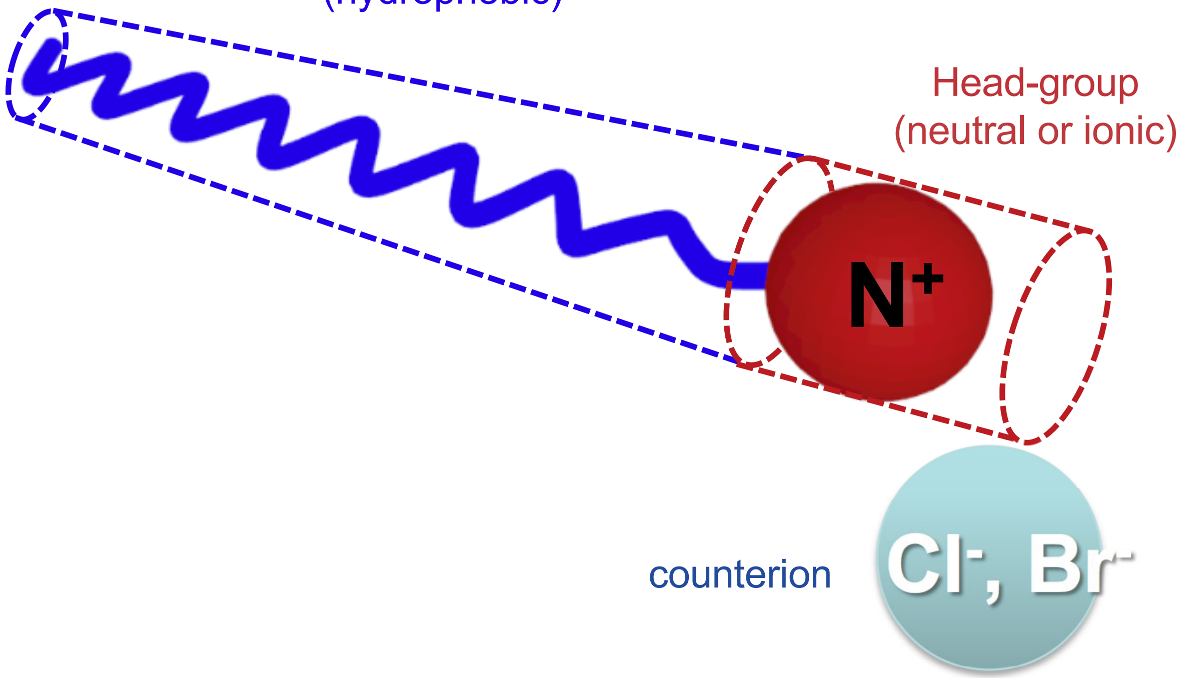
~ 1000% of τ_R

Blanchard A et al.: PRL 95 (2005) 166001

Example: Shear banding in surfactant solutions I

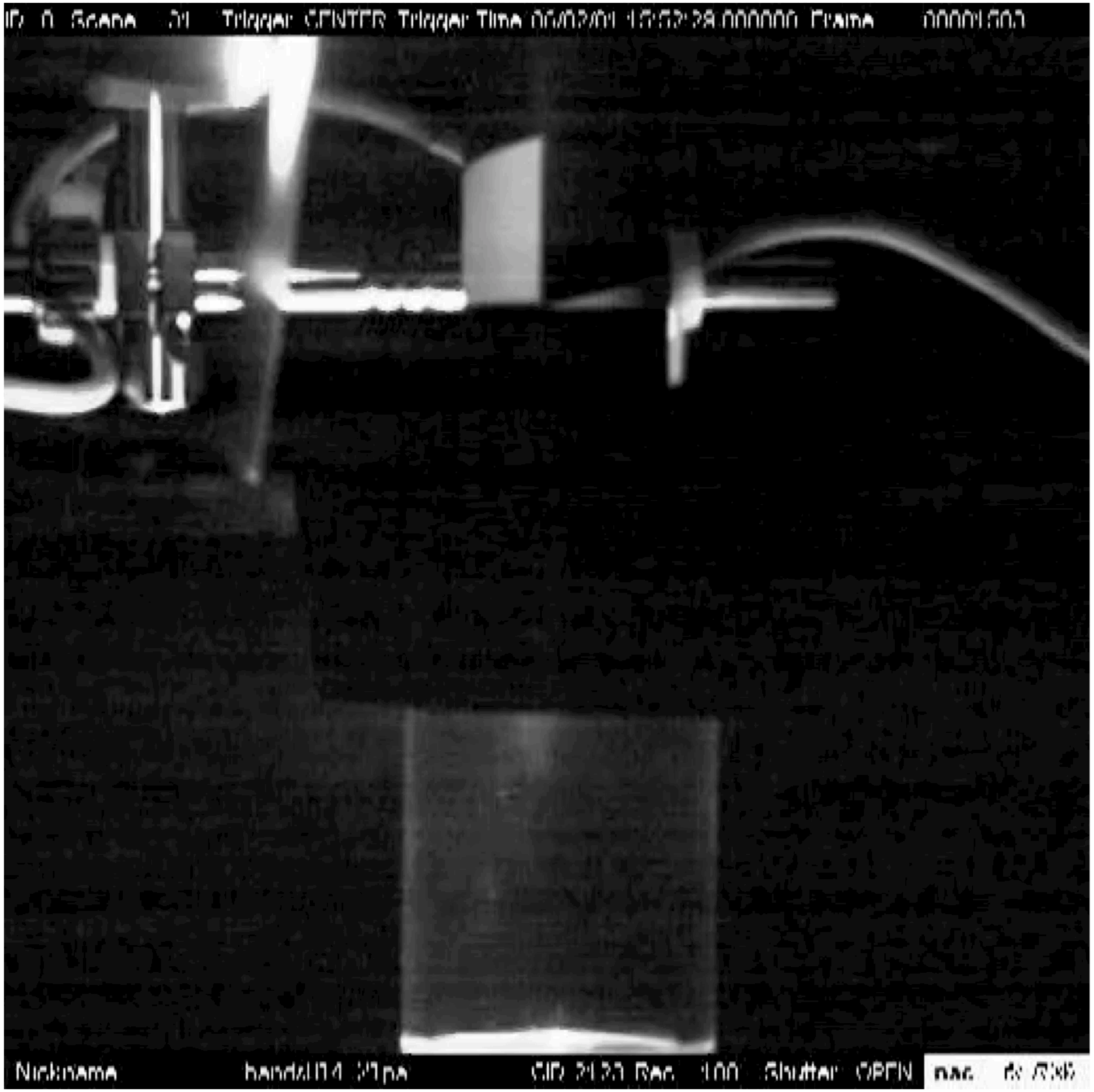
Micellization is a balance of:
- Hydrophobic forces
- Electrostatics

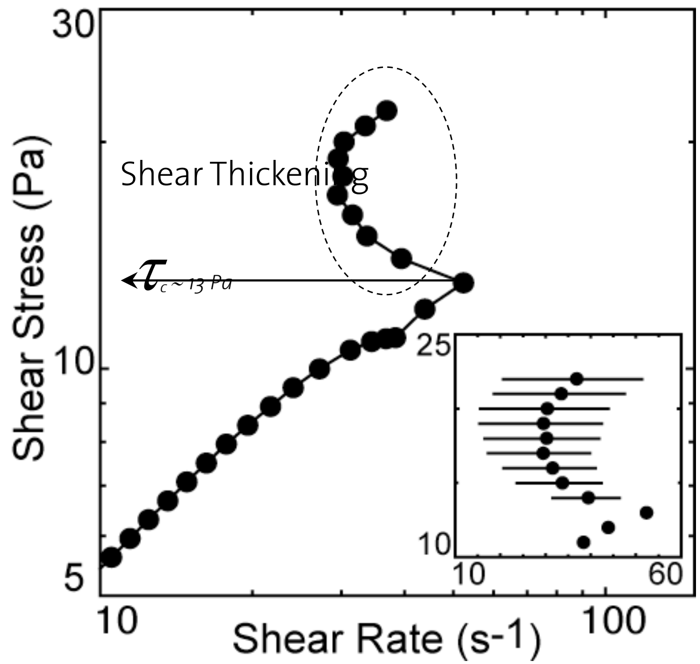




Phase diagram defined by
- Surfactant and counterion
- Concentration and its ratio
- Packing parameter
- Additional components

