Structure and rheology of a shear-thickening wormlike micellar system [1-4]

Simultaneous formation of vorticity and velocity bands studied by birefringence measurements [1, 5, 6]

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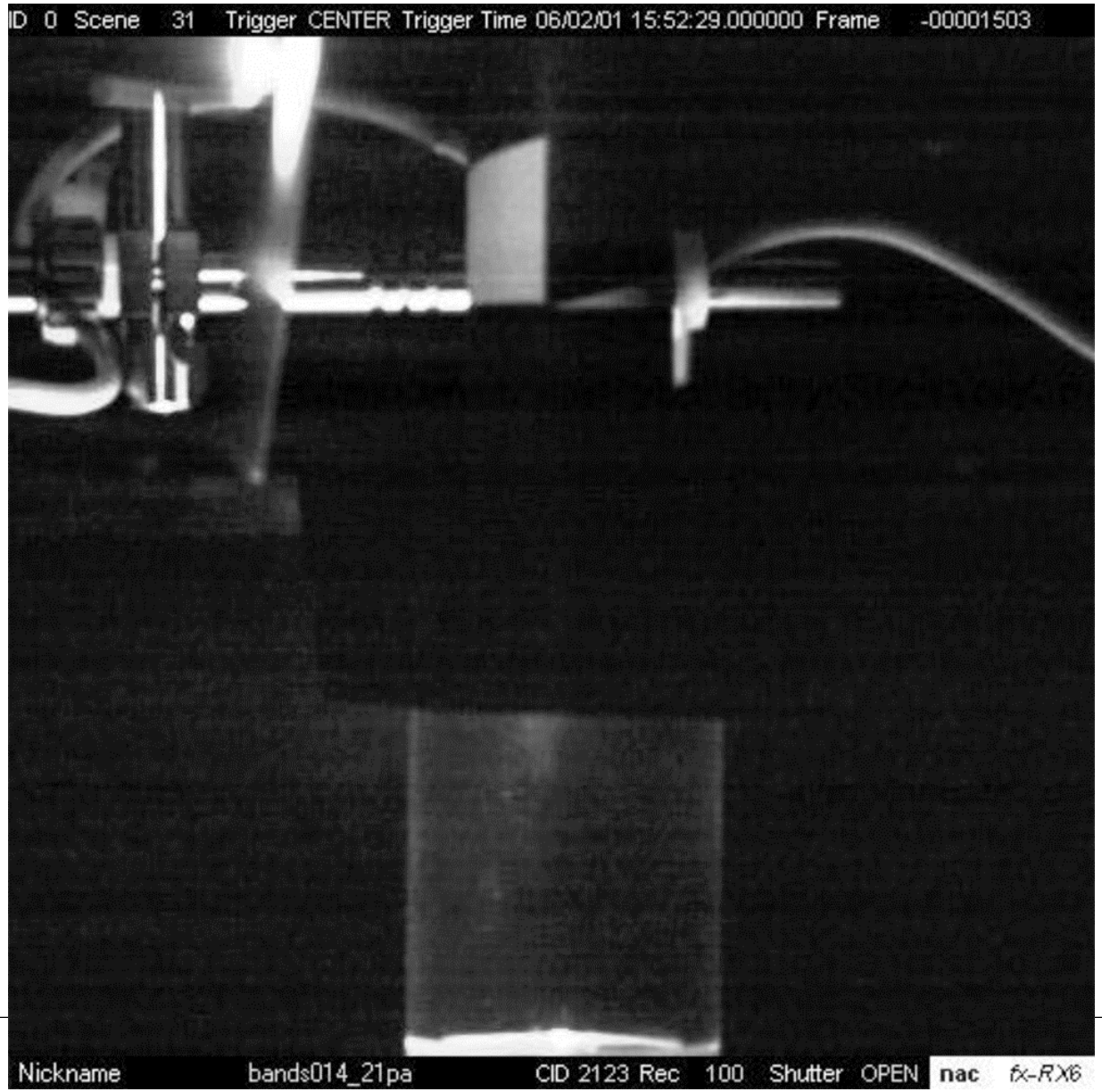
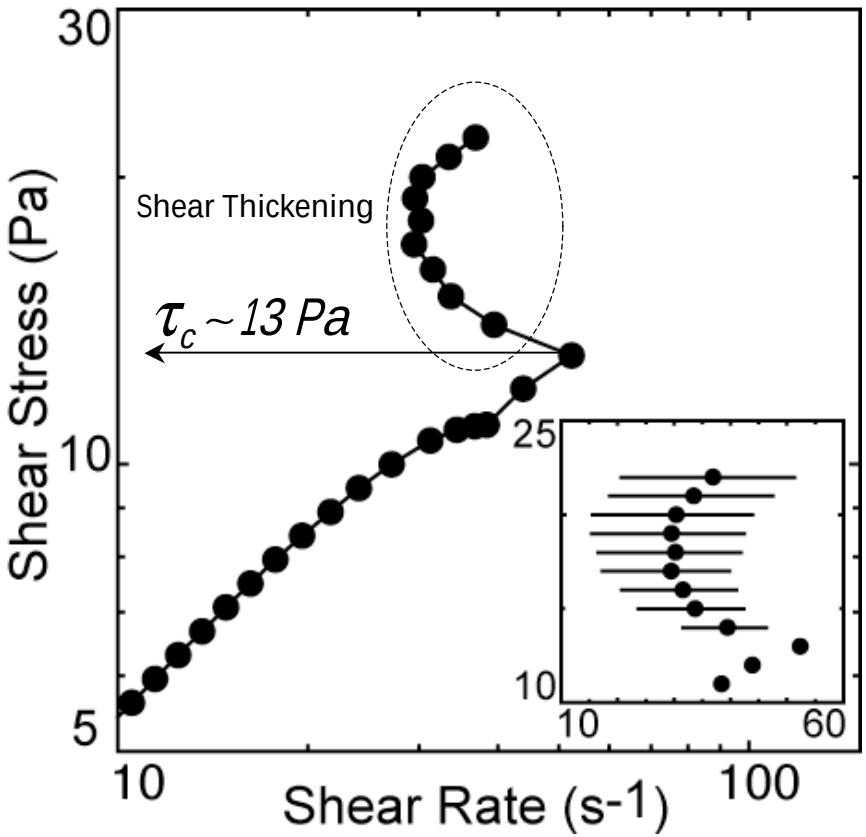
A boring afternoon in the lab



Micellar system under study

System: 40 mMol/L Cetylpyridinium chloride - Sodium salycilate

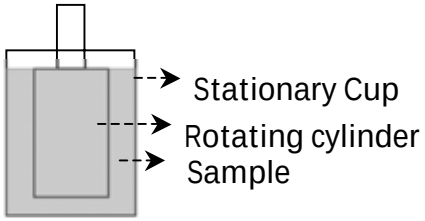


Newtonian
↓
Shear thinning
↓
Shear thickening

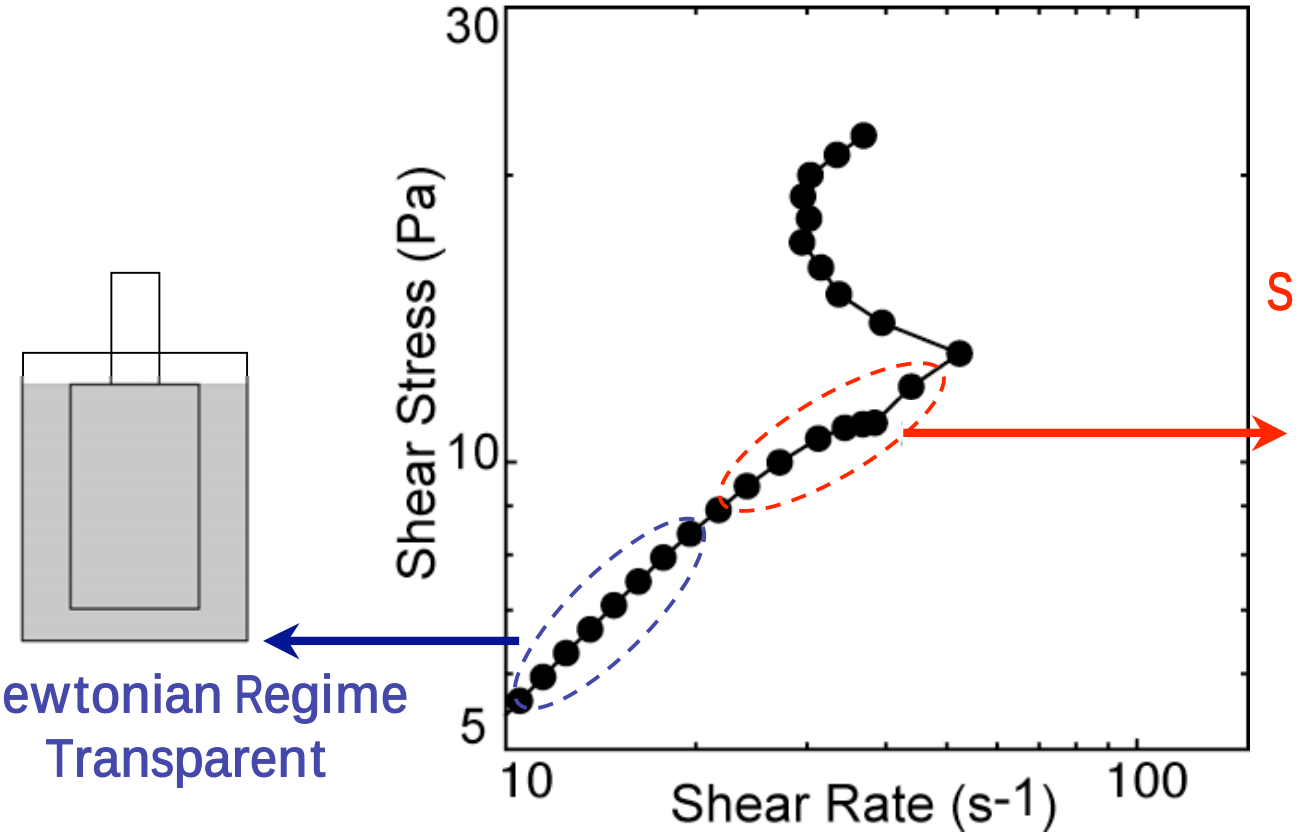
Formation of alternating vorticity bands

Herle, V., Fischer, P., and Windhab, E. J. Langmuir 2005, 21, 9051

Newtonian and shear thinning regime

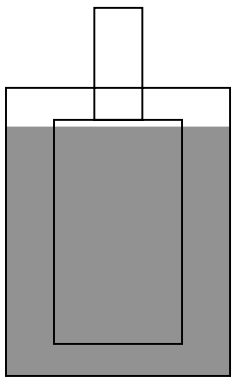


Optical appearance

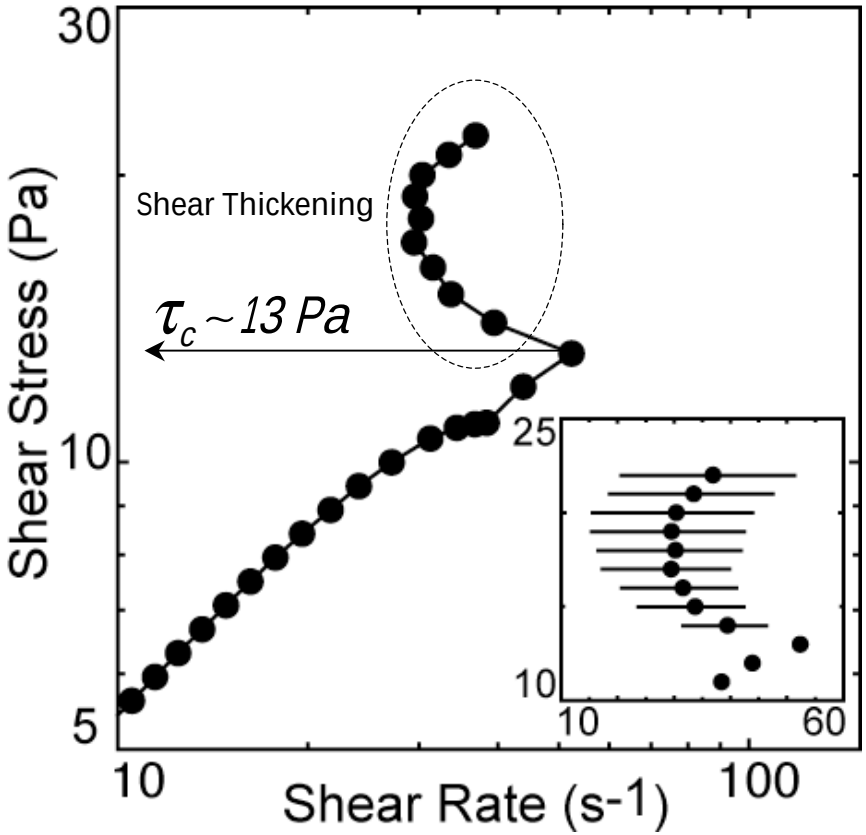


Newtonian Regime
Transparent

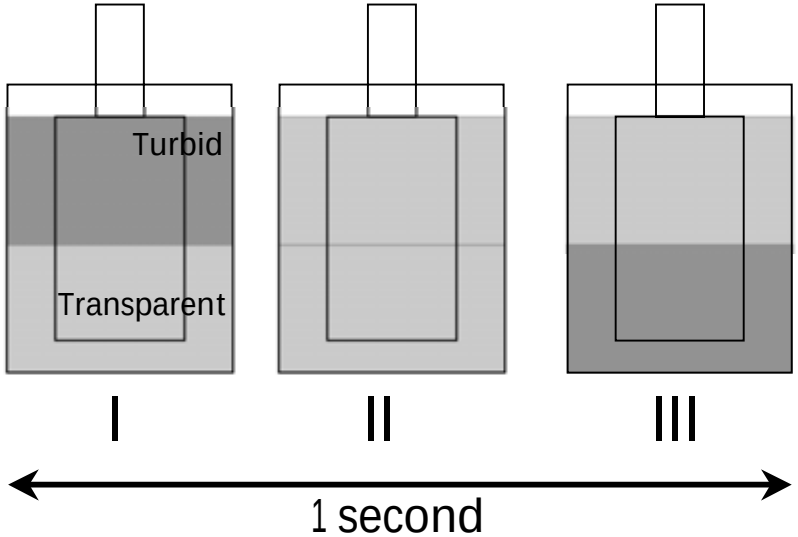
Shear thinning regime
Slightly turbid



Shear thickening regime ($\tau > \tau_c$)



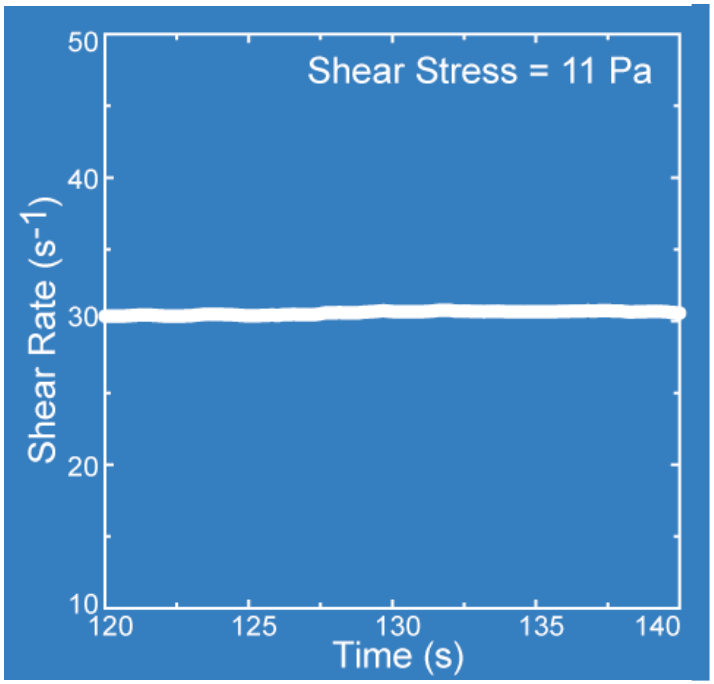
- Formation vorticity bands
- Bands alternate in position
- Shear rate and η oscillates



Rheology, flow visualization and SALS -> Stress induced bands

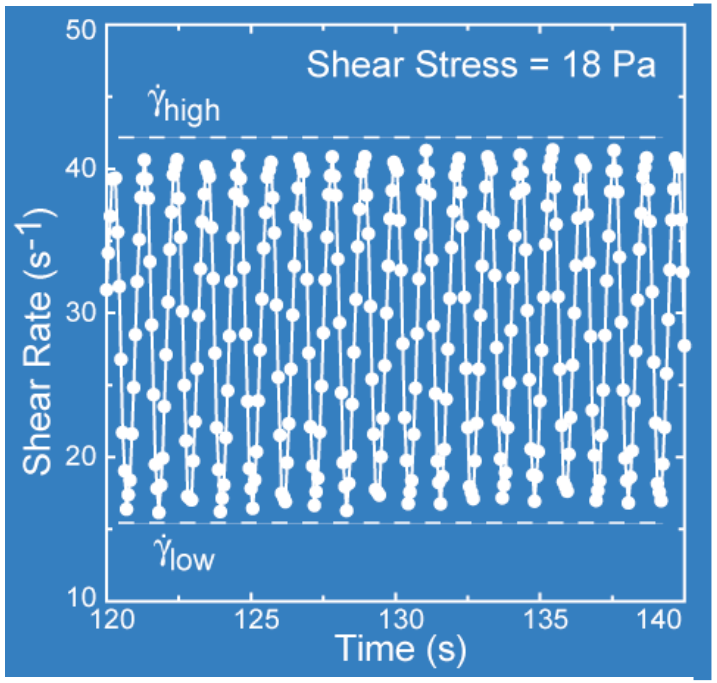
Rheology - transient shear flow

$\tau < \tau_c$



No shear rate oscillations

$\tau > \tau_c$



Shear rate oscillates
Sample never equilibrates!

