

# Instabilities at “zero” Reynolds number: experiments from shear-thinning in surfactant solutions to shear-thickening in dense suspensions

---

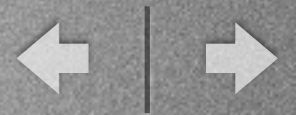
Sébastien Manneville

*Laboratoire de Physique  
École Normale Supérieure, Lyon, France*

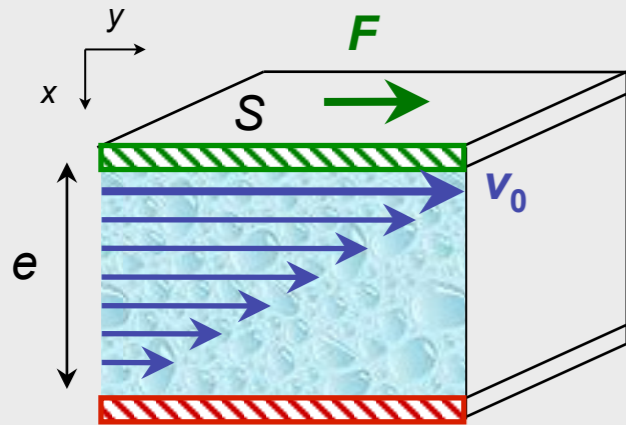




# Flow-microstructure coupling



simple shear

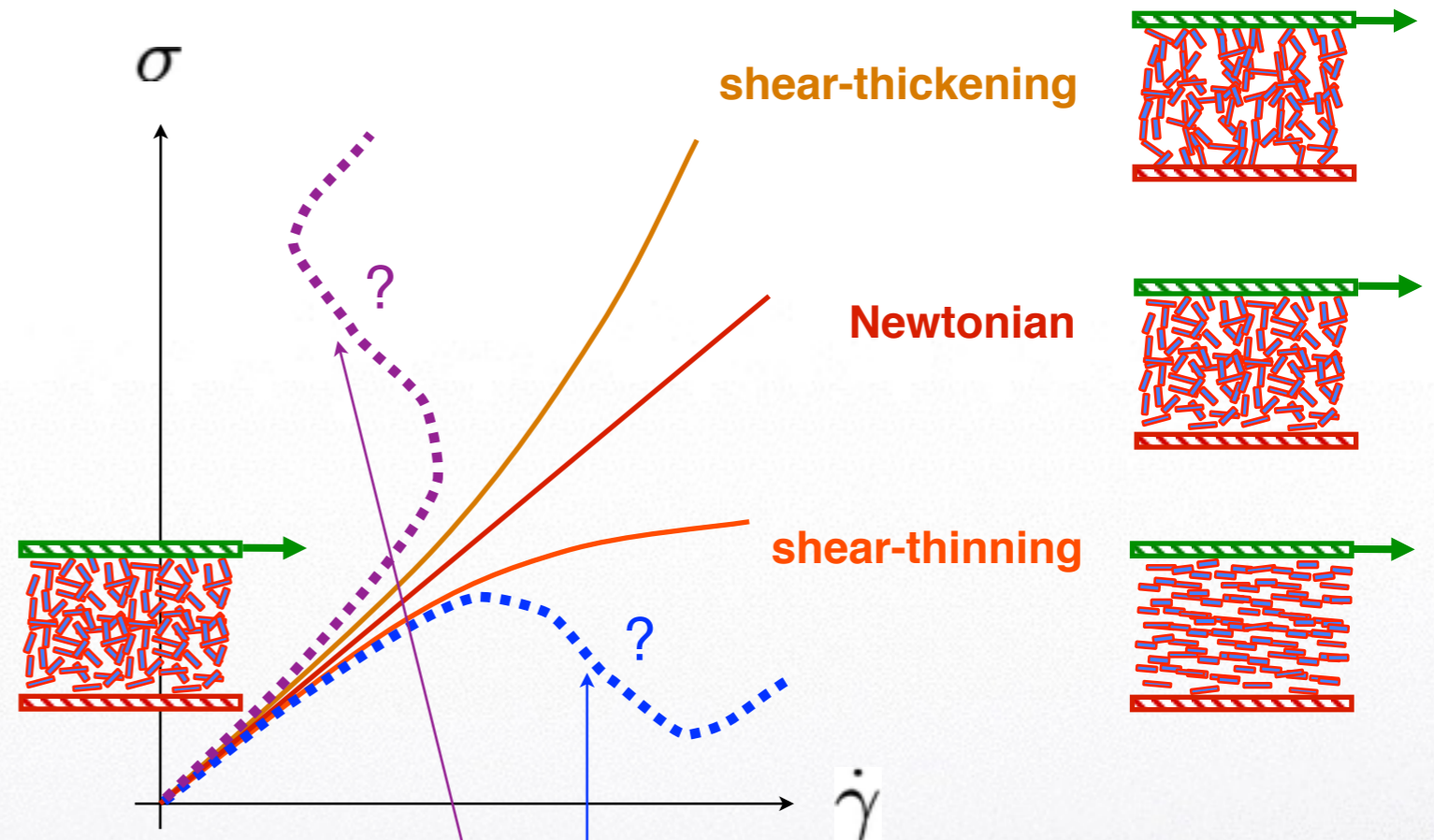


$$\text{shear stress : } \sigma = \frac{\partial F_y}{\partial S_x} \simeq \frac{F}{S}$$

$$\text{shear rate : } \dot{\gamma} = \frac{\partial v_y}{\partial x} \simeq \frac{v_0}{e}$$

$$\text{shear viscosity : } \eta = \frac{\sigma}{\dot{\gamma}}$$

flow curve : shear stress vs shear rate



unstable when  $\frac{\partial \sigma}{\partial \dot{\gamma}} < 0$

feedback between flow and microstructure  
⇒ possibility of mechanical instabilities