Example: Shear banding in surfactant solutions II



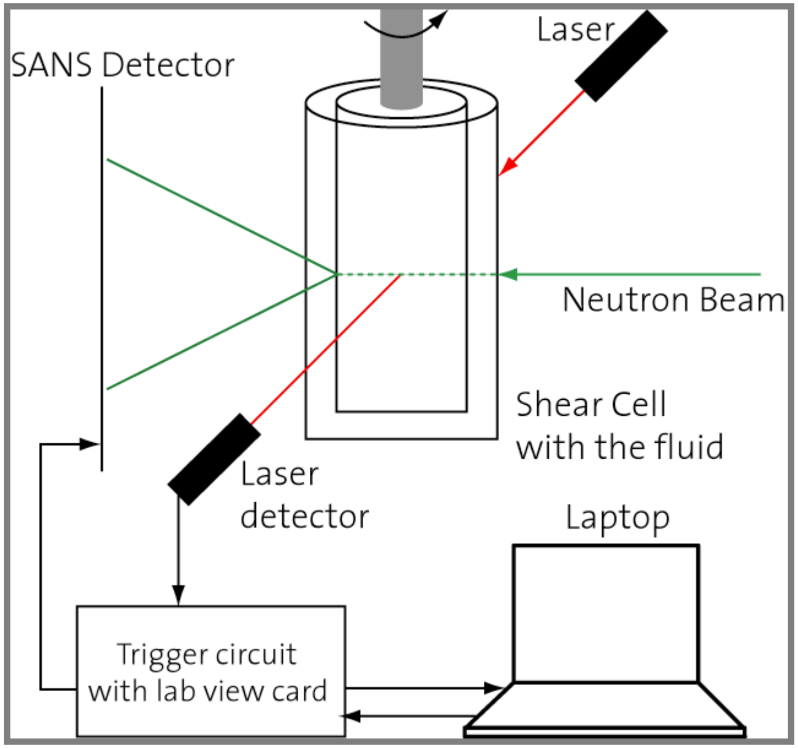


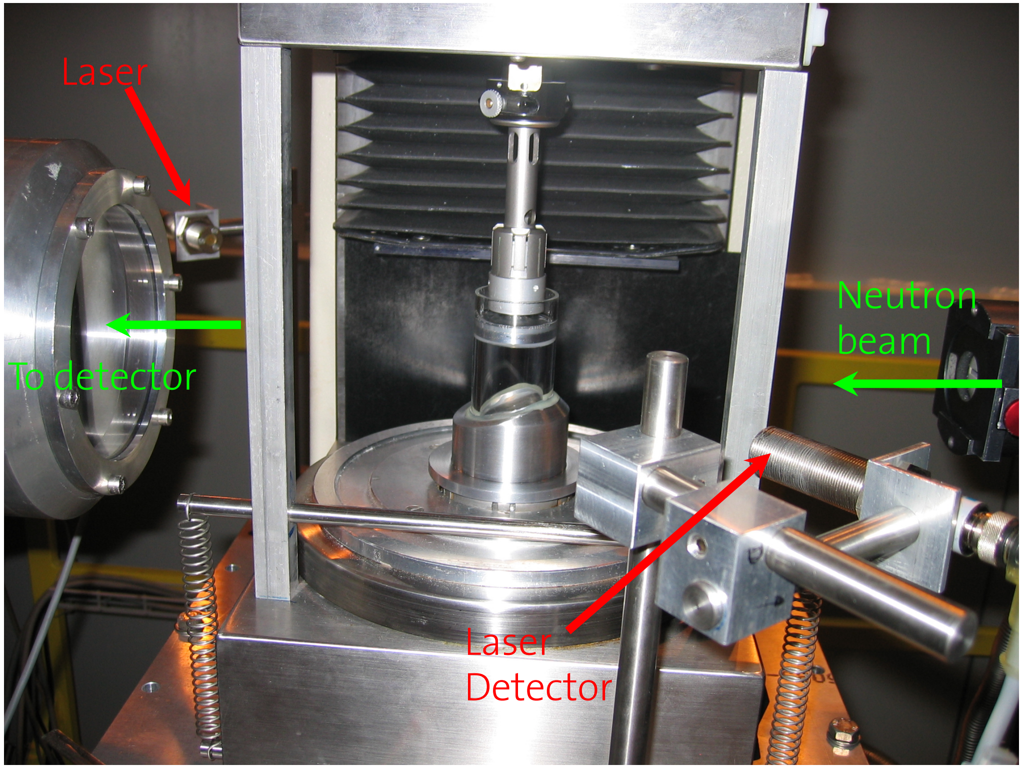
The freaky surfactant solution:

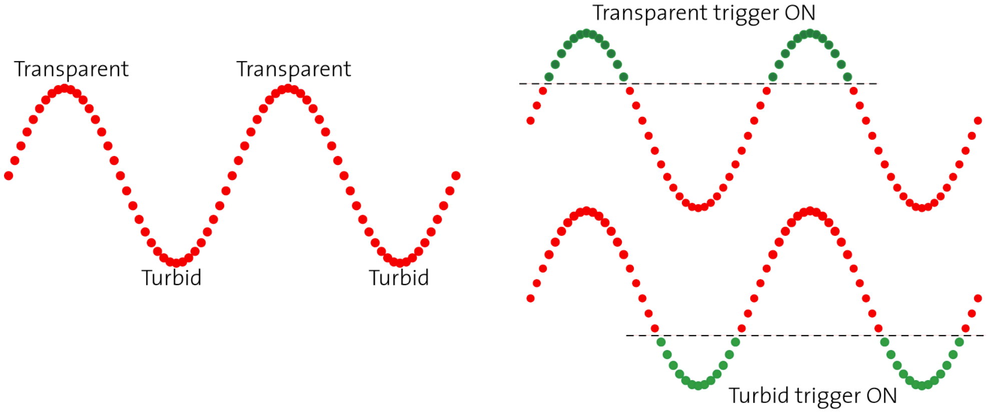
Equimolar solution, e.g.
CPyCl-NaSal, CTAB-NaSal, …
(20-20 to 60-60 mM)

Herle V et al.: Phys Rev. Lett. 99 (2007) 158302
Mütze A et al.: J. Rheol. 58 (2014) 1647