Methods used & questions asked

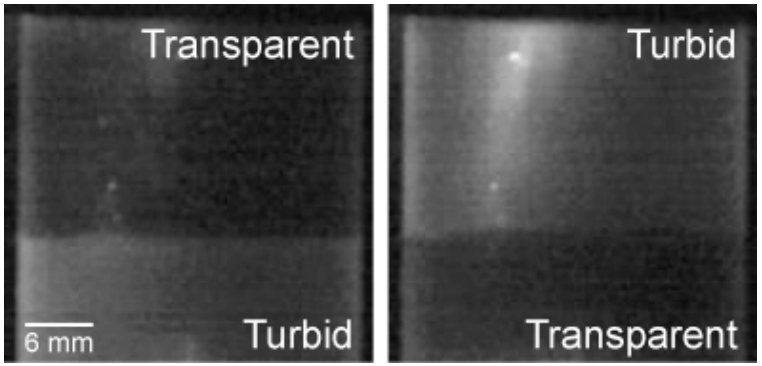
Rheology & Flow visualization

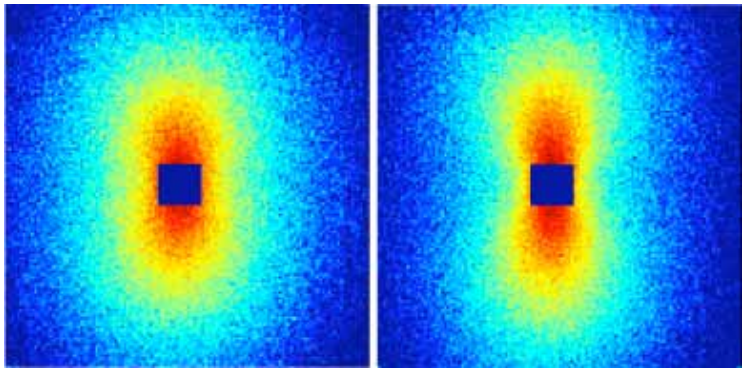
Optical appearance (flip-flop) of bands correlated to rheological oscillations?

Influence of geometry?

Triggerd Rheo-Small Angle Neutron Scattering (Rheo-SANS)

Newtonian clear =
shear thickening clear?
Shear thinning turbid =
shear thickening turbid?

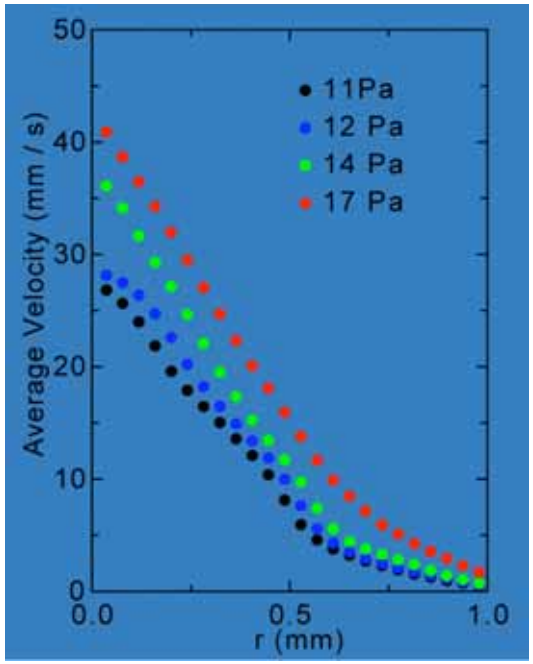


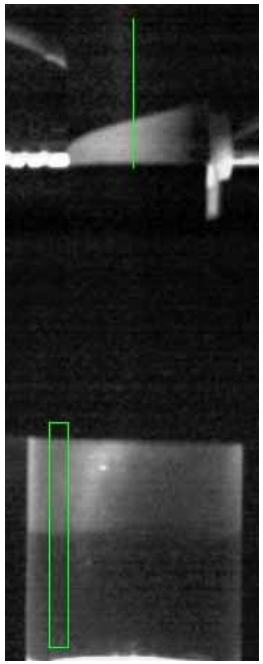


Methods used & questions asked

Fast camera, ultrasound Velocity Profiling (UVP), and Rheo-NMR

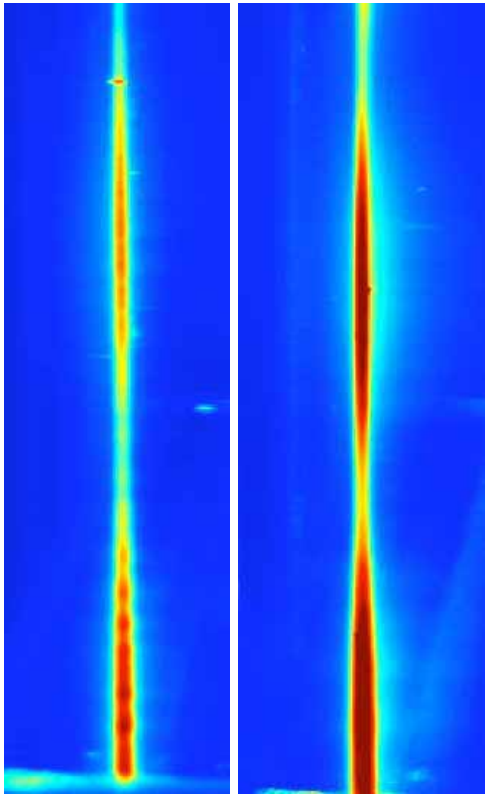
Wahst is the individual rheology of the clear and turbid bands?



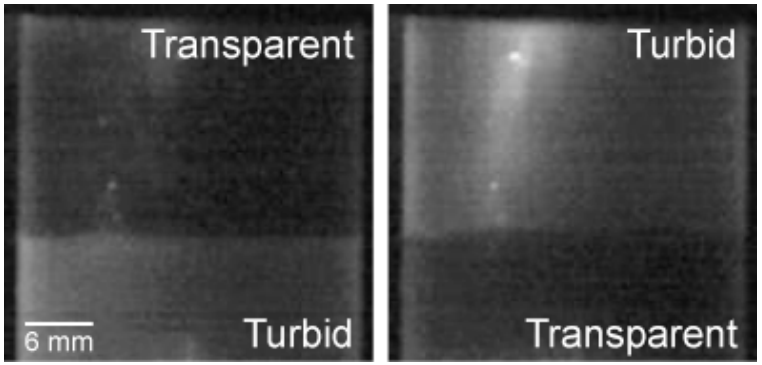


Direct birefringence measurements

Is there really a radial band within the vorticity band (sub-banding)



Vorticity bands & Rheology and SALS

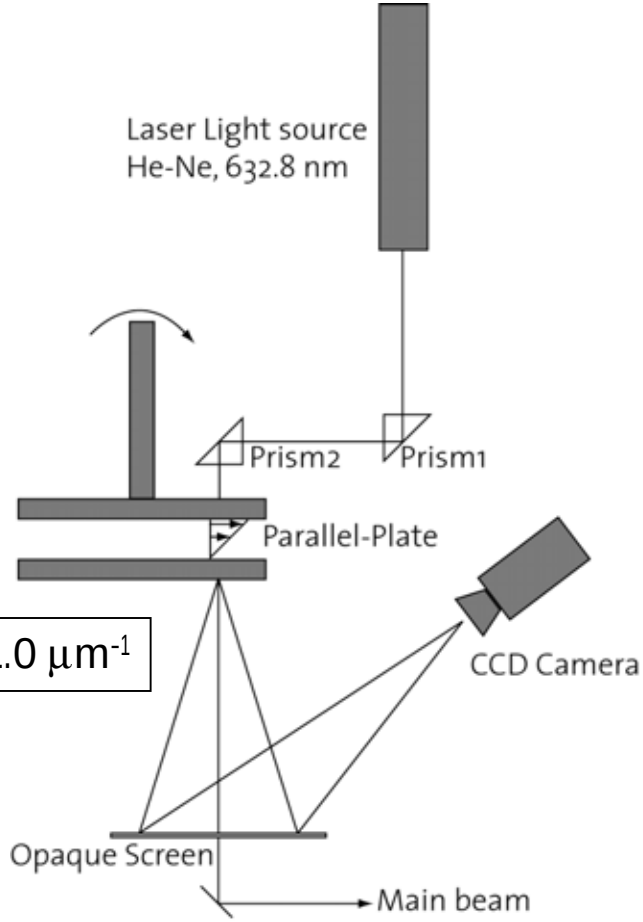


Are the oscillations in viscosity and shear rate the same as in the optical appearance of the bands?

Establish via optical rheometry and SALS the (obvious) link between ring formation and oscillation of the free parameter

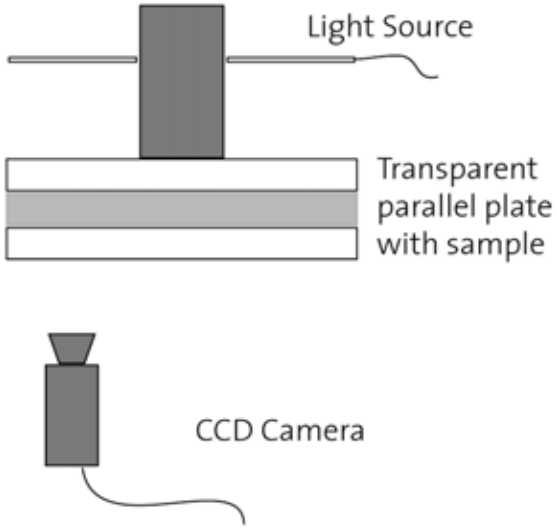
Instrumentation (optical rheology)

Rheo-Small Angle Light Scattering



$|q|=0.25 - 1.0\ \mu m^{-1}$

Optical Imaging set up



Both set-ups are designed for the Stress controlled rheometer (DSR)

Analysis of the oscillating signal - FFT

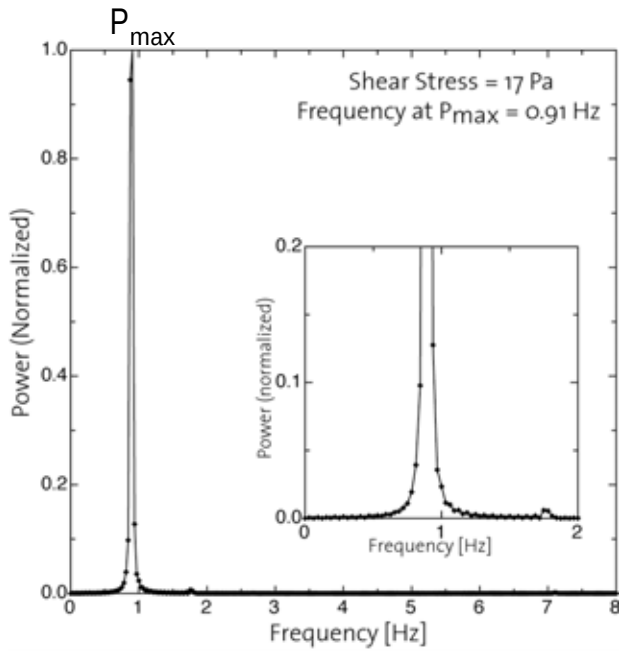
Oscillating shear rate signal from flow curves
and
Oscillating intensity signals from the shear bands

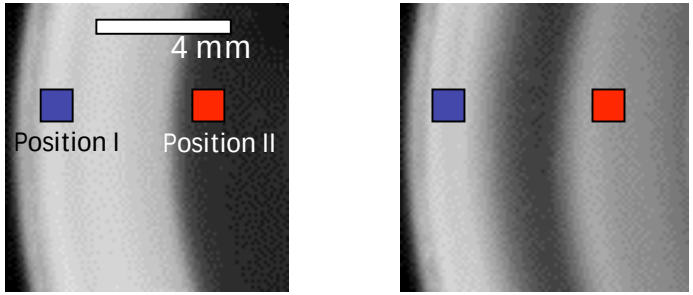
↓

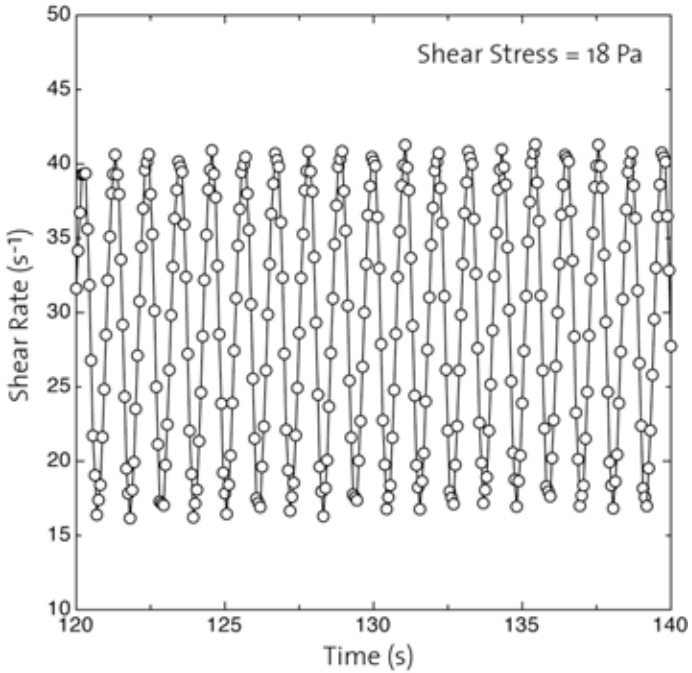
Fast Fourier Transform

↓

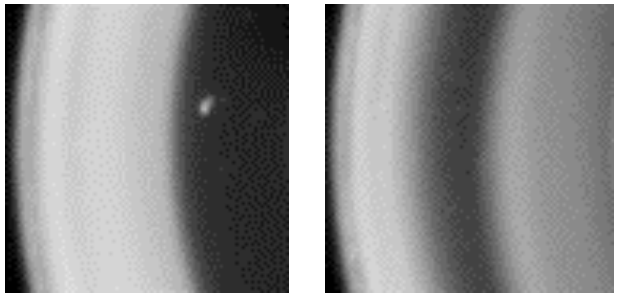
Power Spectrum



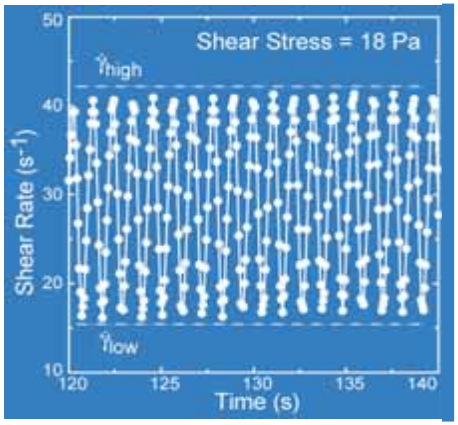




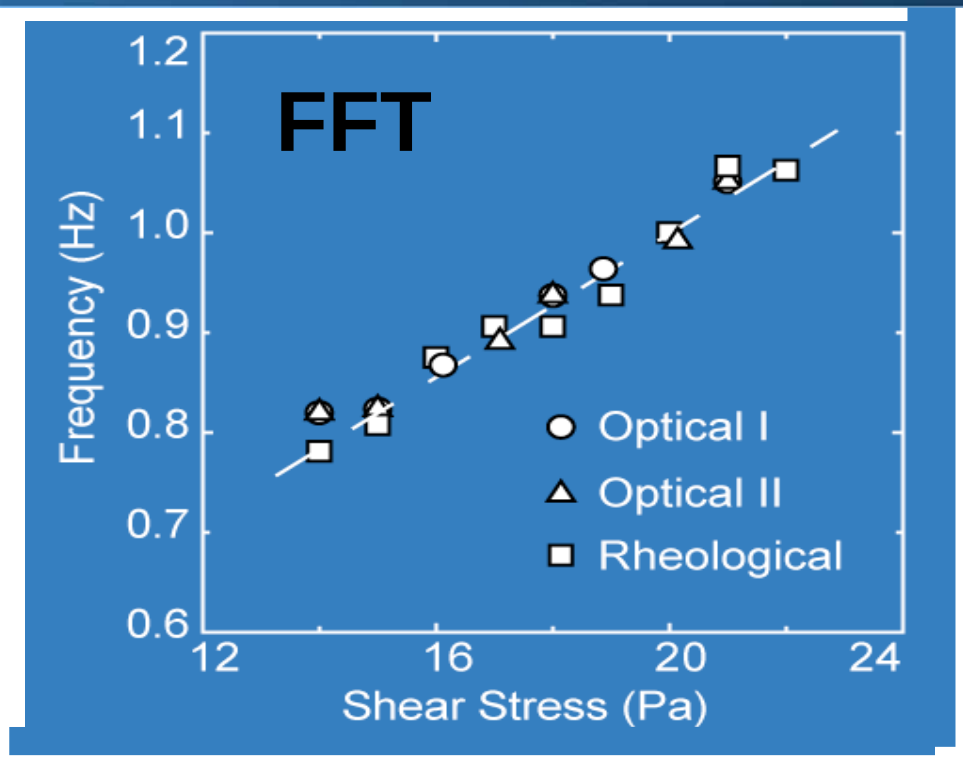
Flow visualization & Rheology



Oscillating shear bands in parallel plate device



Rheological signal

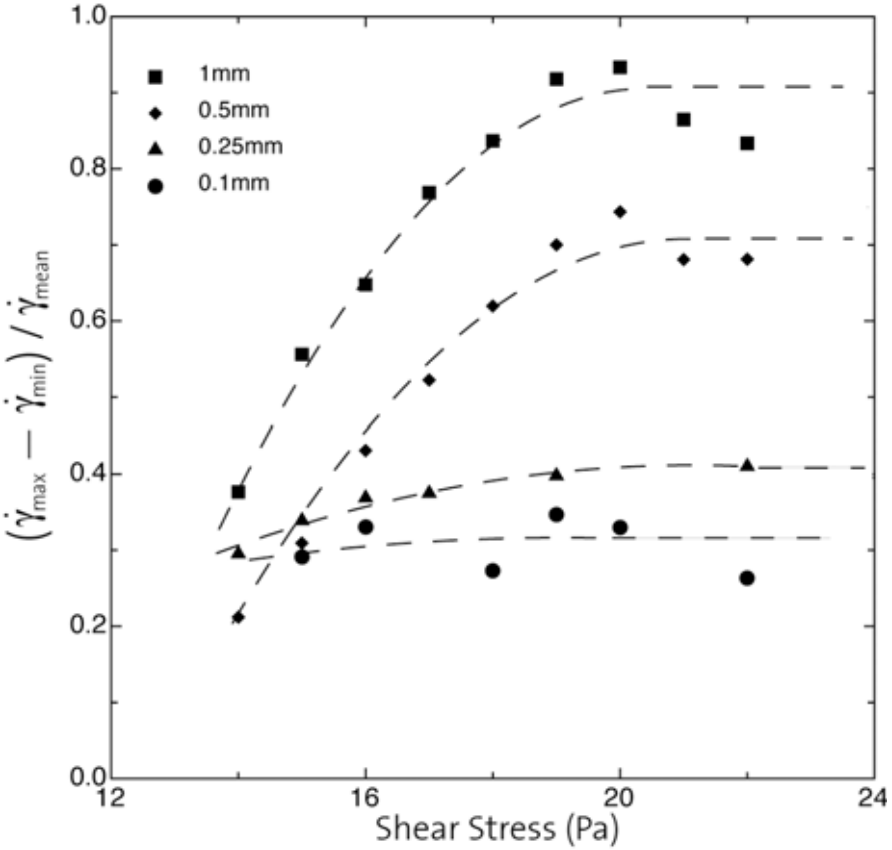


Optical and mechanical signals superimpose!