Example: Shear banding in surfactant solutions III



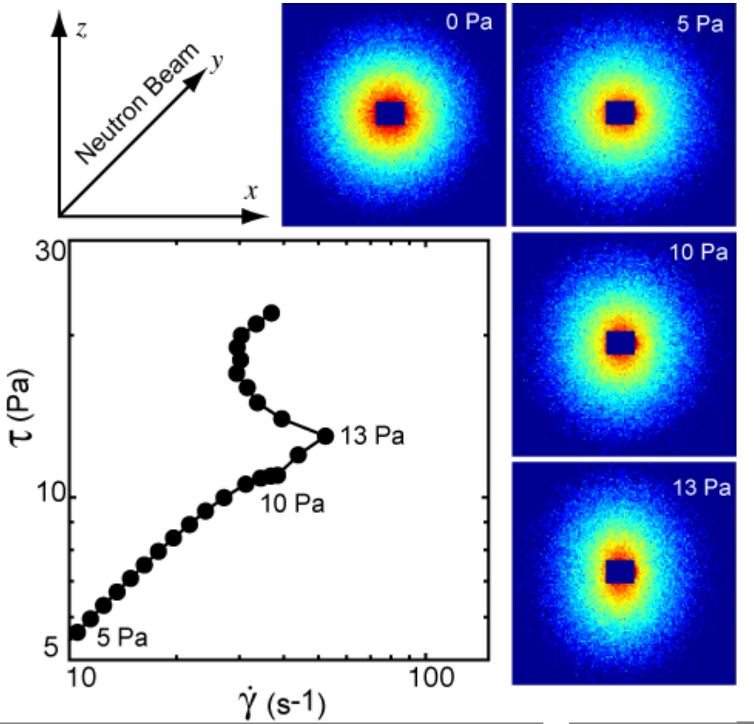


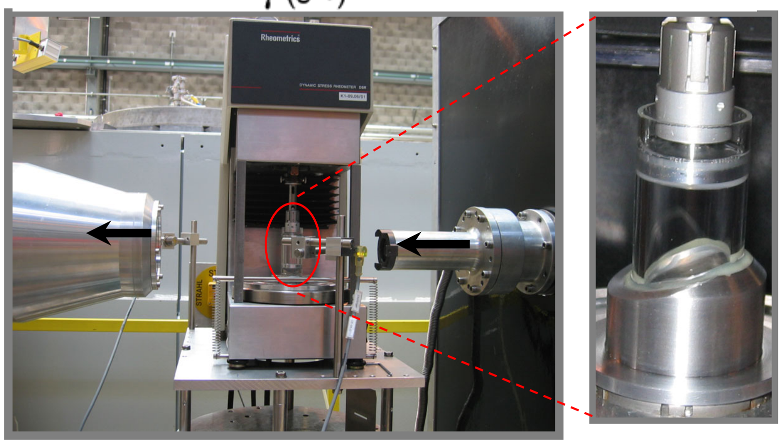


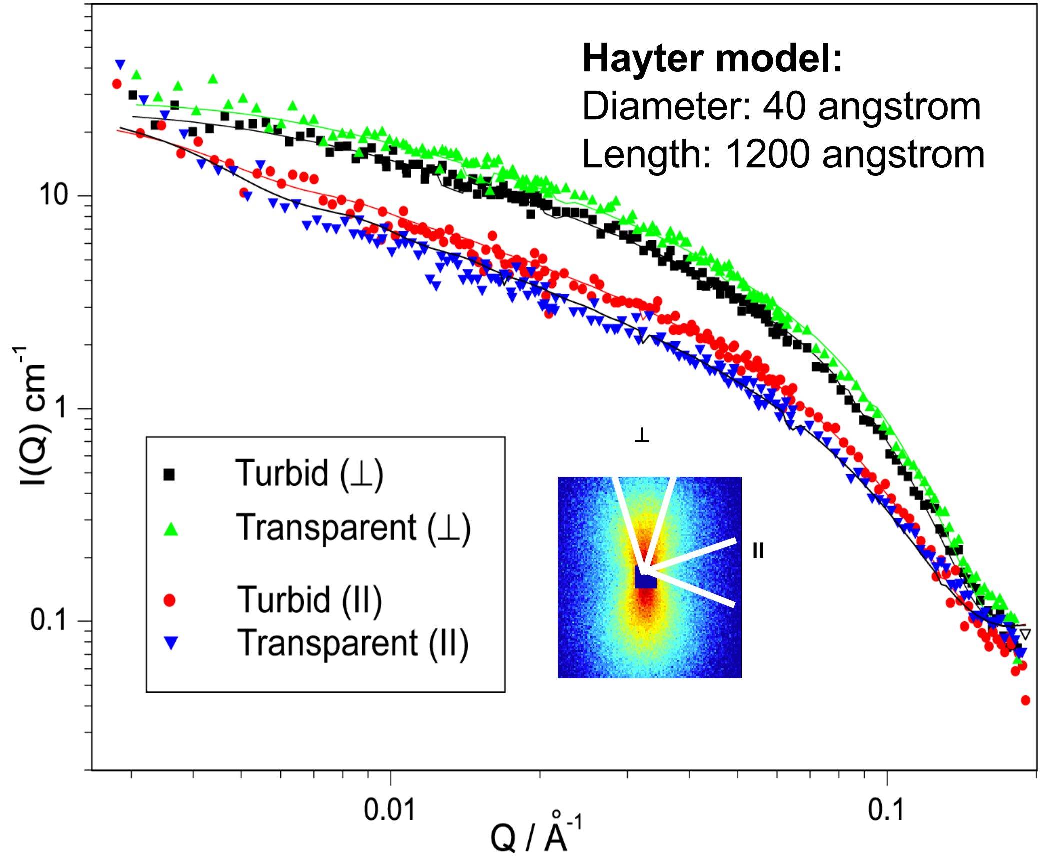
Triggered SANS setup:
- Set a threshold value
- Trigger the SANS detector
- Collect the data

Herle V et al.: Phys Rev. Lett. 99 (2007) 158302
Mütze A et al.: J. Rheol. 58 (2014) 1647

Example: Shear banding in surfactant solutions IV







Data analysis:

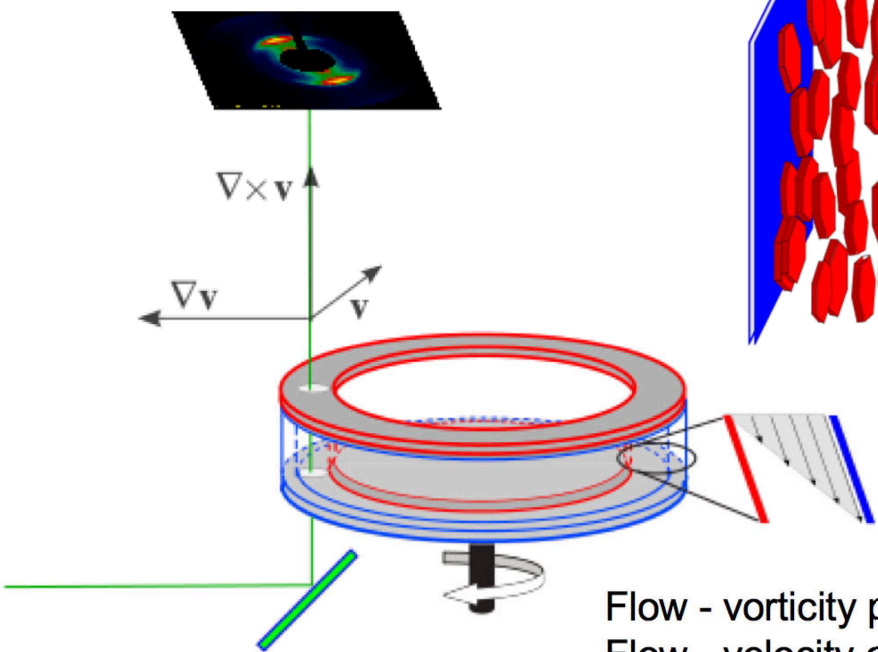
Pattern analysis (flow mapping, orientation)

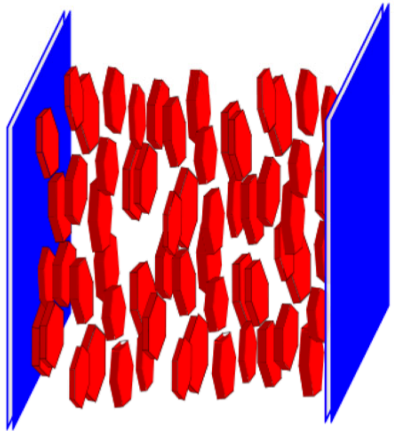
Modeling: (Structure and form factor, size, contrast, ...)

Herle V et al.: Phys Rev. Lett. 99 (2007) 158302
Mütze A et al.: J. Rheol. 58 (2014) 1647

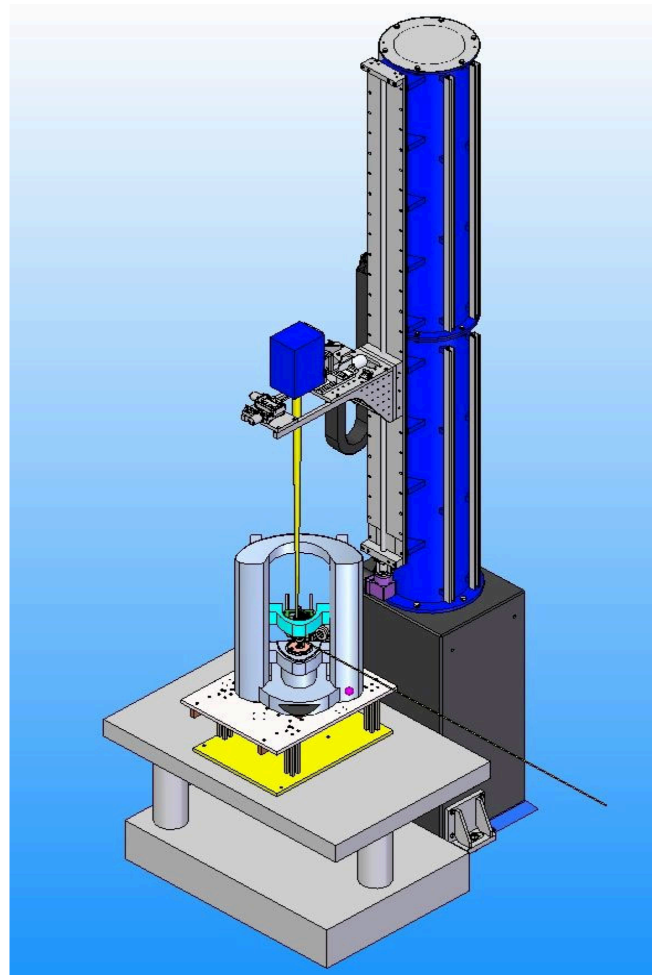
Example: LAOS and scattering I

Rheo-structural response of nematic colloidal platelets in LAOS





Flow - vorticity plane
Flow - velocity gradient plane



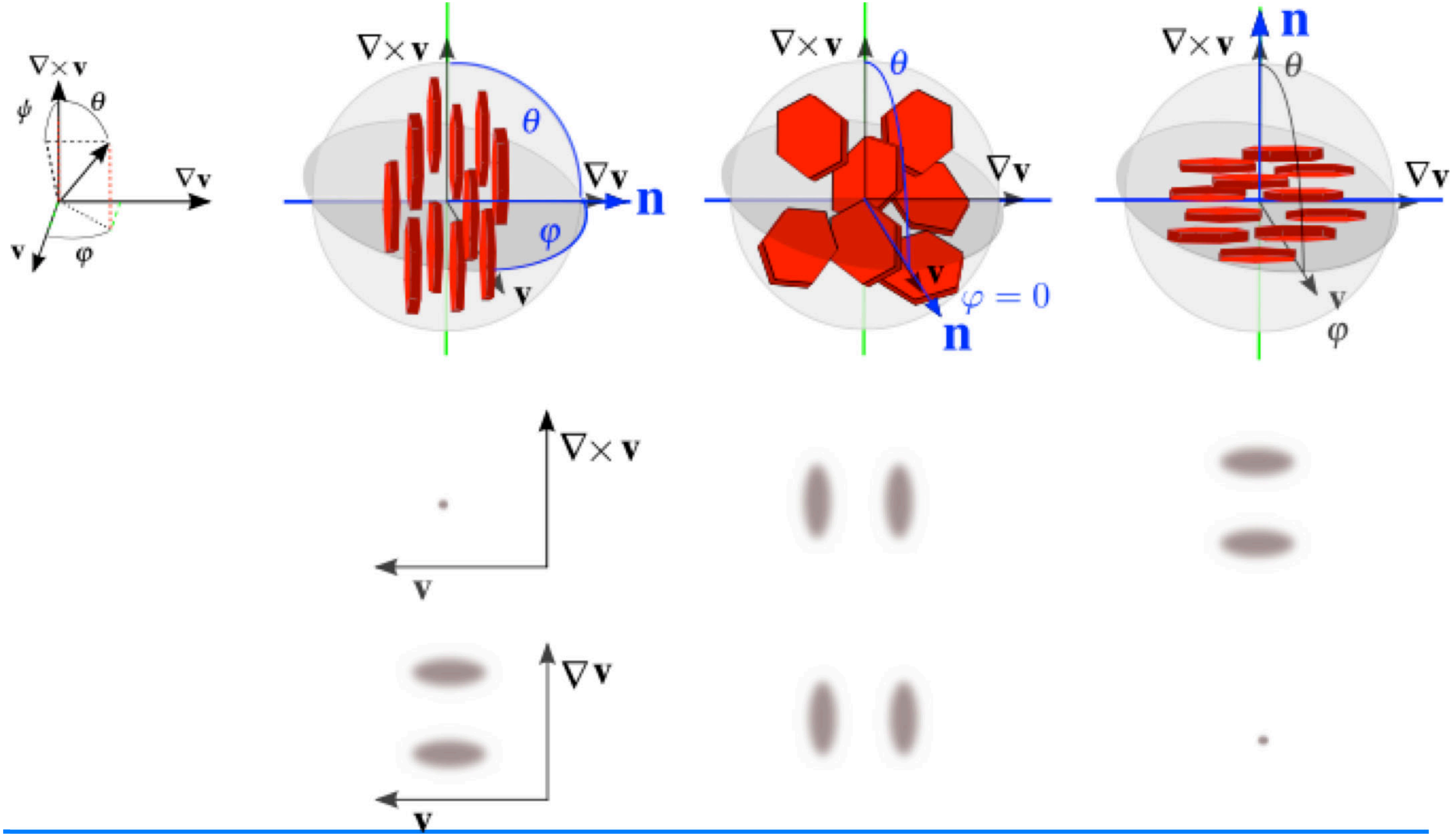
Gibbsite platelets (AlOOH)

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

Slide by Pavlik Lettinga, FZ Jülich
Physics of Fluids 29 (2017) 023102

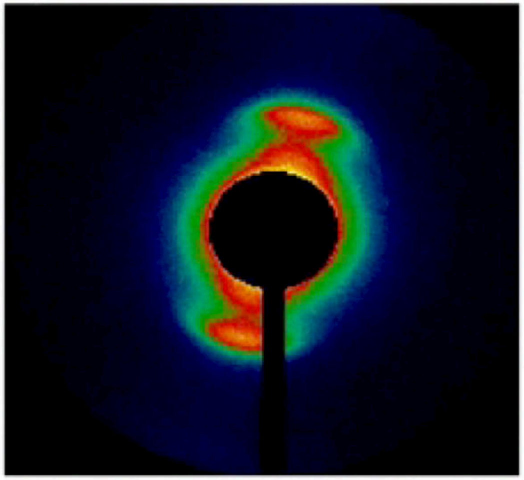
Example: LAOS and scattering II

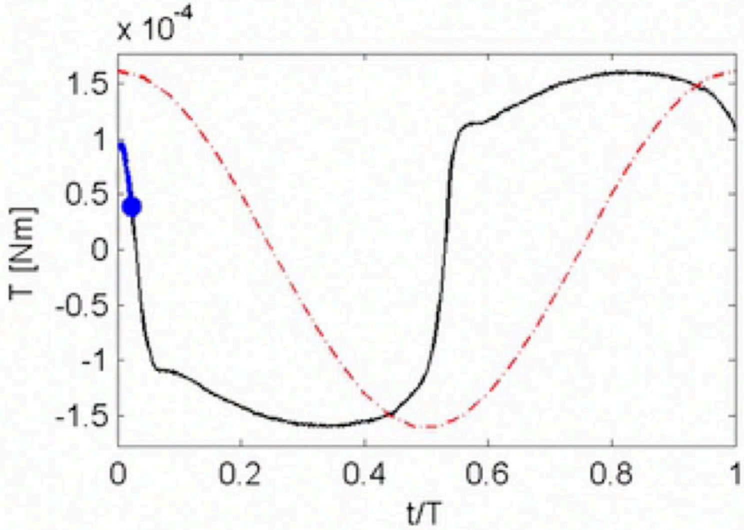
Rheo-structural response of nematic colloidal platelets in LAOS

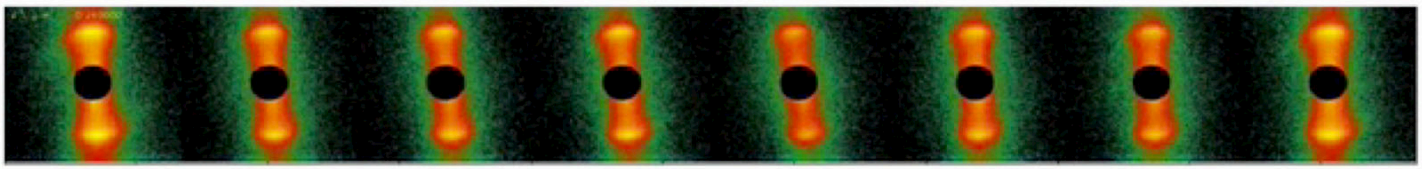


Slide by Pavlik Lettinga, FZ Jülich
Physics of Fluids 29 (2017) 023102

Example: LAOS and scattering III

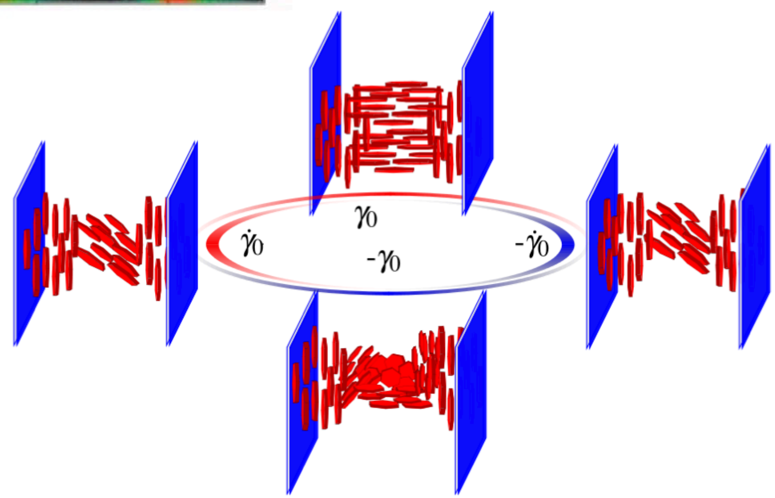






Transient stress signal and **flipping SAXS** patterns indicate:

- Disorder in gap
- Huge effect of wall anchoring



Slide by Pavlik Lettinga, FZ Jülich
Physics of Fluids 29 (2017) 023102

Scanning SAXS

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

Marianne Liebi[1], Marios Georgiadis[2], Andreas Menzel[1], Philipp Schneider[3], Joachim Kohlbrecher[1], Oliver Bunk[1] & Manuel Guizar-Sicairos[1]

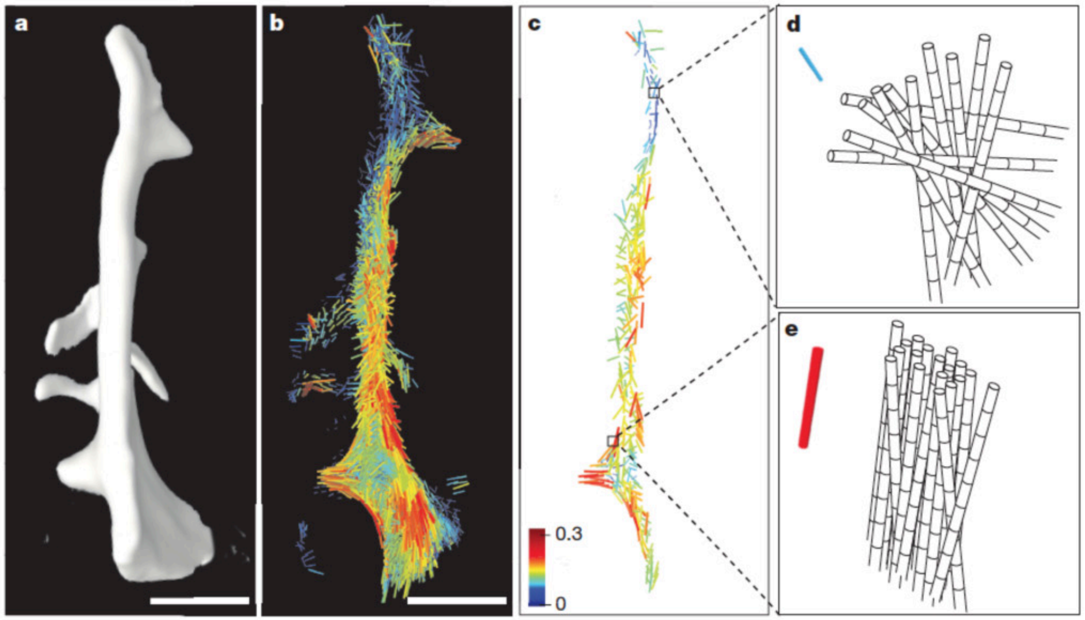
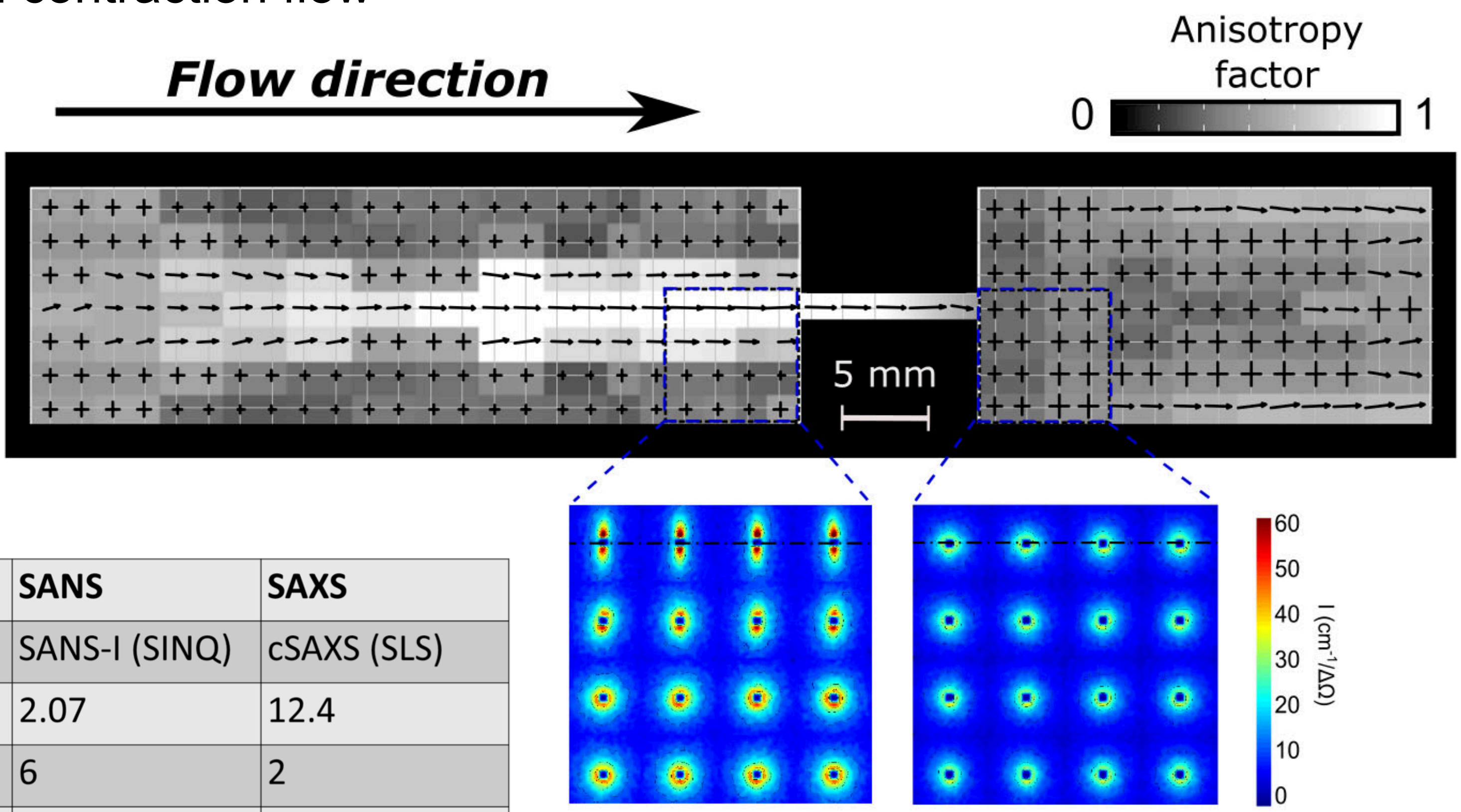