Oscillations are indeed due to the flip-flop of the bands

Herle, V., Fischer, P., and Windhab, E. J. Langmuir 2005, 21, 9051

Effect of gap size - Amplitude

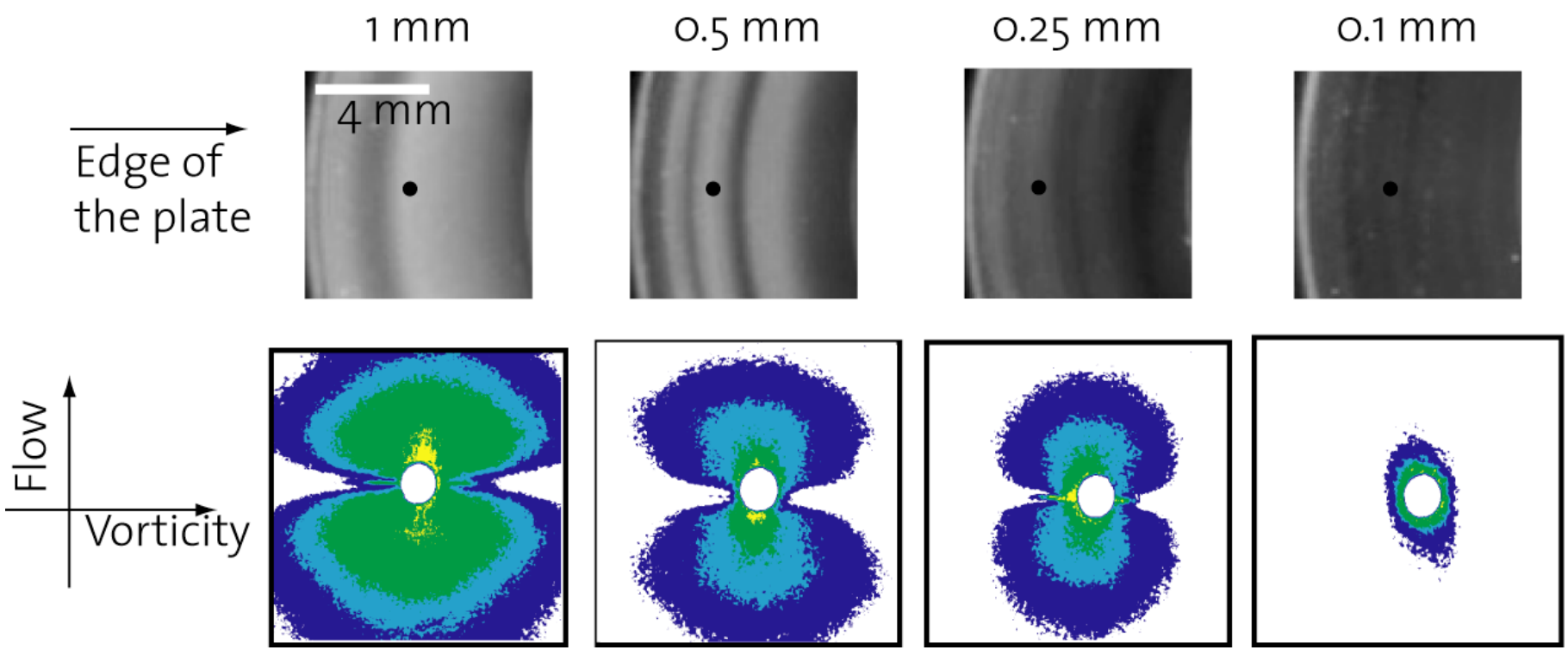


Amplitude of rate oscillation increases with stress @ constant gap (except for 0.10 mm)

Decrease in gap suppresses the rate oscillations
For a gap of 0.10 mm-> NO
0.10 mm is an exception!

Certain length scale is required for band formation

Flow visualization & Rheology

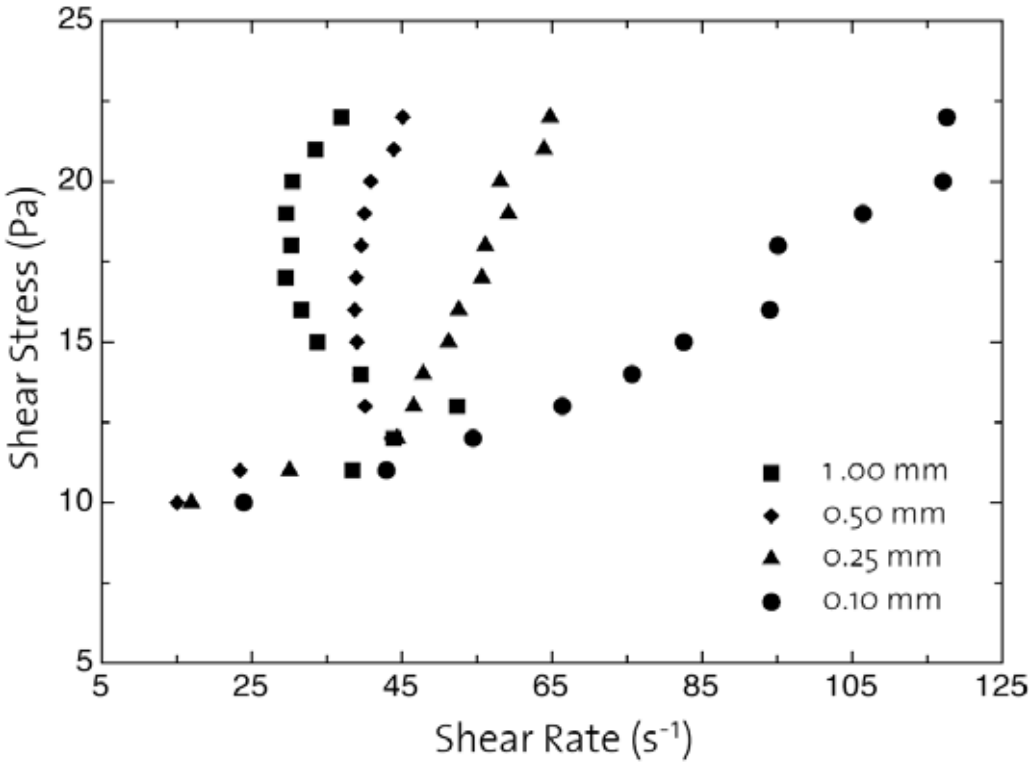


Structural buildup is determined by the rheometer gap

Herle, V., Fischer, P., and Windhab, E. J. Langmuir 2005, 21, 9051

Flow visualization & Rheology

Shear induced structures <---> Length scales

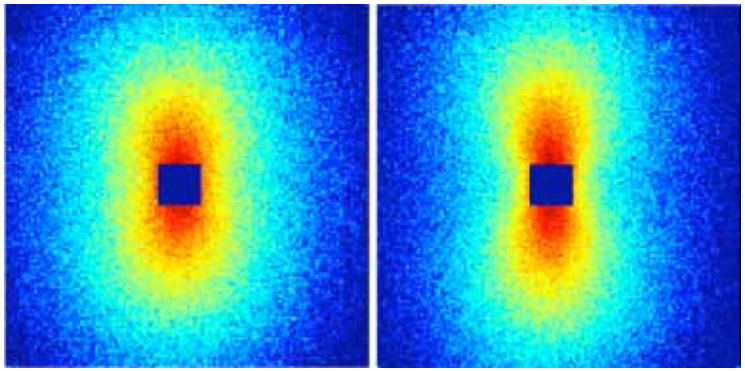


Lowering the gap

- Shear thinning instead of thickening
- Intensity of turbid bands decreases
- More number of less intense bands
- Oscillations of the $\dot{\gamma}$ are dampened

Herle, V., Fischer, P., and Windhab, E. J. Langmuir 2005, 21, 9051

Vorticity bands & SANS

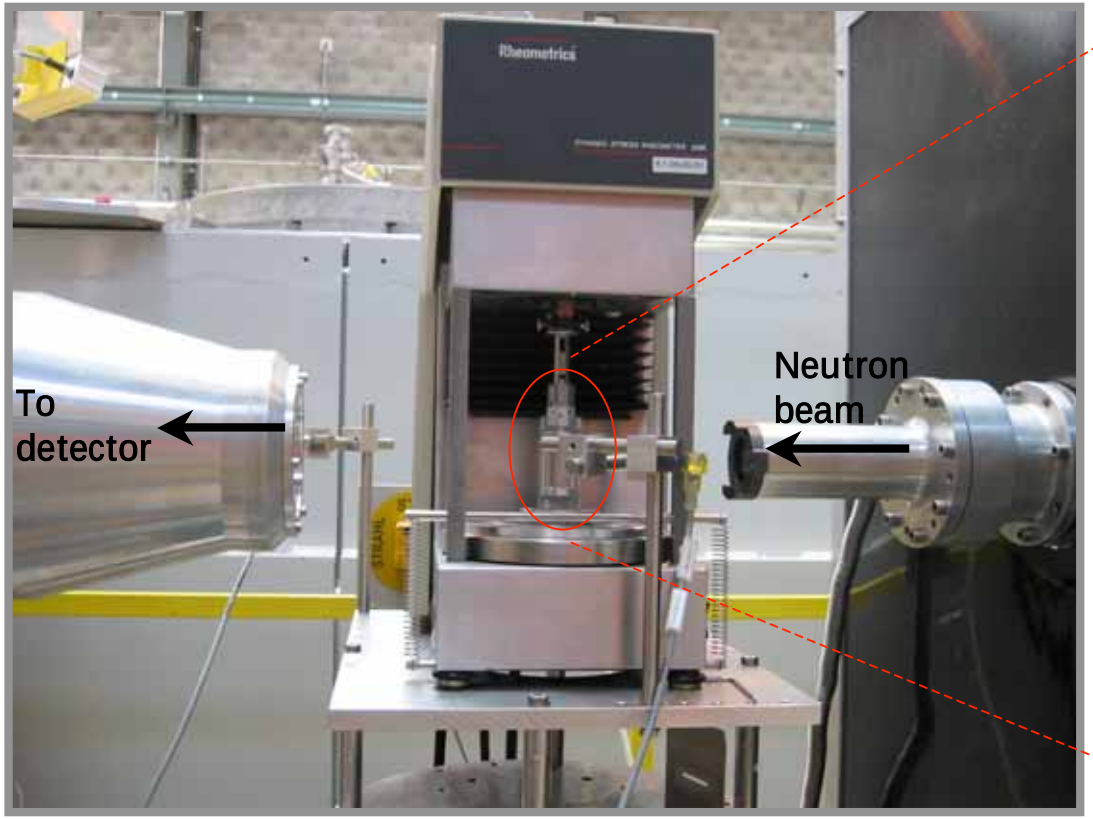


What are the **structures** in these bands?

How to access the structural information in each band?

By triggering the SANS detector and selectively collecting the scattering for each band

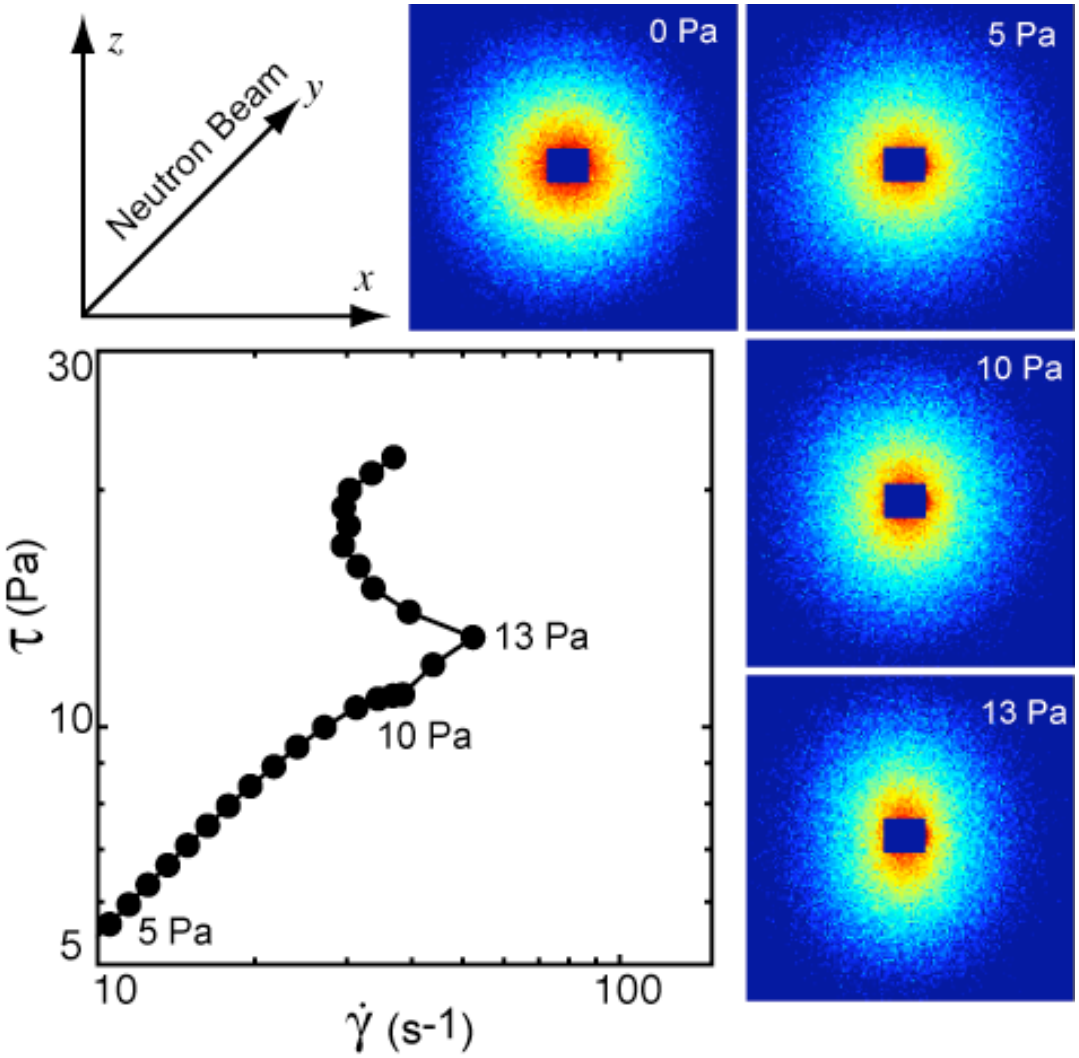
SANS - Set up



Neutron source: PSI SANS-I
$\lambda = 8$ Å
Detector dist. = 2, 6, and 18 m
q range = 0.003 - 0.15 $Å^{-1}$

Suprasil Glass
Outer cylinder dia = 32 mm
Inner cylinder dia = 30 mm
Gap = 1 mm

Newtonian and Shear thinning regime

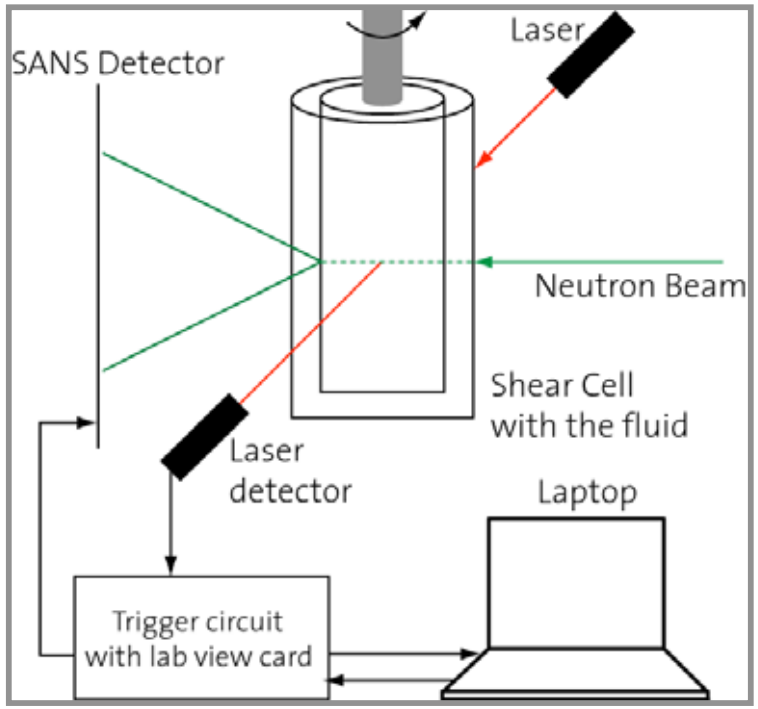


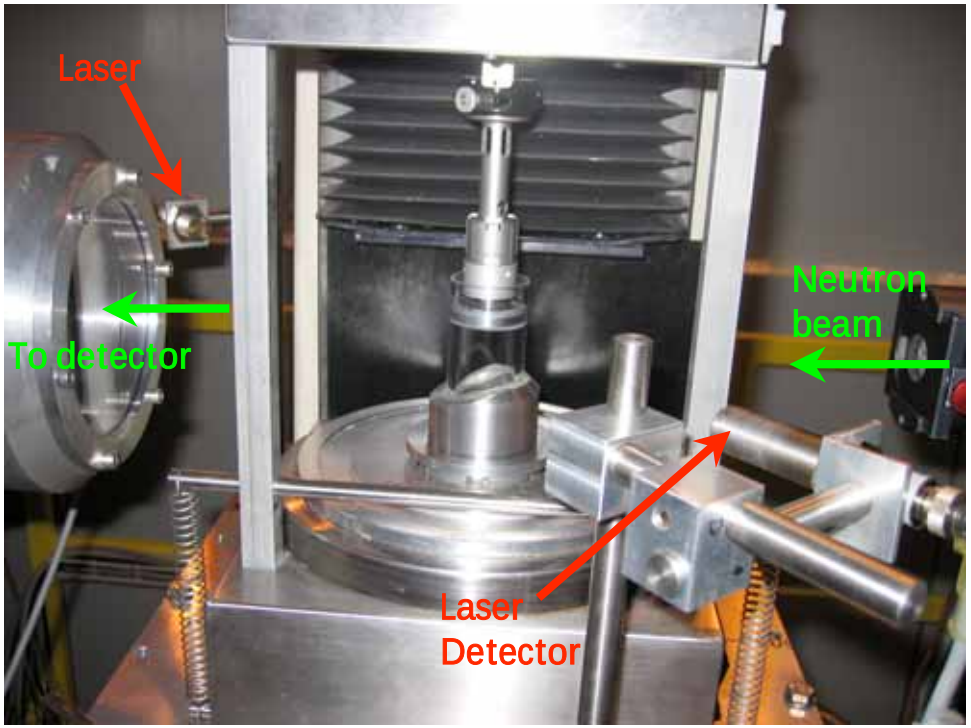
x = Flow direction
y = Vel. gradient direction
z = Vorticity direction

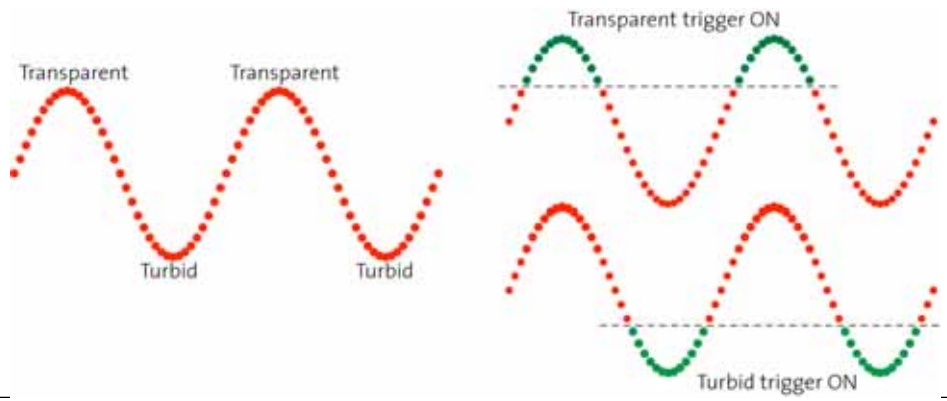
1. No significant anisotropy is observed
2. Partial alignment of micelles

Herle, V., Fischer, P., et al.: Phys. Rev. Lett., in press.

SANS-Trigger Set-up

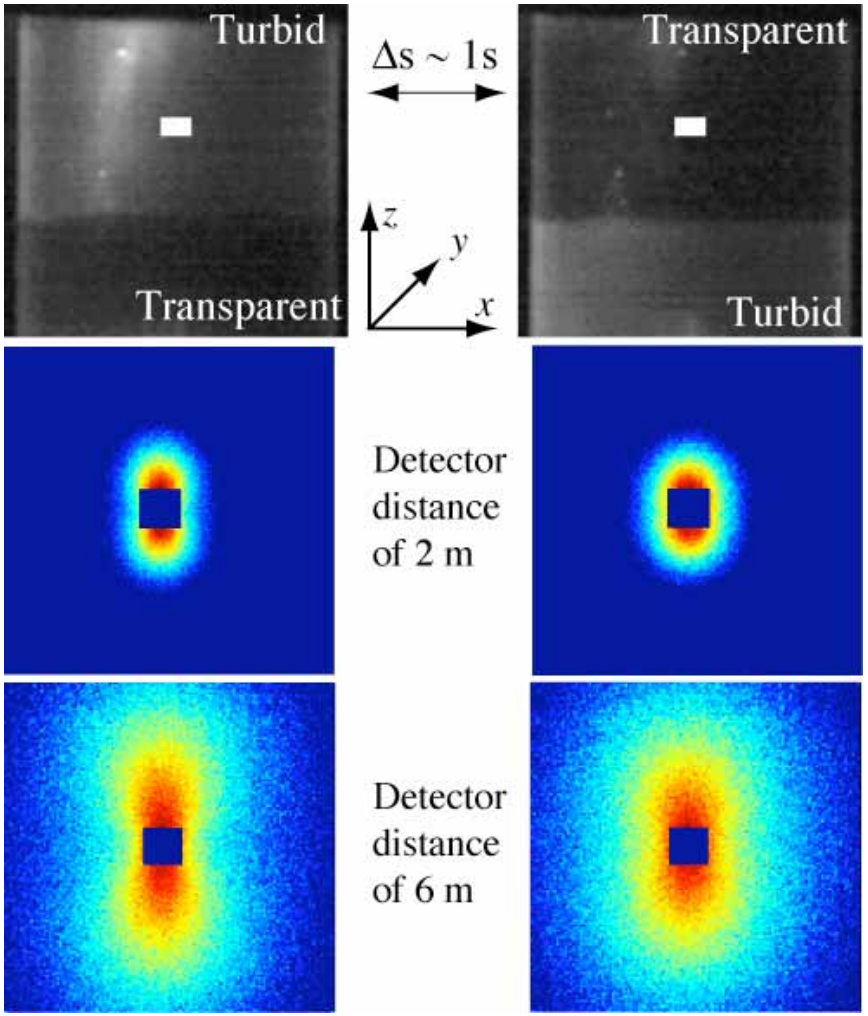






- Set a threshold value
- Trigger the SANS detector
- Collect the data

Triggered SANS measurements

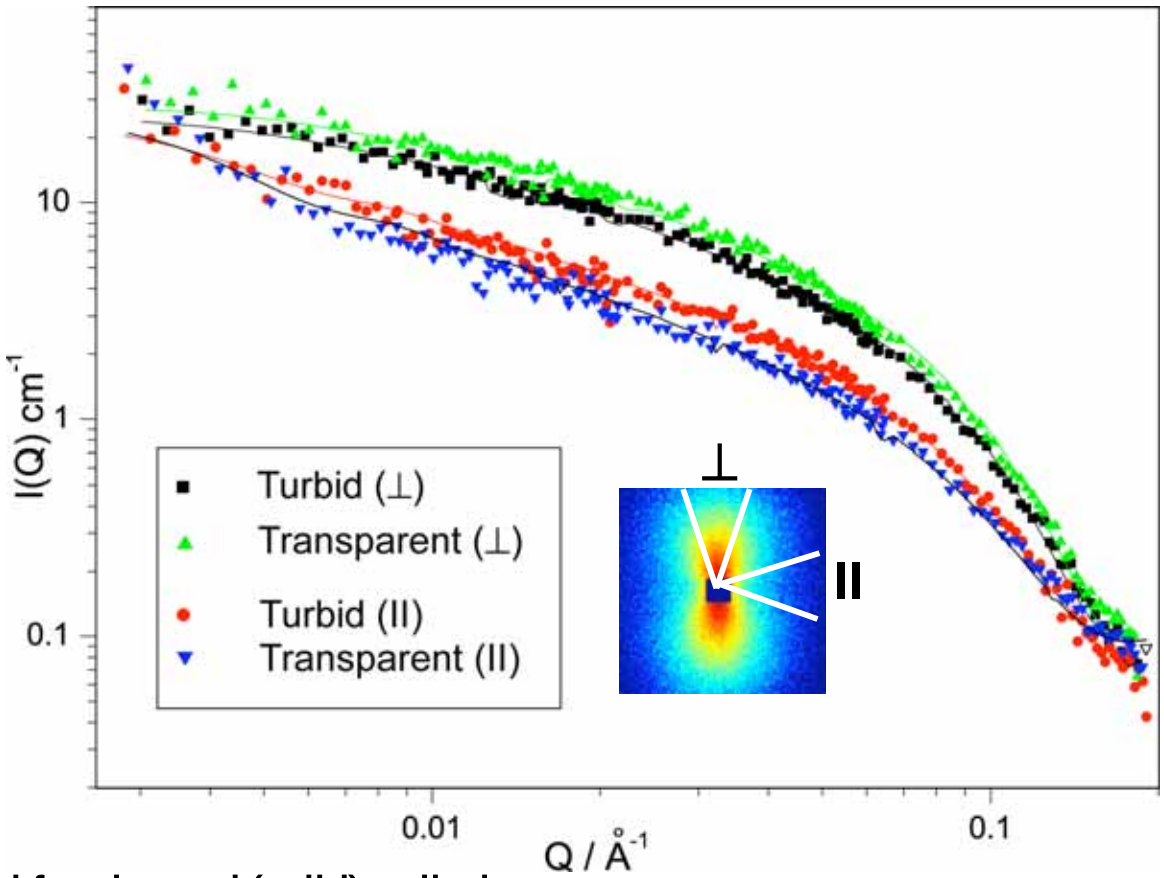


1. Triggering the detector helps to separate the scattering information
2. Transparent state in this regime is structurally different from the one in the Newtonian or shear thinning regime
3. Both transparent and turbid bands are highly anisotropic
4. Turbid state is more anisotropic than transparent one

Herle, V., Fischer, P., et al.: Phys. Rev. Lett., in press.

SANS Analysis for flip-flop bands

I vs *q* plot

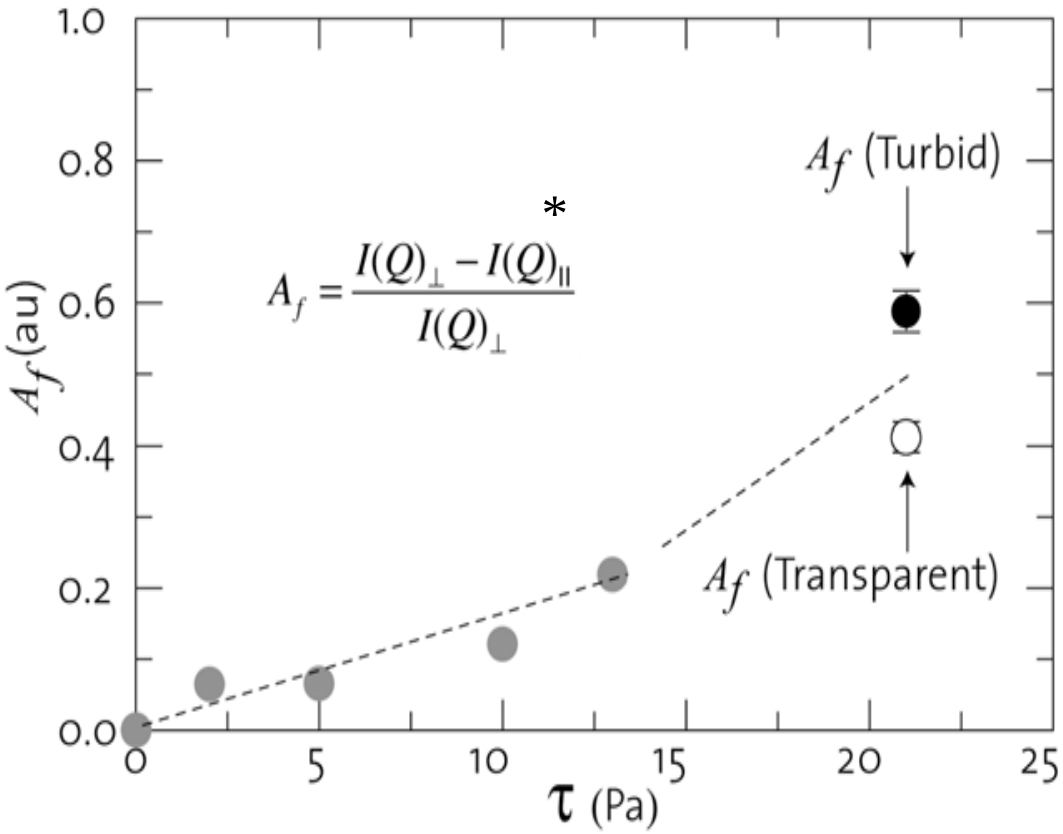


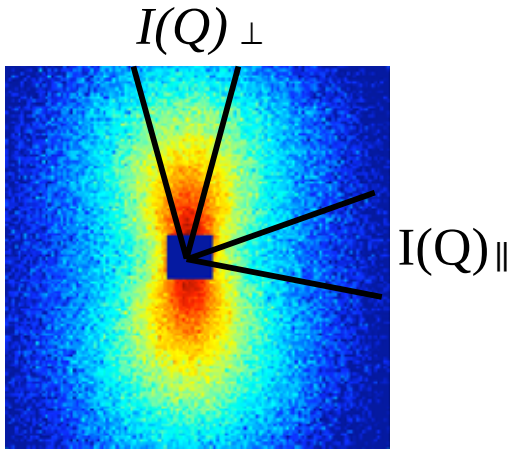
Hayter model for sheared (solid) cylinders
Dia of micelles ~ 40 angstrom
Approx. length of micelles ~ 1200 angstrom

Hayter, J.B. and Penfold, J.: J. Phys. Chem 88 (1984) 4589

SANS Analysis for flip-flop bands

Anisotropy





Turbid band correspond to a more anisotrope state

* Croce et. al. 2005, Langmuir
Schubert et. al. 2004, Langmuir

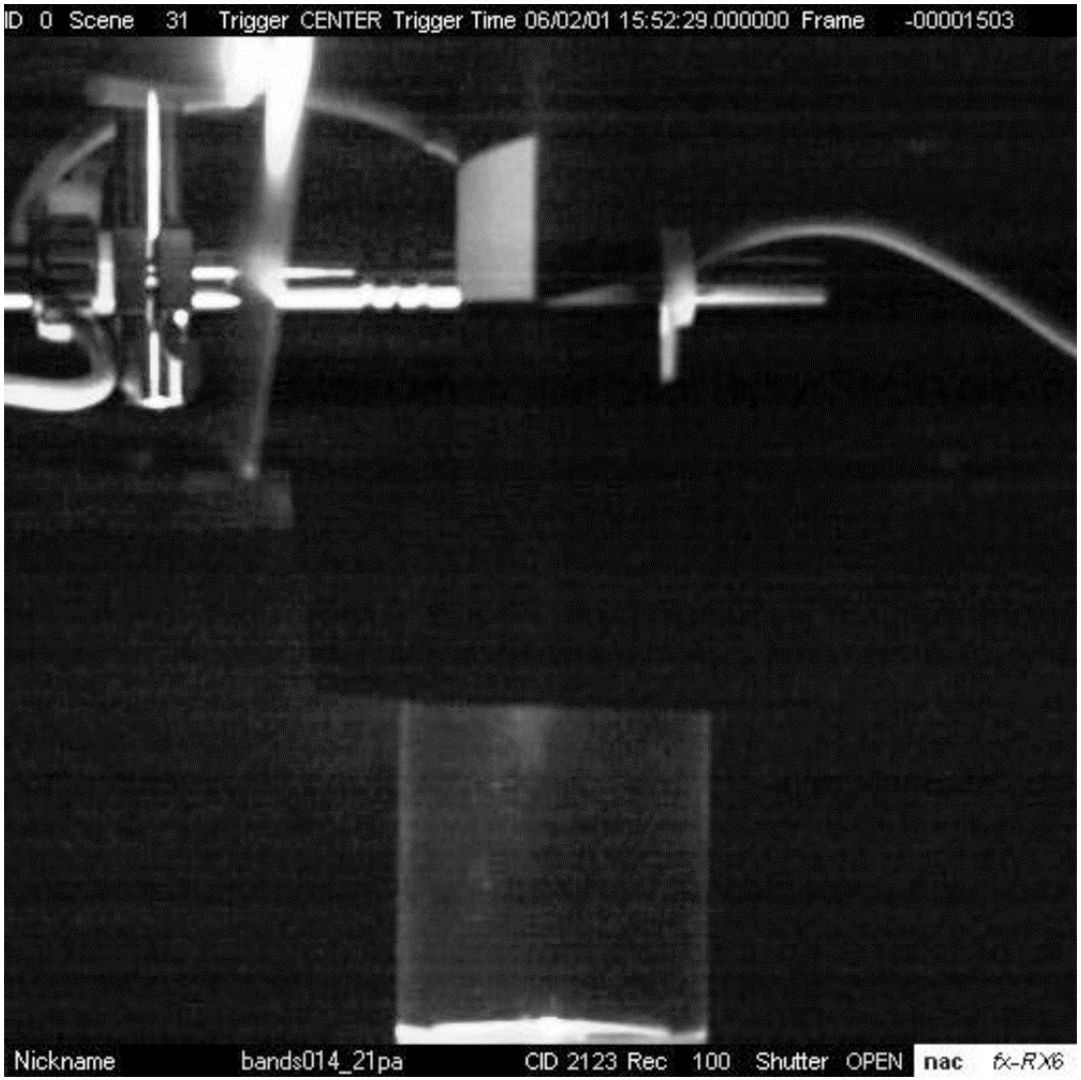
High speed camera

What are the **viscosity** in the individual bands (Part I)?