Figure 3 | Orientation of collagen fibrils within a human trabecular bone sample. **a**, Computed-tomography reconstruction obtained from the transmitted intensity using standard filtered backprojection. **b**, Orientation of bone ultrastructure as determined using SAS tensor tomography (see also Supplementary 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.

Liebi M et al.: Nature 527 (2015) 350

Scanning SAXS: Mapping complex fluids under flow I

Worm-like micelle in contraction flow

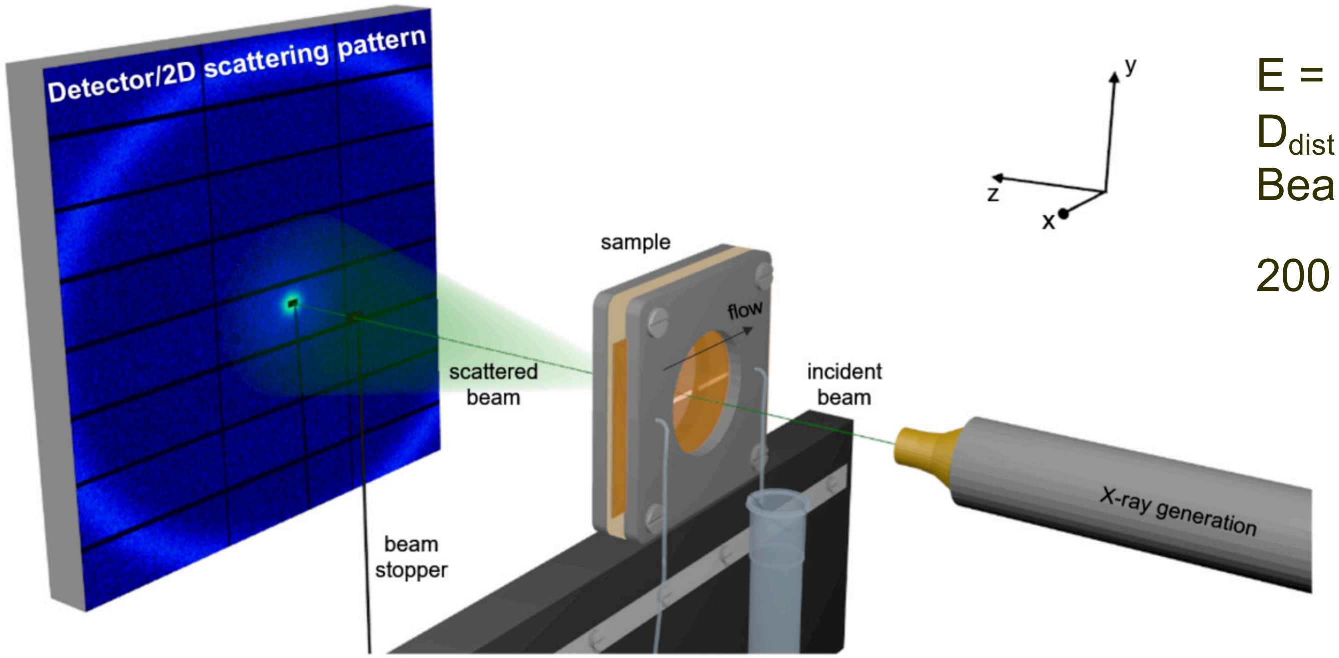


Technique	SANS	SAXS
Beamline	SANS-I (SINQ)	cSAXS (SLS)
Energy (keV)	2.07	12.4
Detector distance (m)	6	2
Beam size (μm²)	3.1 x 10^6	1.6 x 10^3
Acquisition time (s)	≈ 720	0.1
Scattering volume (μm³)	3.1 x 10^9	0.16 x 10^6
Number of scanning points	275	6030
Total measurement time (h)	≈ 55	≈ 0.2

Lutz-Bueno et al.: Lab Chip 16 (2016) 4028

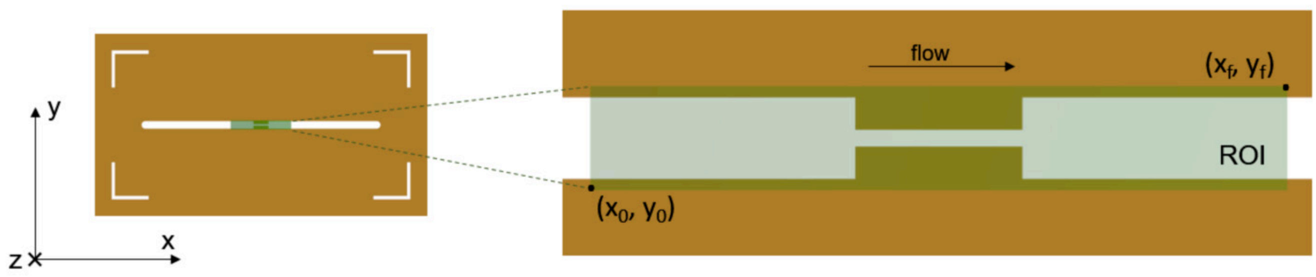
Scanning SAXS: Mapping complex fluids under flow II

Experimental setup Scanning SAXS (cSAXS at PSI)