How to access the rheology of each band?

Motion of rotation tool captured by
high speed camera images

Alternating Vorticity bands

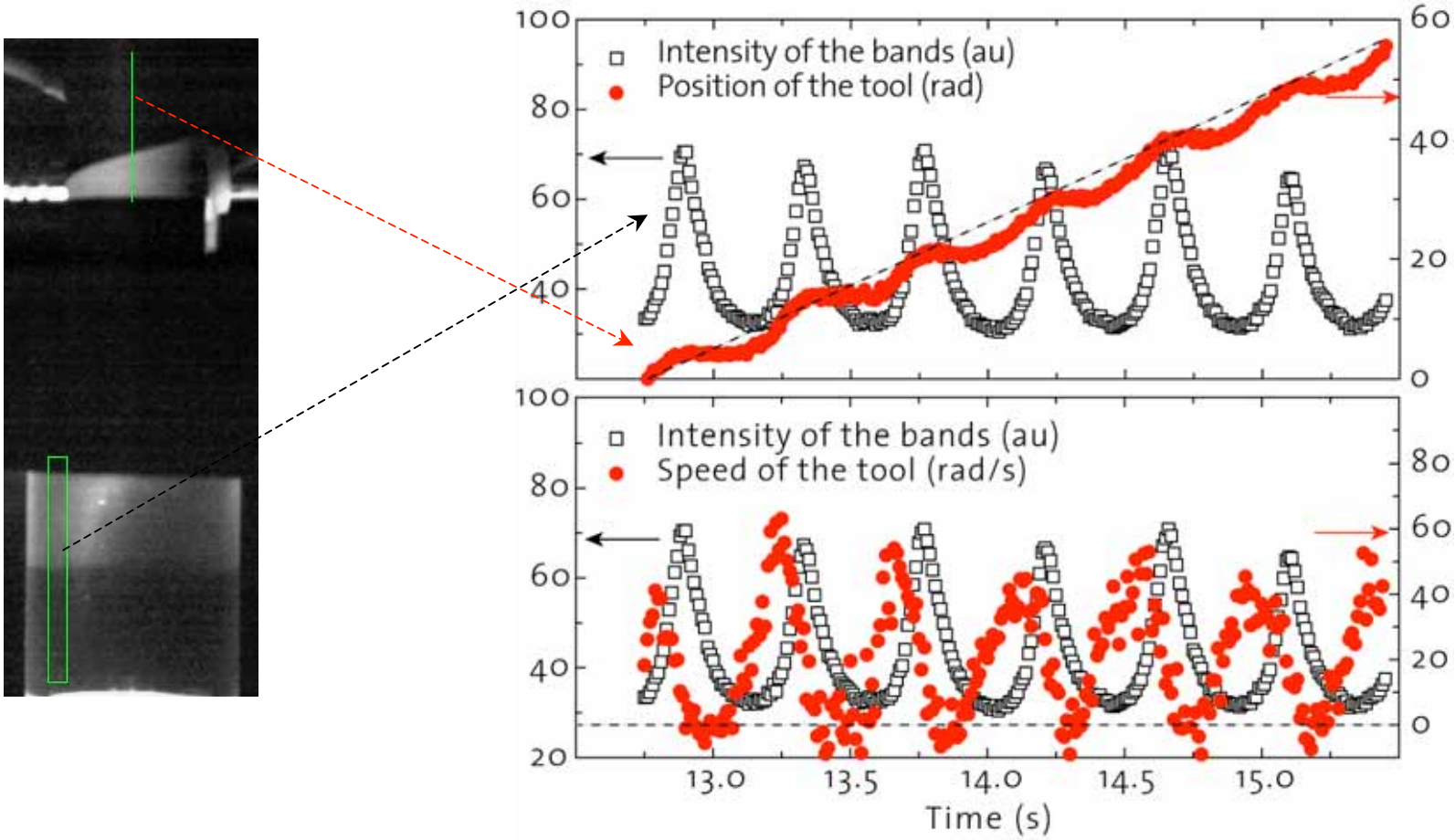


Problems and Questions

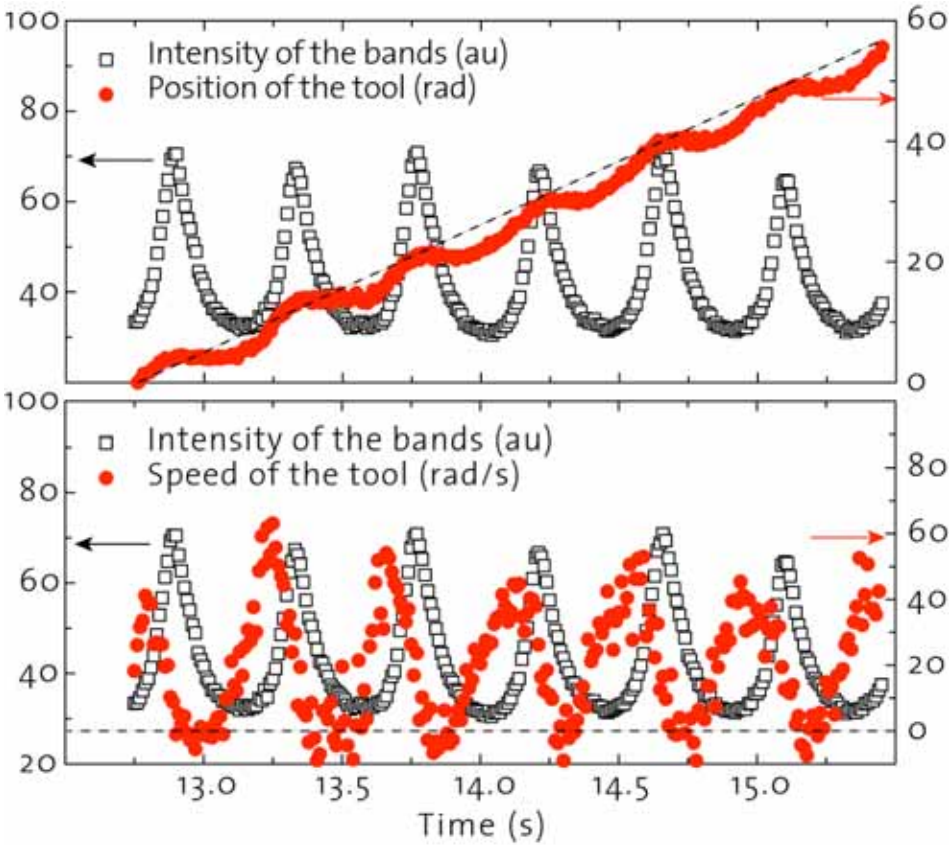
- It is difficult to capture the dynamics of the process
- Does the oscillation in the tool really corresponds to the bands?
- If yes, then, when the tool slows down and when it accelerates?
- Finally, what are the structures in these bands?

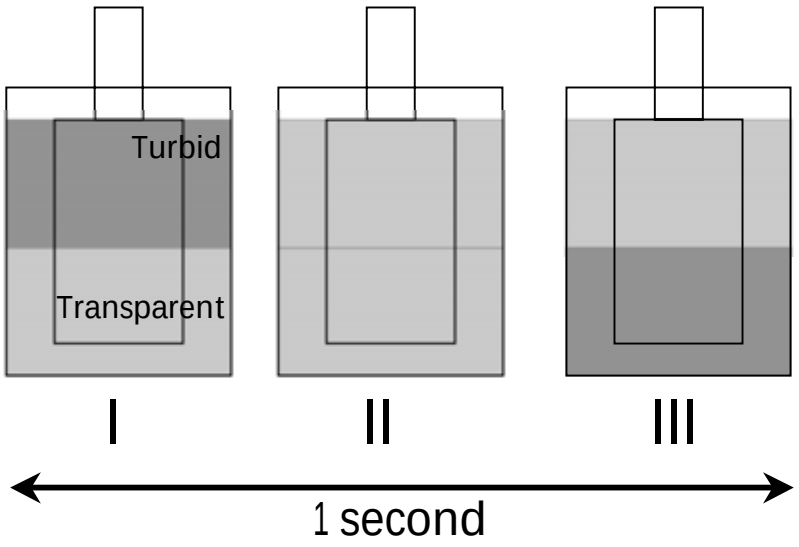
Vorticity bands- Analysis

Analysis of the bands and the position of the tool using LabView program



Vorticity bands- Analysis



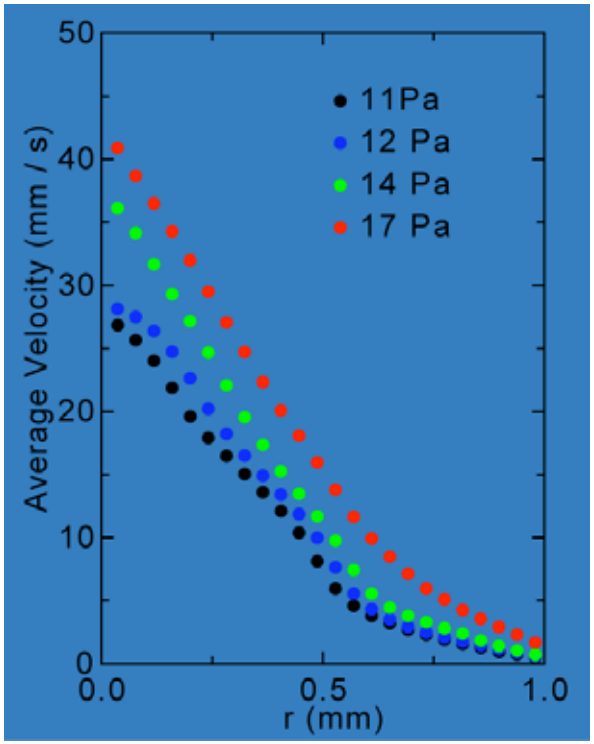


Lower intensity -> transparent band
Higher intensity -> turbid band

- As the turbid band appears velocity approaches zero
- Implying turbid bands may be of higher viscosity!

Herle, V., Fischer, P., et al.: Phys. Rev. Lett., in press.

Vorticity bands & UVP



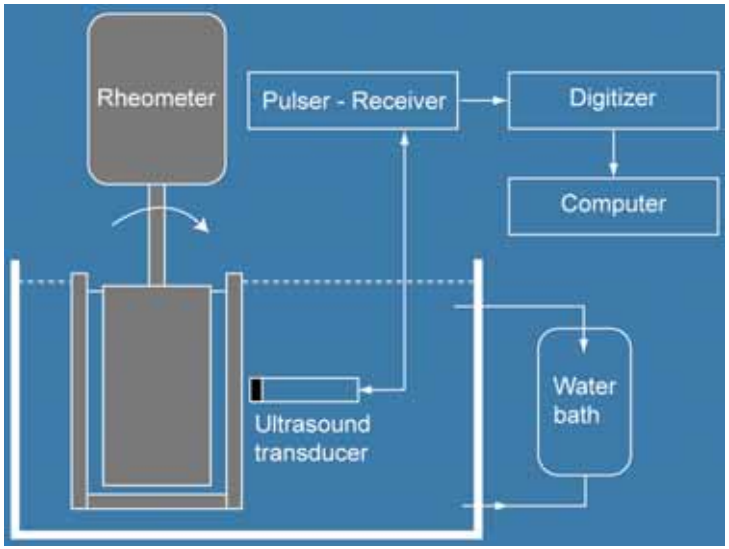
What are the **viscosity** in the individual bands (Part II)?

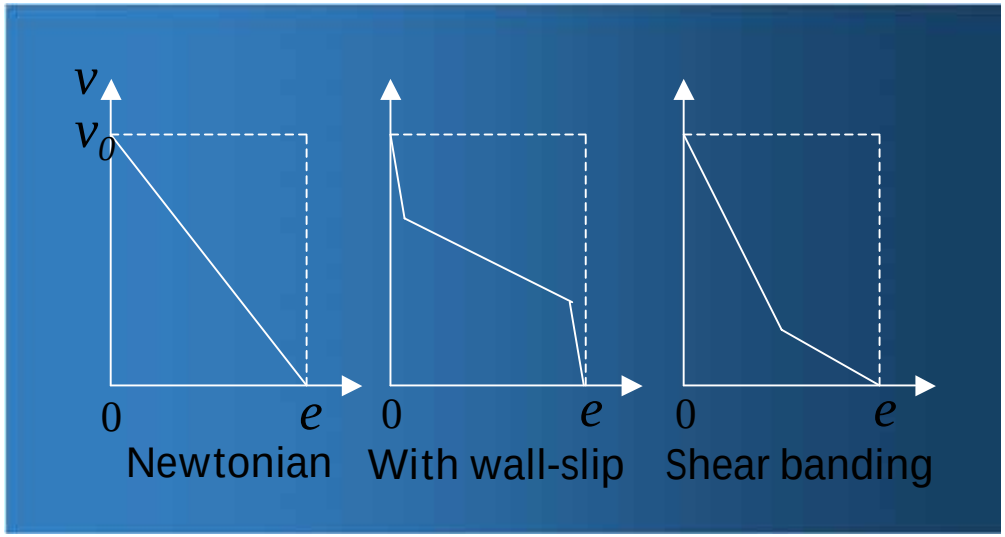
How to access the rheology of each band?

Is the turbid band more viscous than the clear one?

By time-resolved Ultrasound Doppler Velocimetry collecting the shear rate for each band

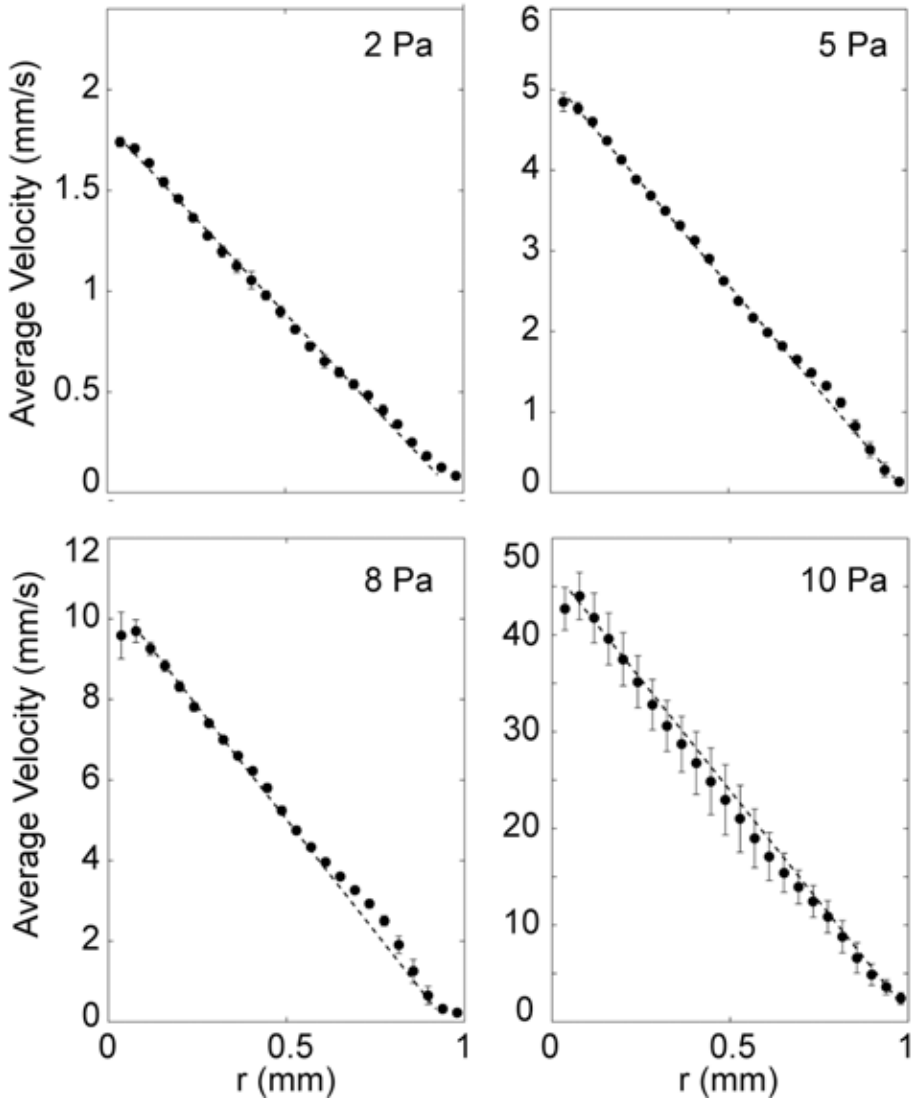
UVP-Experimental Set-up

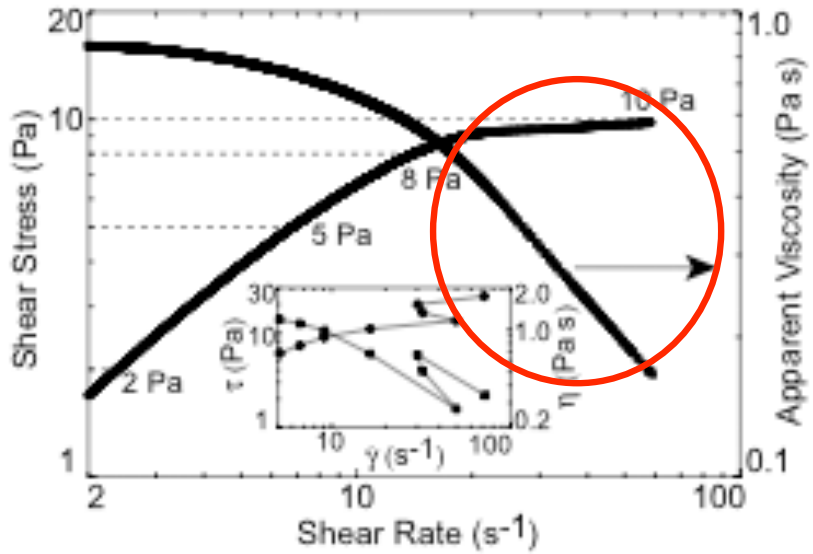




Manneville S: Eur. Phys.J.-Appl.Phys 28 (2004) 361

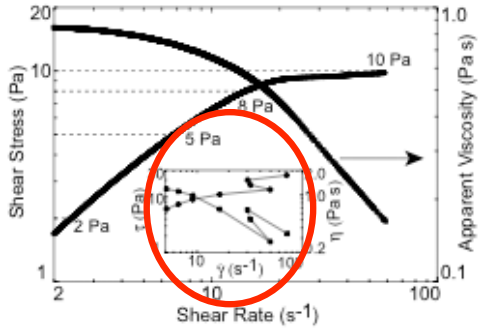
UVP @ Newtonian and Shear thinning regime

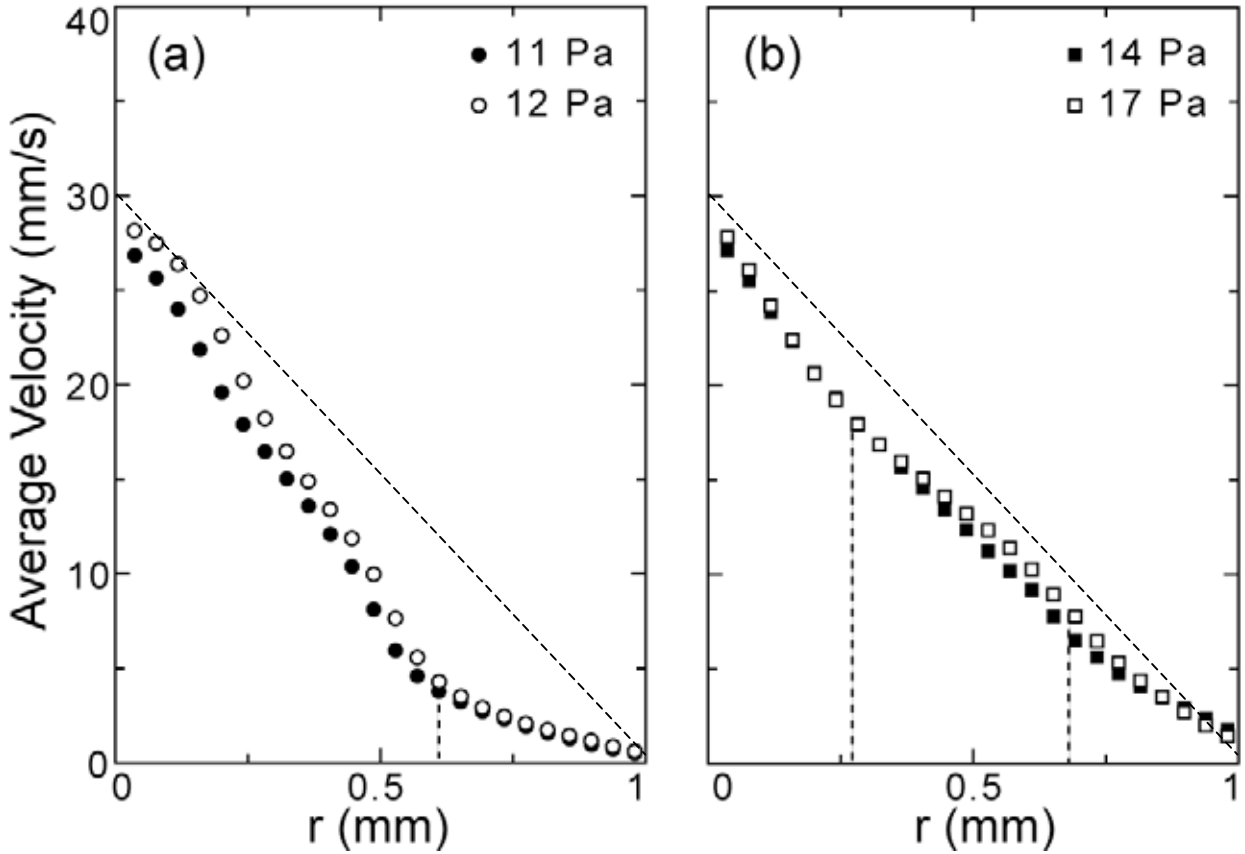




- No radial banding in stress plateau regime as in conventional systems
- Flow is homogeneous

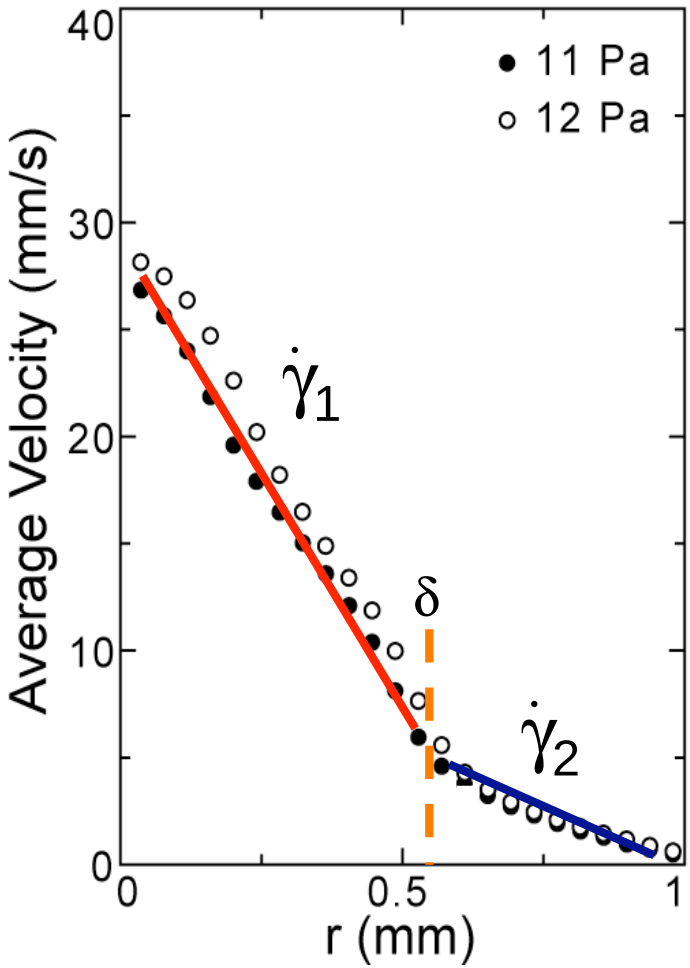
UVP @ Shear thickening regime ($\tau > \tau_c$)

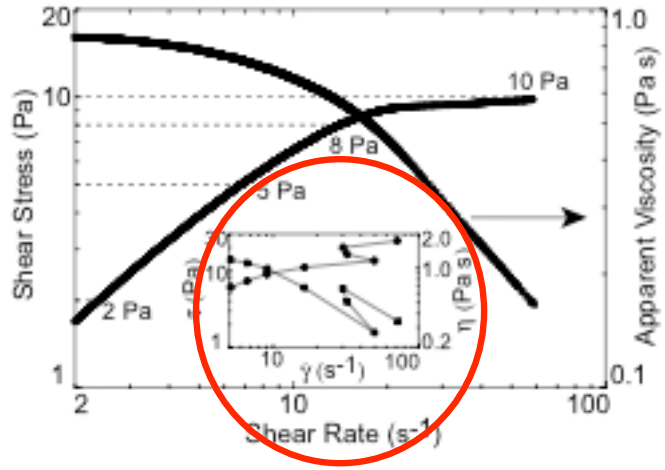




- Radial Banding is present
- Flow is inhomogeneous
- At higher stresses flow becomes chaotic!
- Local velocity fluctuates as a function of time

Local shear rates and time evolution ($\tau > \tau_c$)





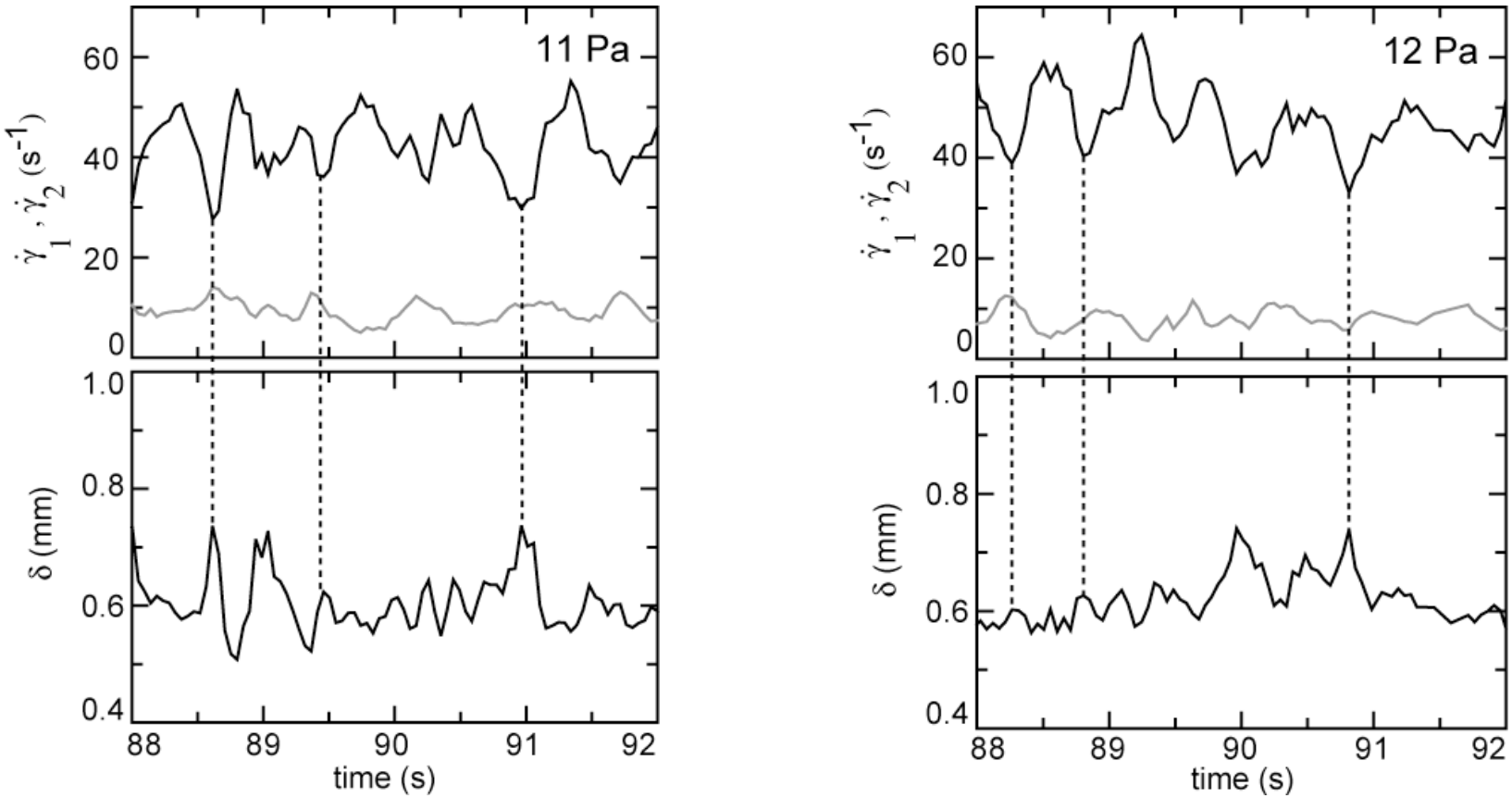
Local shear rates in each band can be calculated

This will give an idea about local shear rates

Position of the interface (δ) was monitored

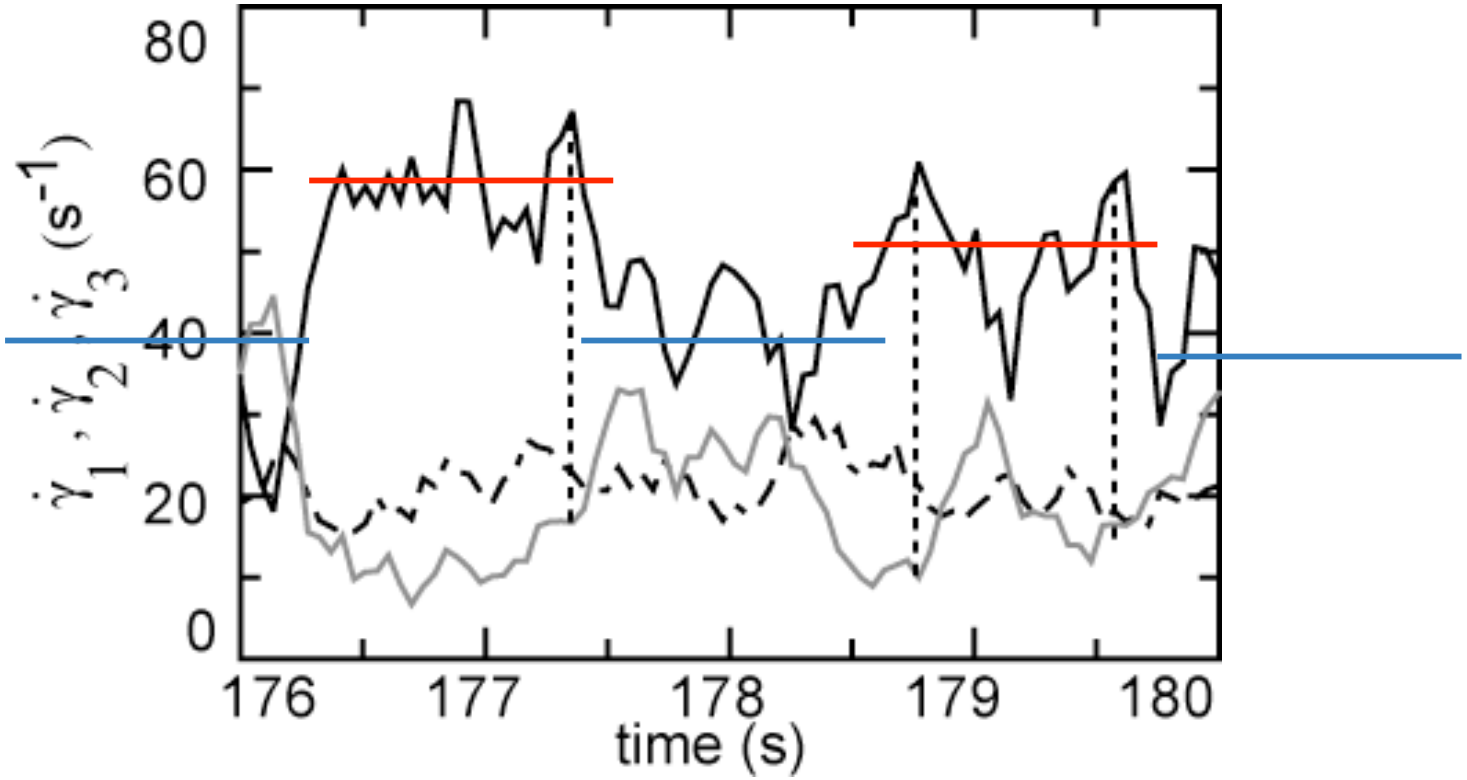
Local shear rates as a function of time ($\tau > \tau_c$)

In the Stress-plateau regime



γ_1 and γ_2 are anticorrelated
γ_2 and δ are correlated

Local shear rates as a function of time @ 17 Pa

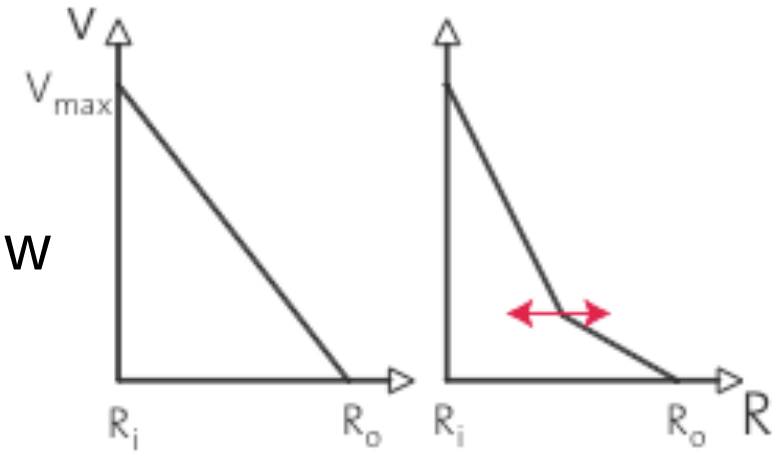


We do not see the vorticity bands (all turbid due to seeding):

- The behavior of local shear rates seems chaotic!
- Is the flip-flop of the macroscopic motion hidden?