E = 12.4 keV
D_{dist} = 7 or 2 m
Beam size = 40 x 40 µm^2

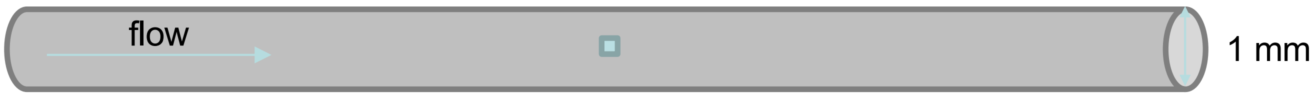
200 x 25 scattering patterns



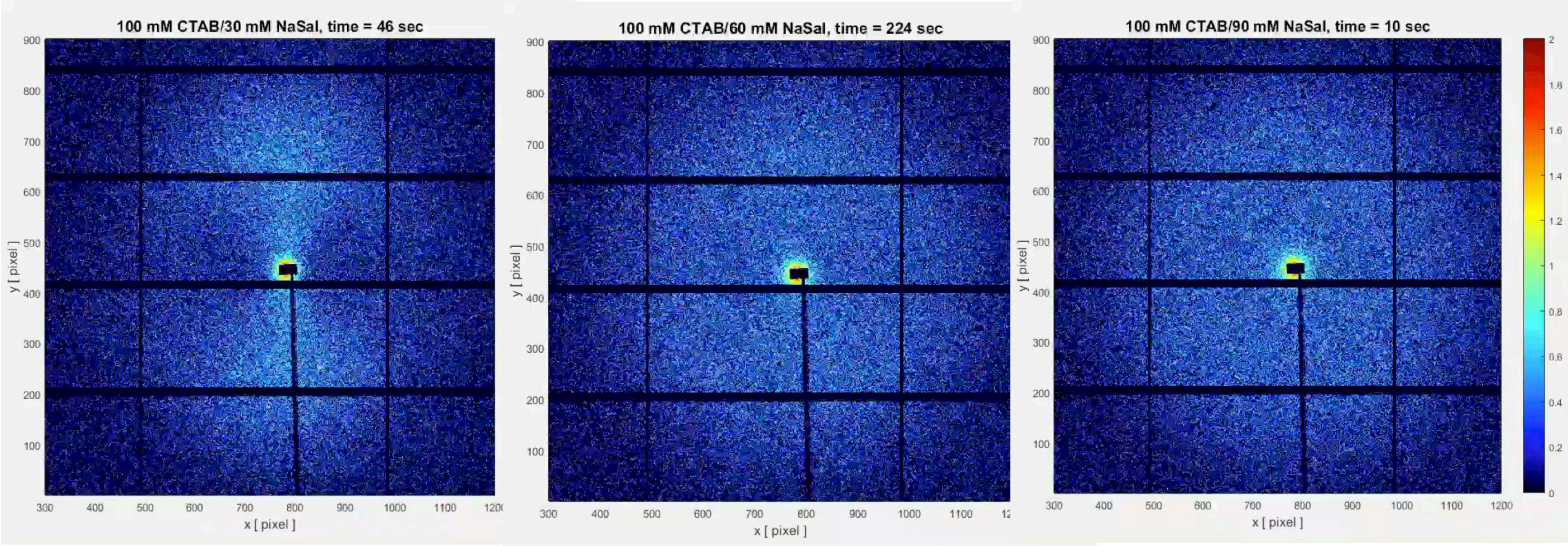
Lutz-Bueno et al.: Lab Chip 16 (2016) 4028

Scanning SAXS: Mapping complex fluids under flow III

Orientation of worm-like micelle in transient flow



100 mM CTAB/30 NaSal | 100 mM CTAB/60 NaSal | 100 mM CTAB/90 NaSal

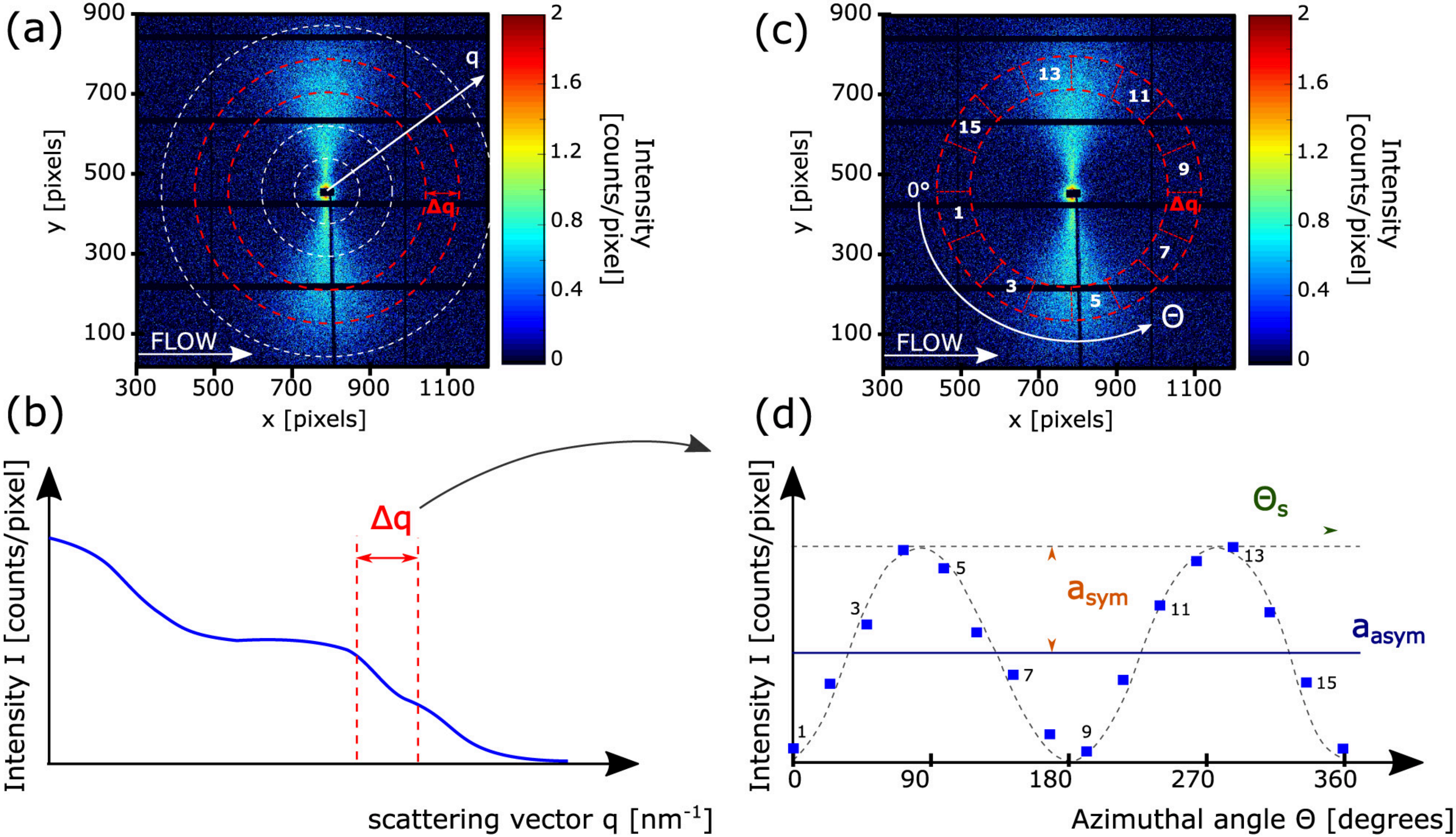


Pressure driven flow: 300-1600 mbar in 120 seconds, Beam size = 200 x 200 μm^2 Exposure time = 0.4 sec

Lutz-Bueno et al.: Lab Chip 16 (2016) 4028

Scanning SAXS: Mapping complex fluids under flow IV

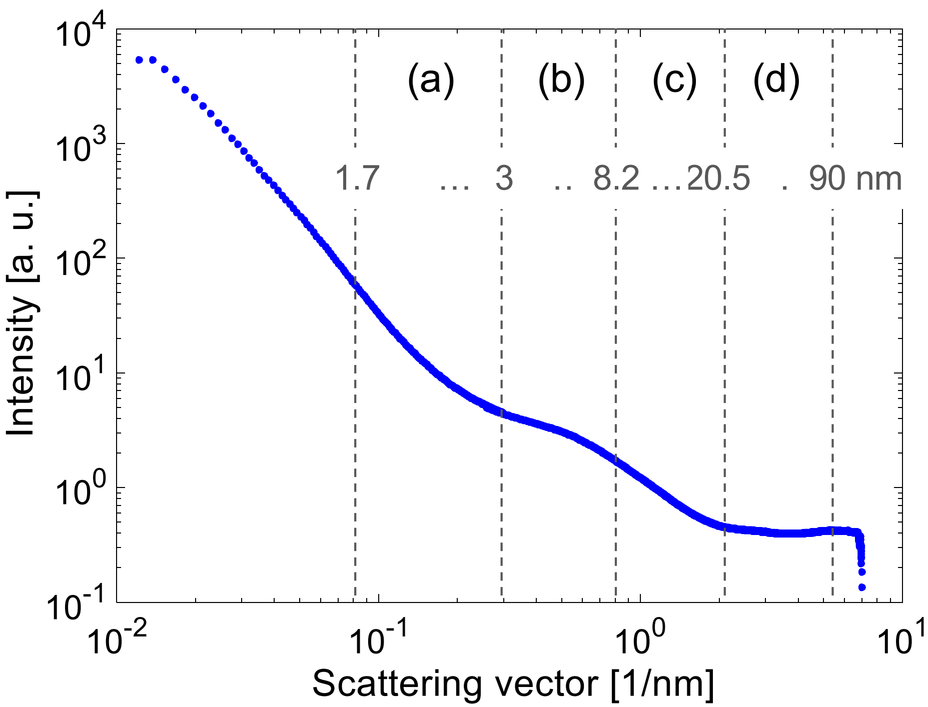
A few Tb of data … and now? - **Color coding** for anisotropy in each scattering pattern