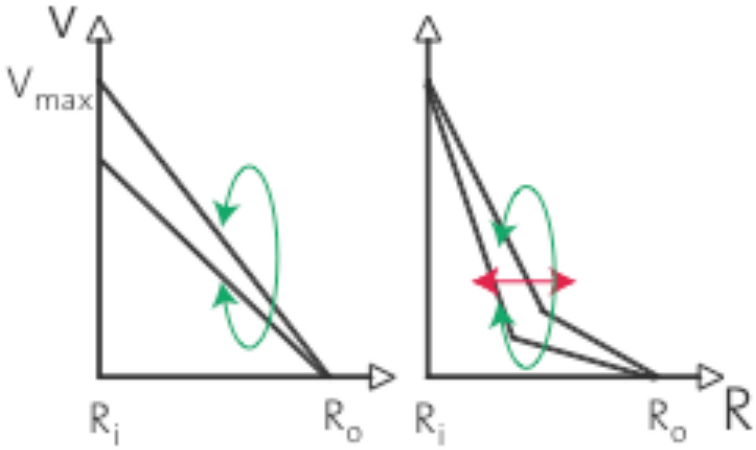
Possible coexistence of radial and vorticity bands?

Newtonian flow
Shear-thinning flow



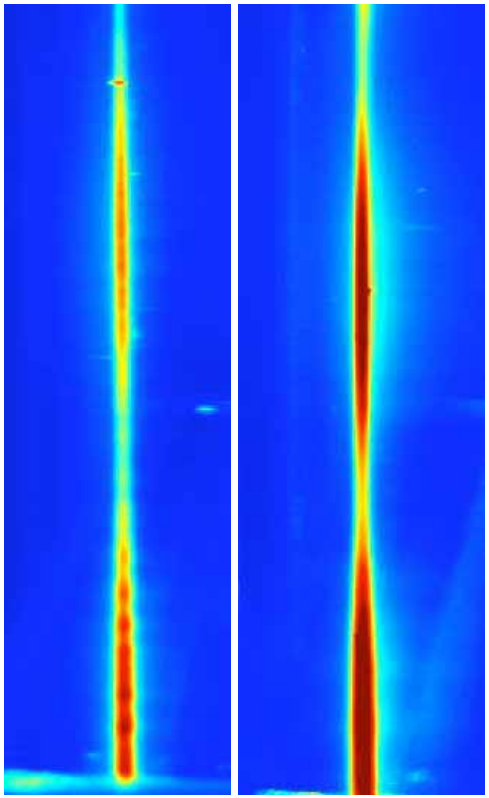
Radial shear banding

Vorticity banding



Coupled radial and vorticity banding plus pretty much noise of rheo-chaos

Vorticity bands & Direct birefringence

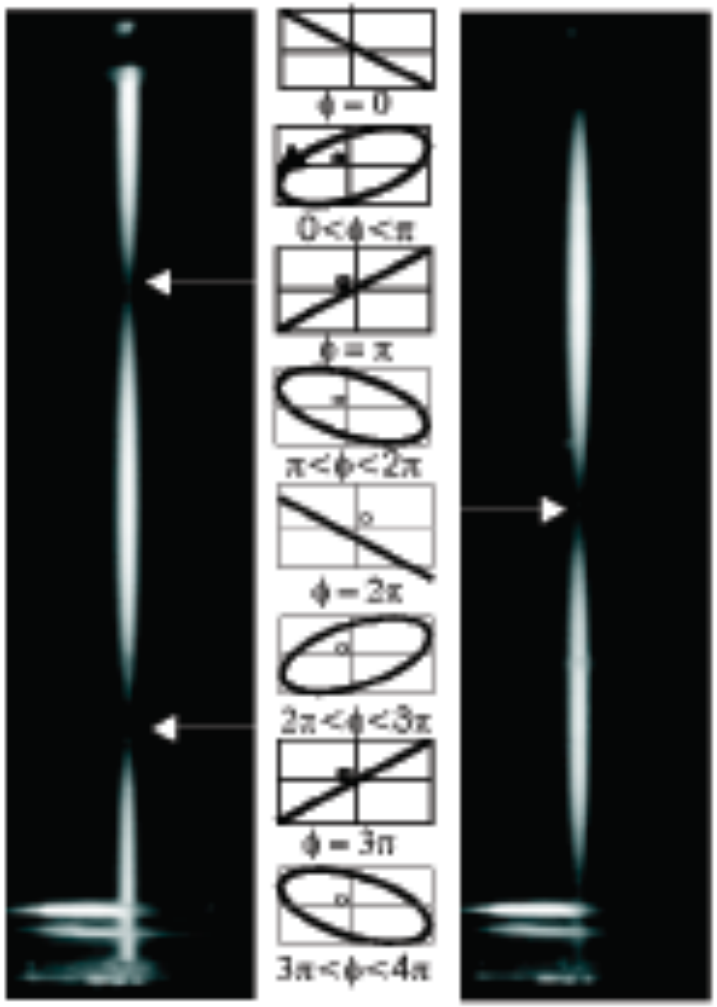


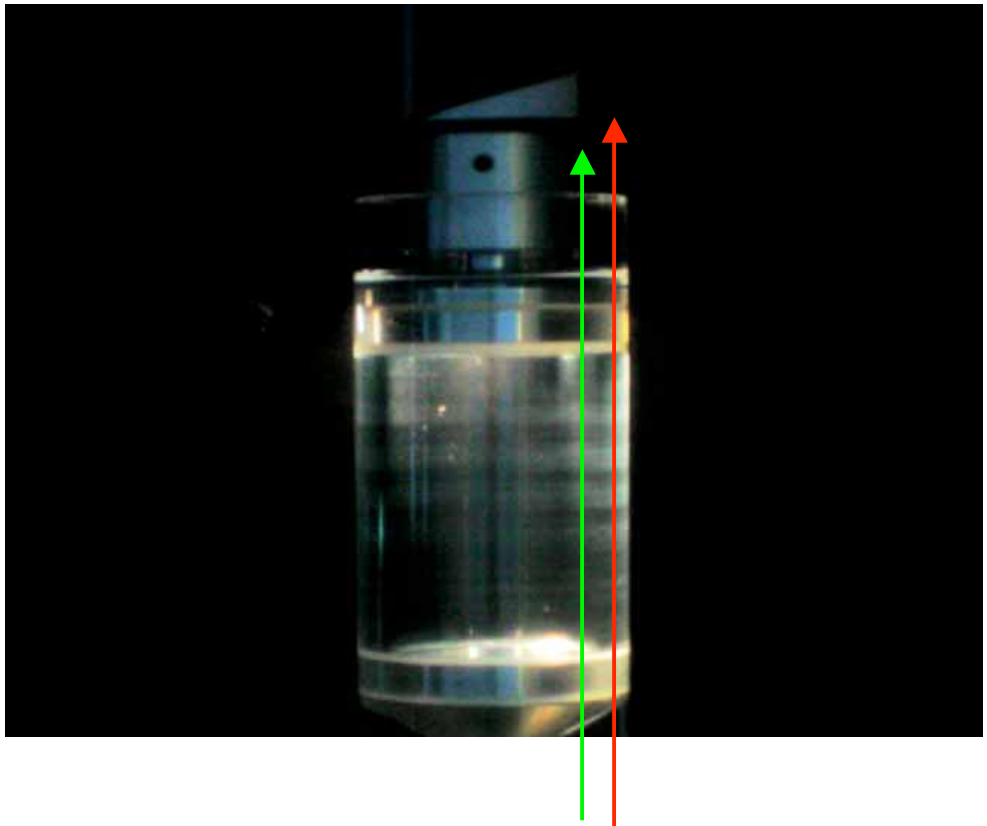
Do the sub-bands flip-flop?

How to access the structural information in each band?

By direct birefringence measurement of each band in the “chaotic regime”

Direct birefringence - Set-up





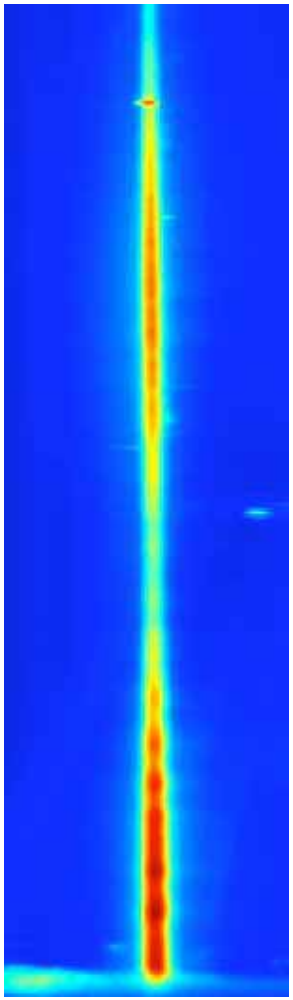
Laser close to inner rotating cylinder

Laser close to outer cylinder

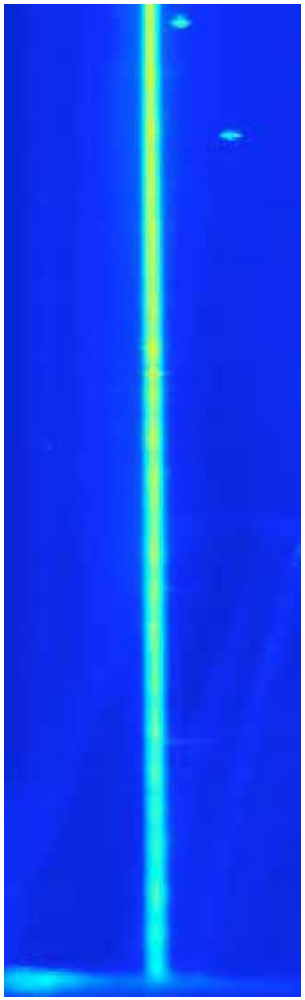
Decruppe J.P. et al.: PRE 71 (2005) 011503

Radial sub-band found in vorticity bands

Inner cylinder (rotating):

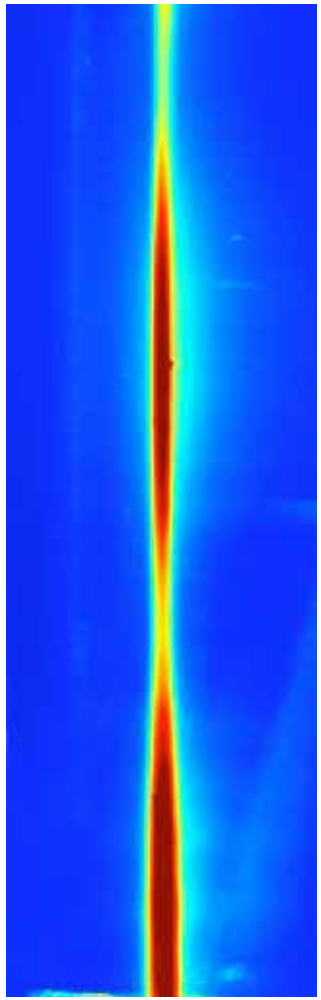


Turbid band

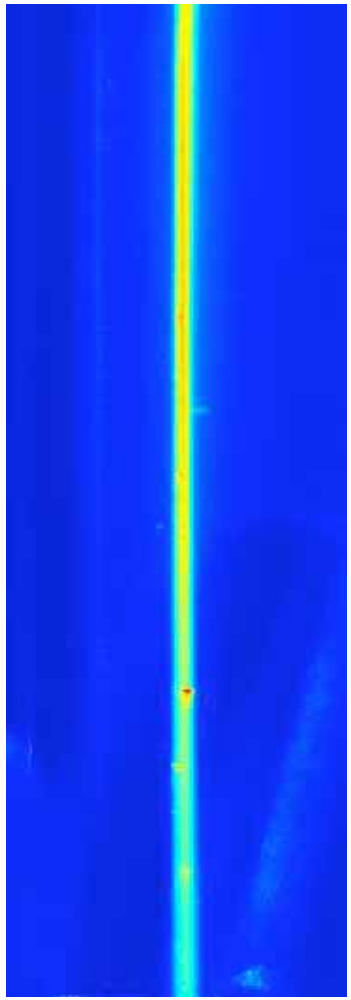


Clear band

Outer cylinder:



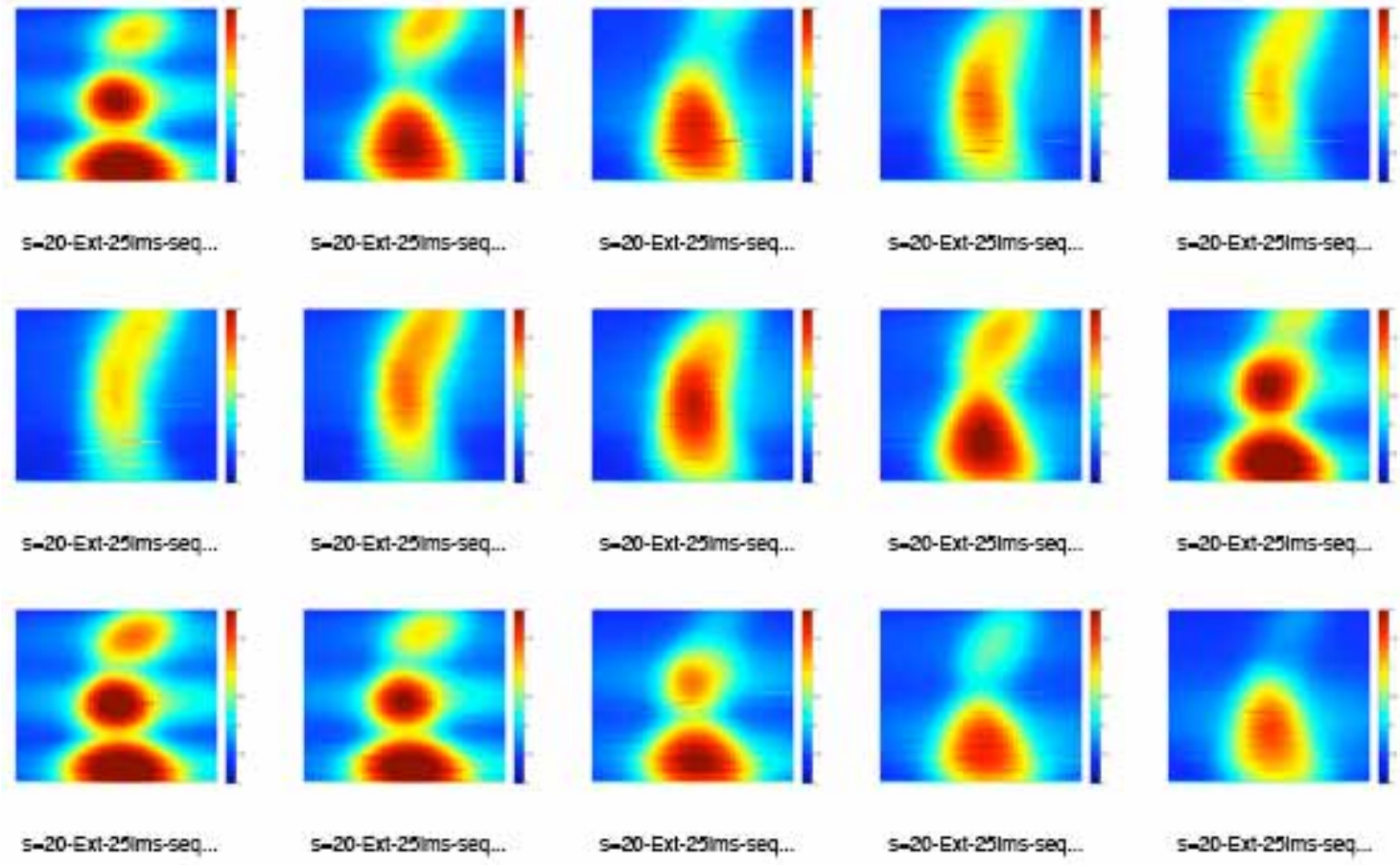
Turbid band



Clear band

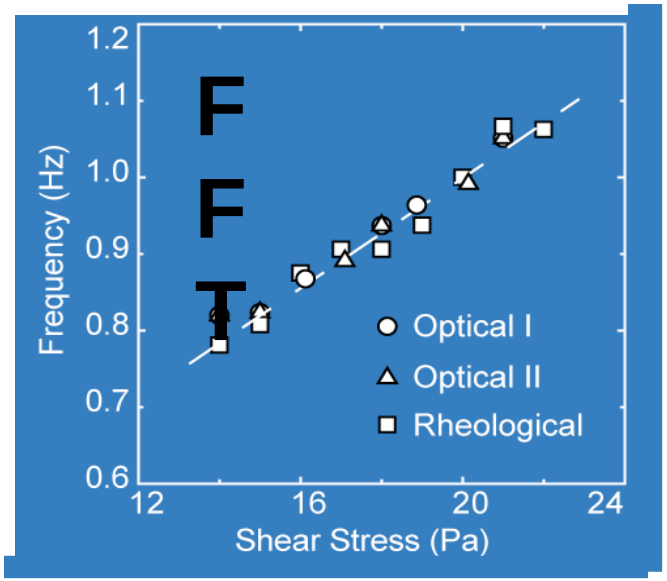
Radial sub-band found in vorticity bands