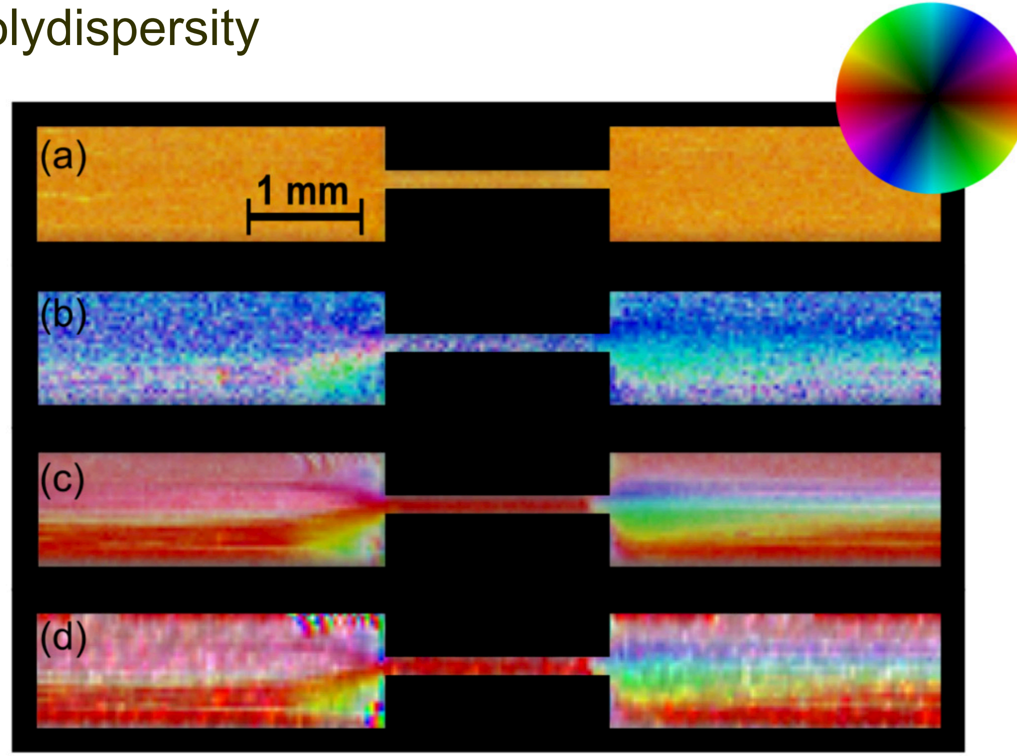


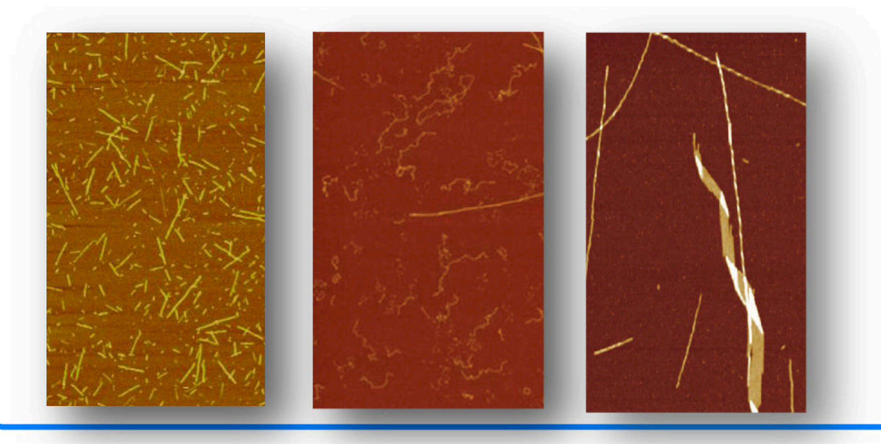
Lutz-Bueno et al.: Lab Chip 16 (2016) 4028

Scanning SAXS: Mapping complex fluids under flow V

Amyloid fiber under flow: Estimate of polydispersity





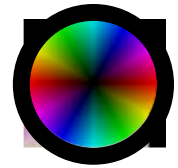


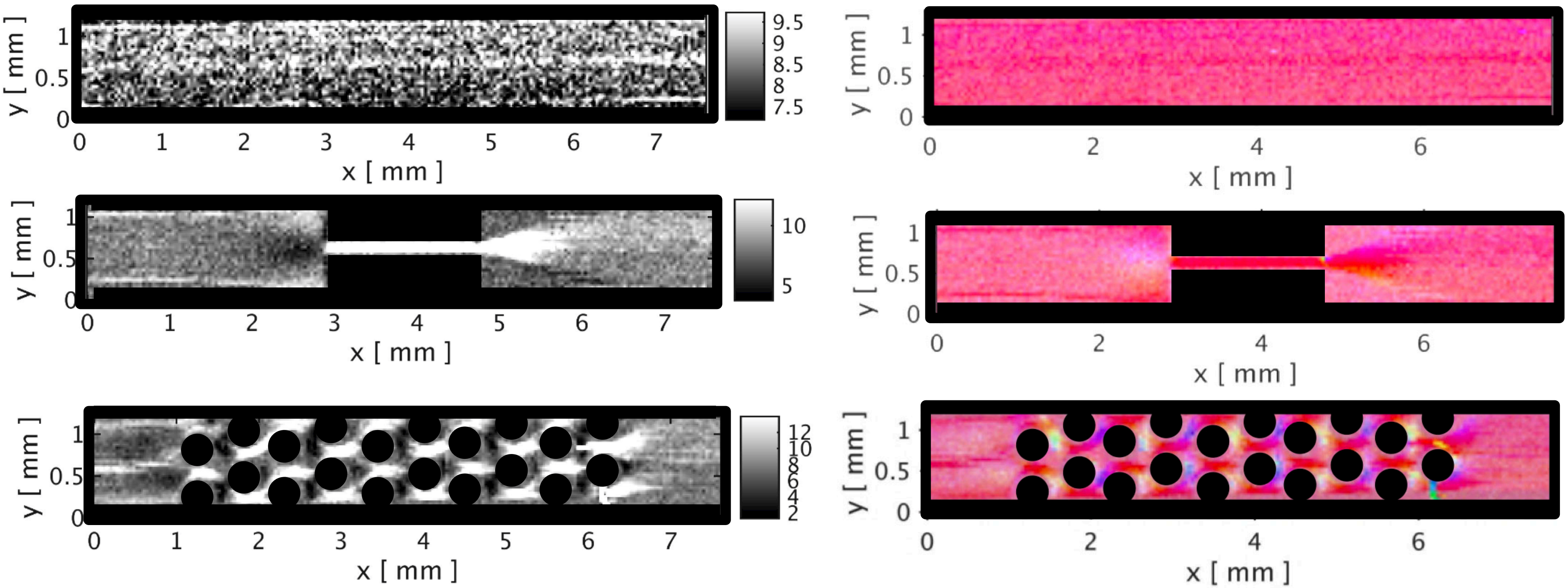
Probing of different dimensions of the fibers from same measurement

Jordens et al.: Langmuir 30 (2014) 10090−10097

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 mm)





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)

Lutz-Bueno et al.: Lab Chip 16 (2016) 4028

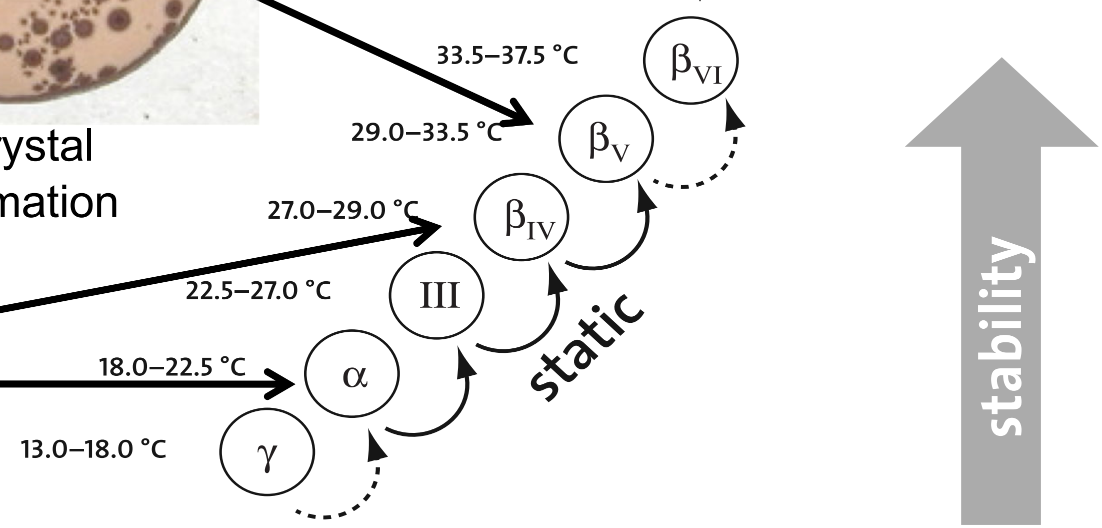
Dessert: Chocolate crystallization under flow I