Inner cylinder (rotating):

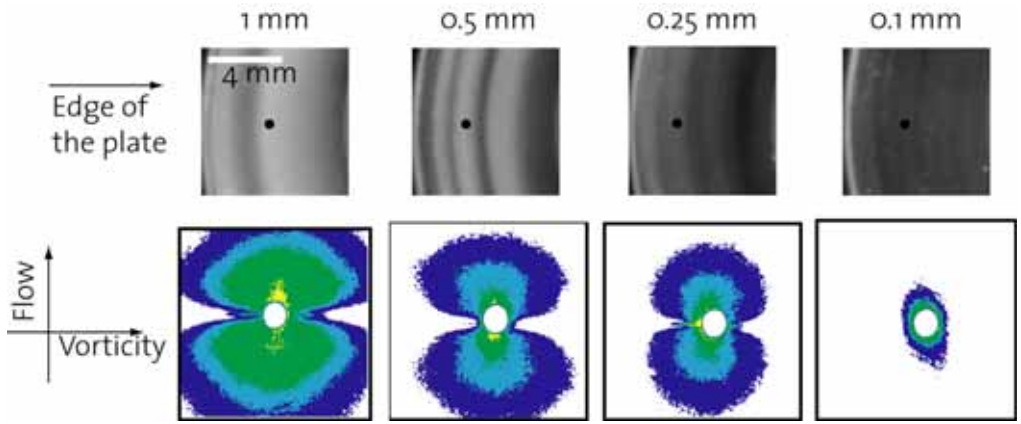


Summary (1)

Vorticity bands correlate with the oscillation of the free rheological parameter
Gap effect suggest different lengthscale are relevant for rheological response



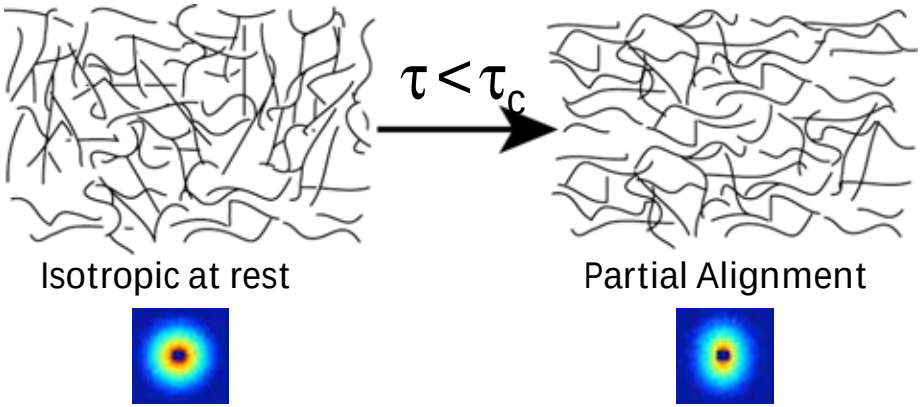
Optical and mechanical signals superimpose!



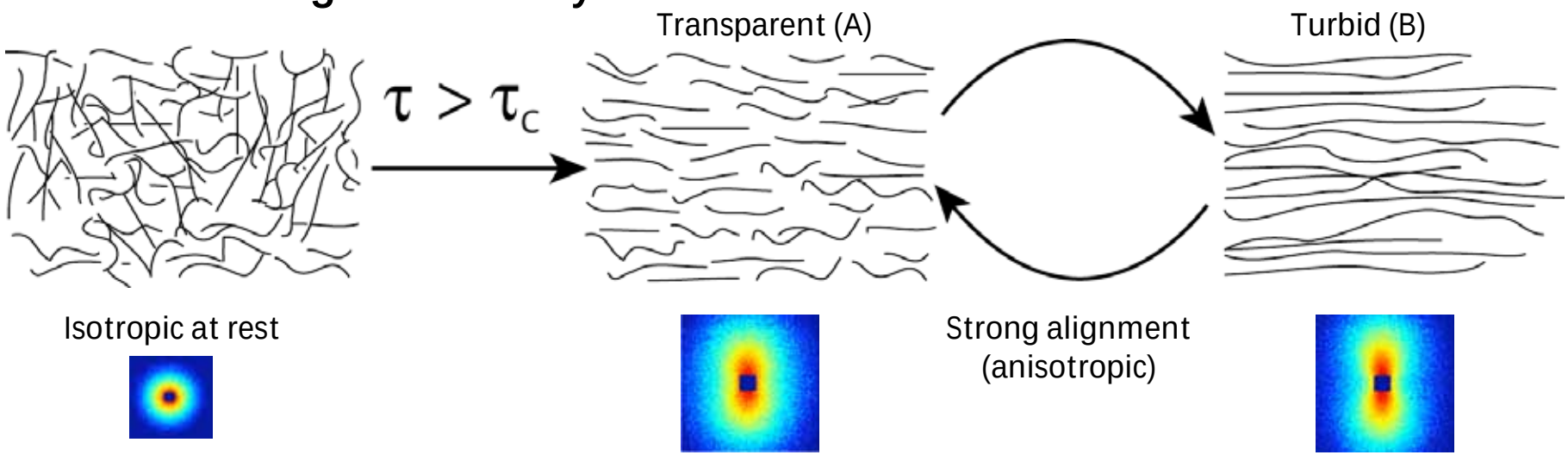
Summary (2)

Rheo-SANS suggest the highest aligned band to be high viscous

Shear Thinning

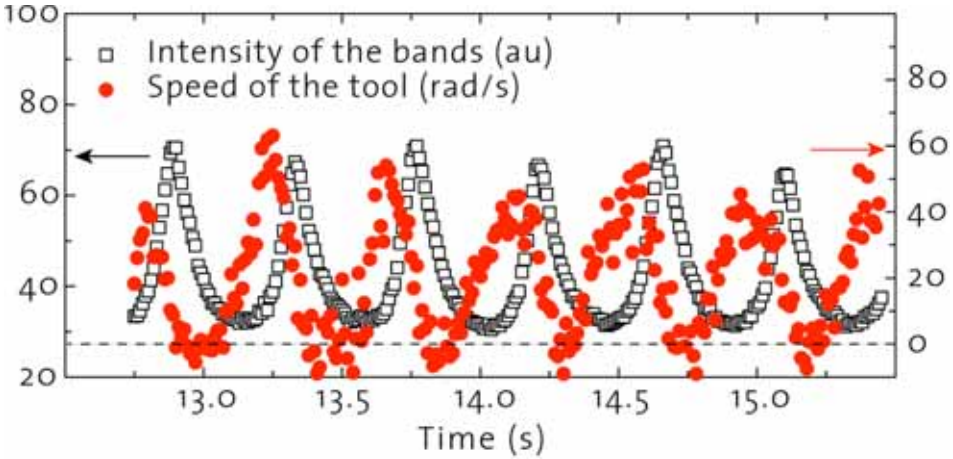


Shear Thickening and vorticity bands

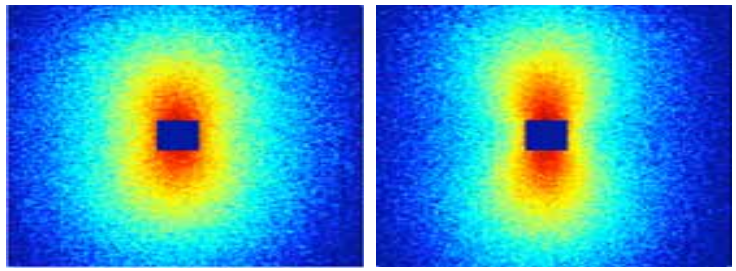


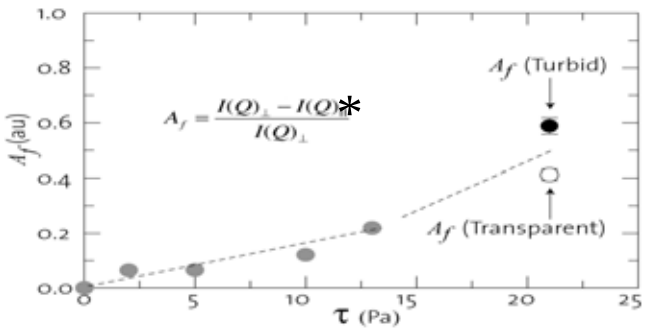
Summary (3)

Fast camera experiments show that the creating of turbid band leads to oscillation in viscosity. Due to a phase difference of $\pi/2$ the system never reaches a steady state.



As the turbid band appears, velocity approaches to Zero

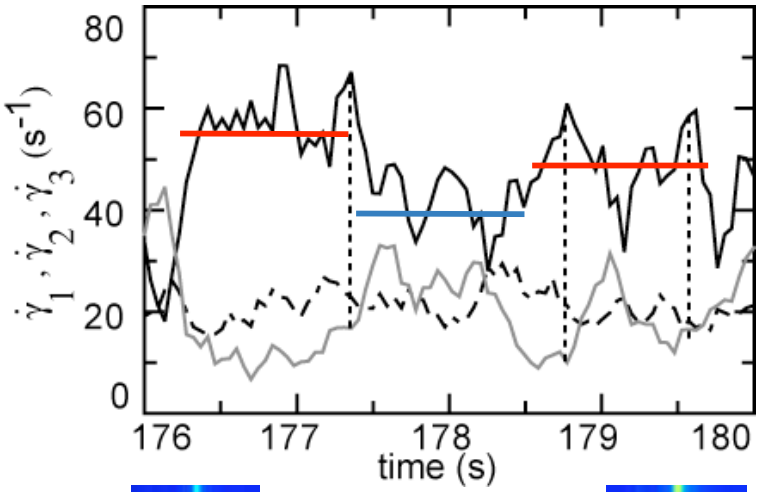


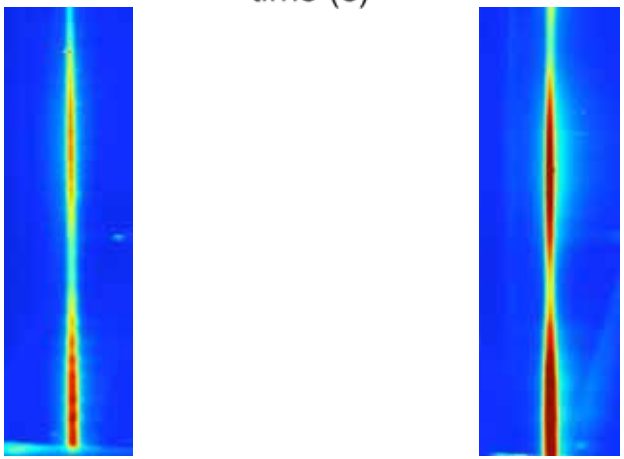


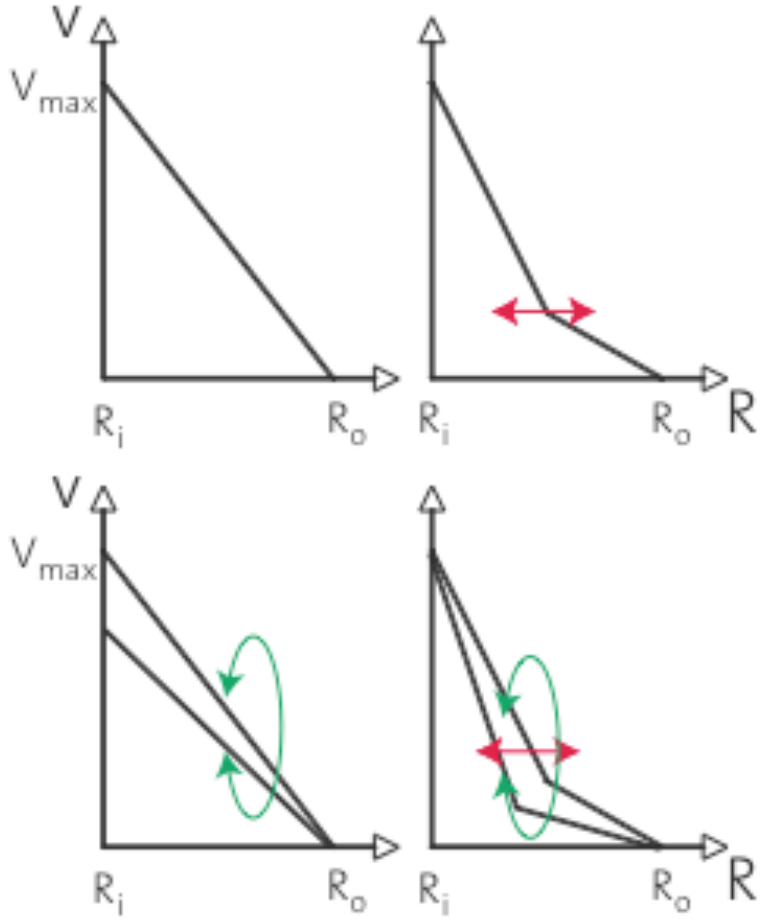
Turbid state is more anisotropic than transparent one

Summary (4)

Local velocity measurements (Rheo-UVP) and Direct Birefringence measurements show the existence of coupled radial and vorticity banding

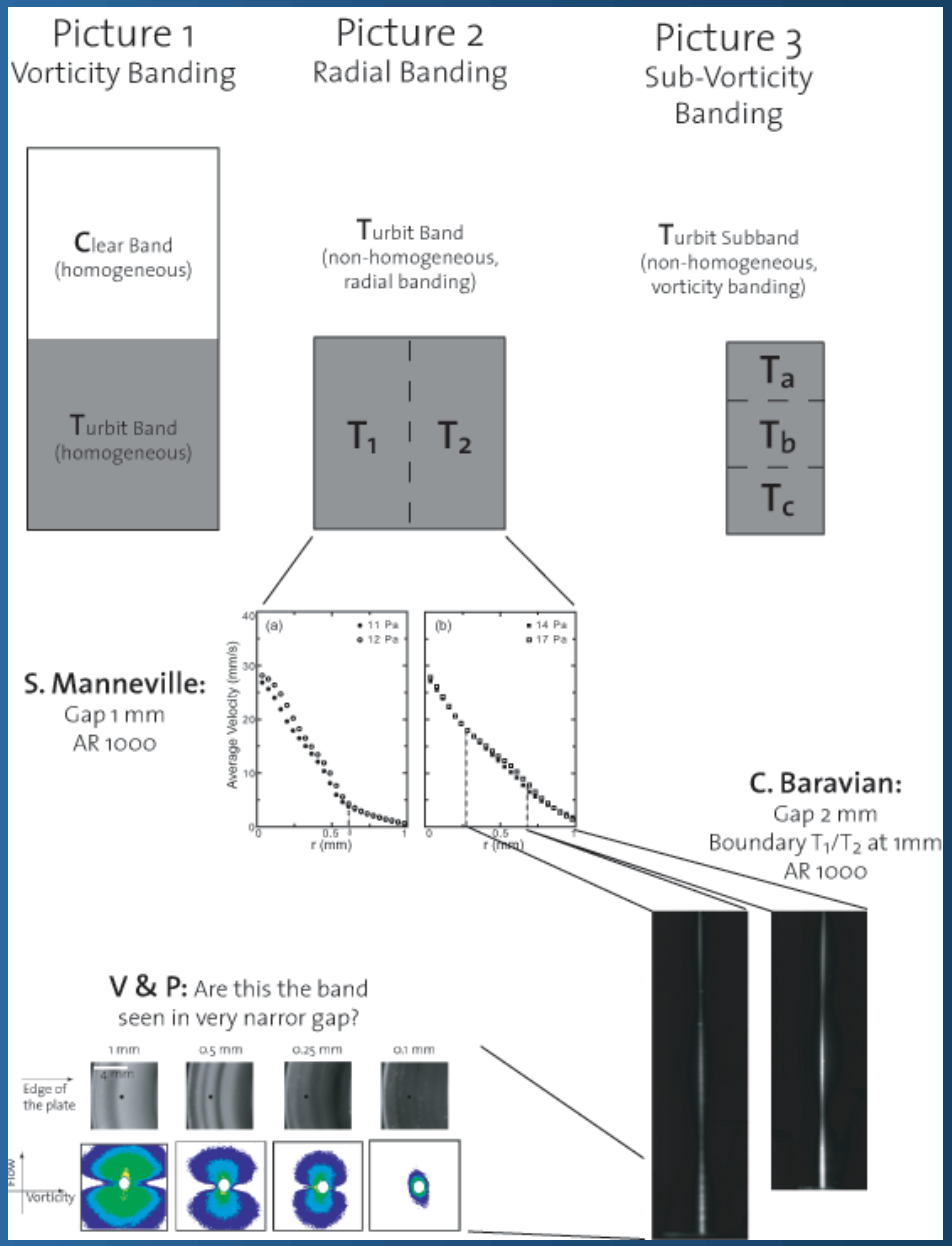






Summary (5)

Is it a Russian Doll …



… or scrap metal to be sold to China?

Richard Nixon
(quoted by Thomas Pynchon in “Gravities Rainbow”,
performed by Ernest in Sherman’s Lagoon)