Pre-crystallized chocolate

After crystal transformation

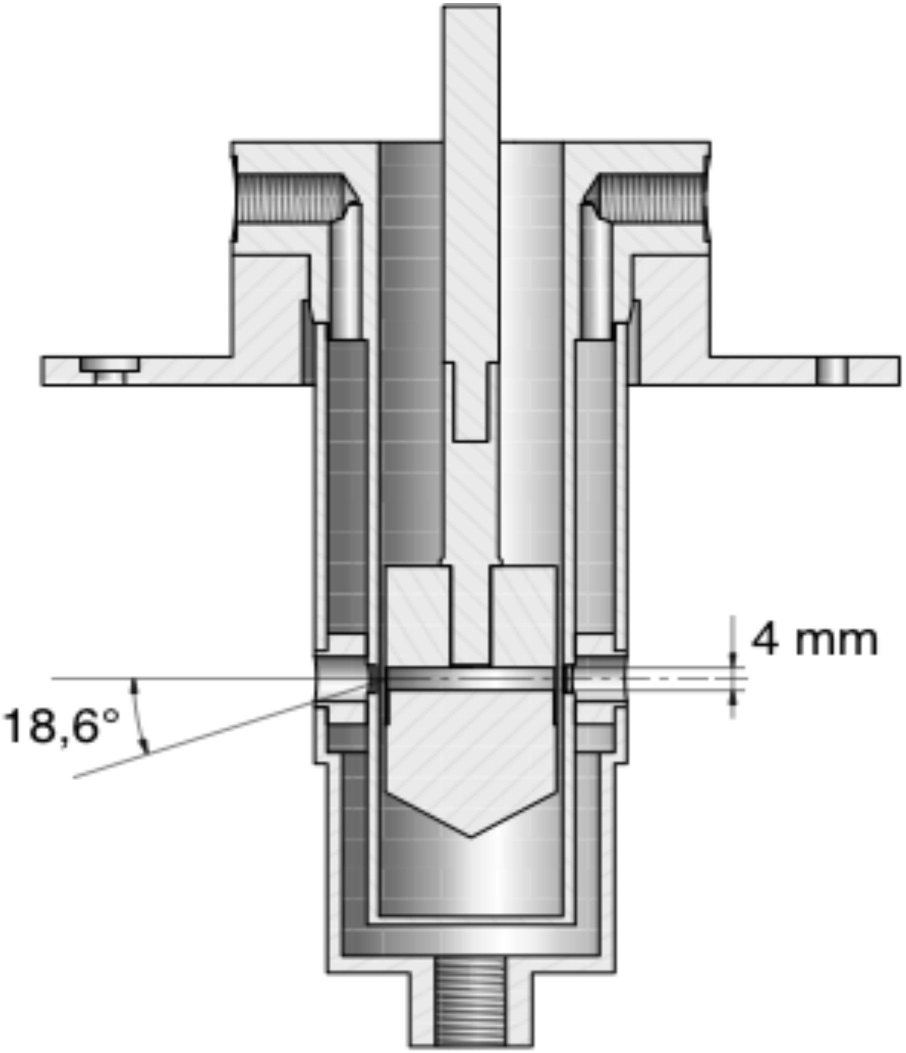
Bloomed chocolate

Non pre-crystallized chocolate

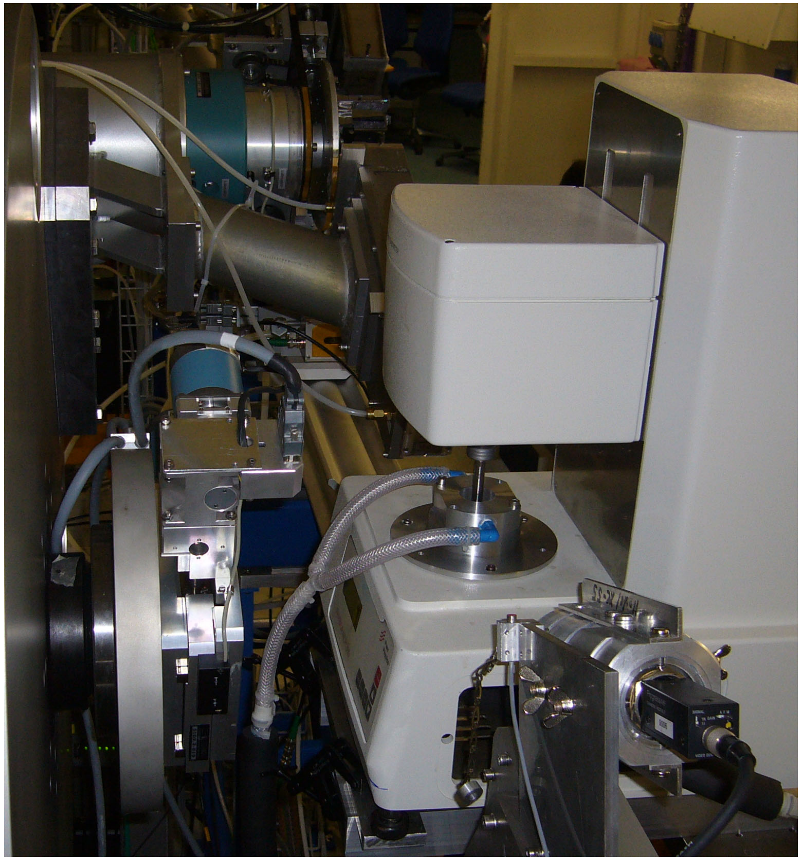


Padar S et al.: Crystal Growth Design 9 (2009) 4023

Dessert: Chocolate crystallization under flow II



Cacao crystal formation is influenced by shear and temperature:
Leads to desired β_{VI} form as function of shear time and temperature profile



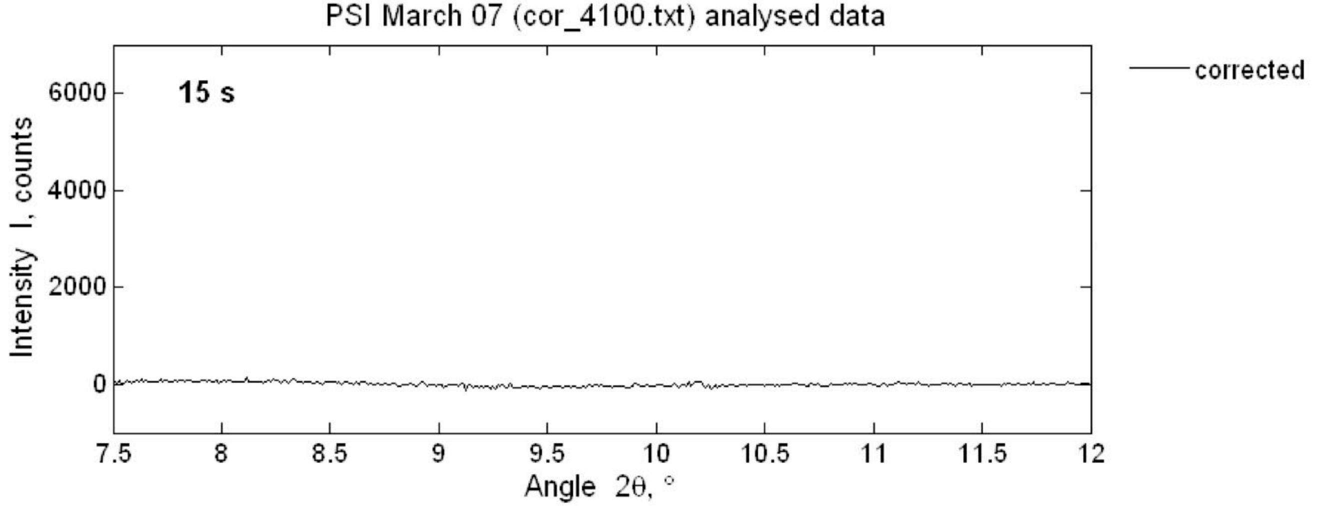
Observation of crystallization (and crystal structure transformation) under shear via SAXS/WAXS

Padar S et al.: Crystal Growth Design 9 (2009) 4023

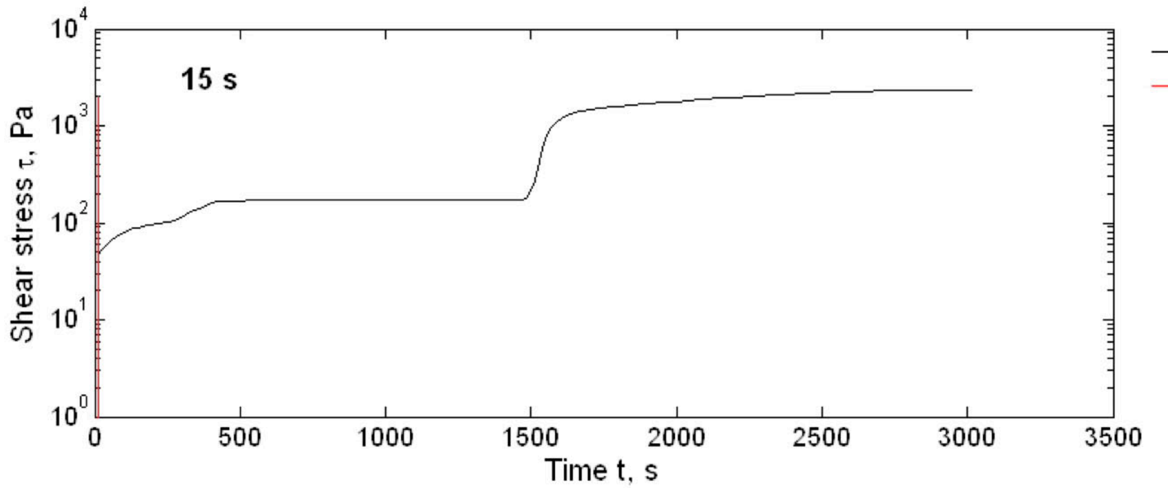
Dessert: Chocolate crystallization under flow III

Scattering intensity as a function of shear stress

WAXS signal:
Peak position
Time information
Crystal structure



Rheology:
Cooling behavior
Crystallization
Flow structuring



Example:
Shear rate = 1000 s^{-1}
T = 21 °C

Padar S et al.: Crystal Growth Design 9 (2009) 4023

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 fundamental aspects 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!