## I. Surfactant solutions

*from gradient banding to elastic turbulence to vorticity banding*

## II. Yielding in soft glassy (“squishy”) materials

*from steady shear localization to critical-like fluidization dynamics*

T. Divoux, M.-A. Fardin, SM & S. Lerouge, *Ann. Rev. Fluid Mech.* **48**, 81–103 (2016)

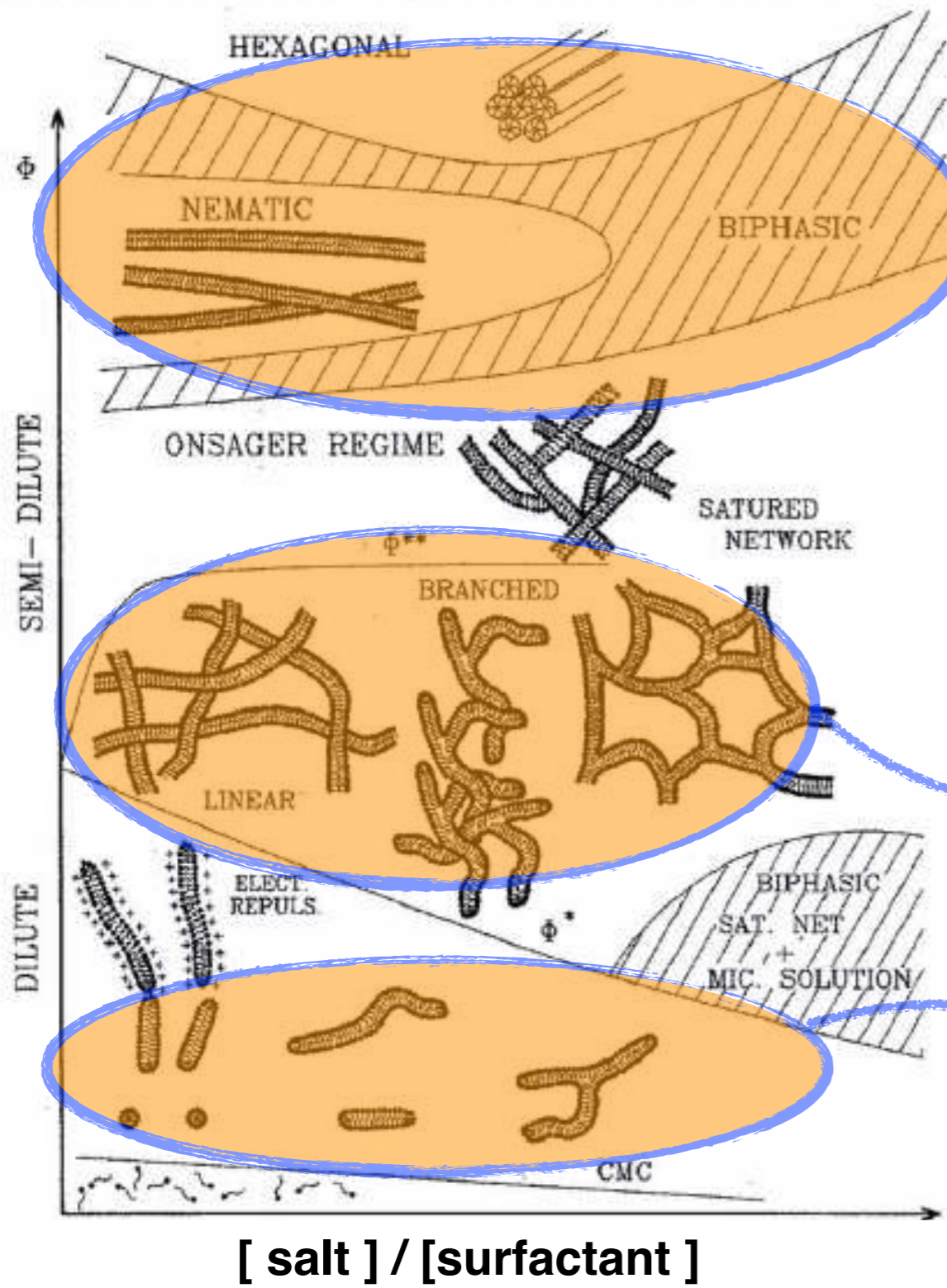
D. Bonn, M. Denn, L. Berthier, T. Divoux & SM, *Rev. Mod. Phys.* **89**, 035005 (2017)

## III. What about dense suspensions?

*similarities and differences with other complex fluids*



# Structure and rheology of wormlike micelles



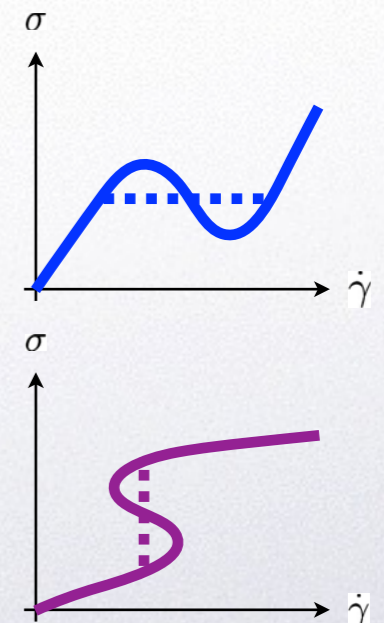
“suspensions” of Brownian “particles”  
 anisotropic, deformable & breakable  
 radius  $\approx 1$  nm & length up to  $\approx 1$   $\mu$ m

crowding of self-assembled structures  
 $\Rightarrow$  **yield stress**

flow-concentration coupling, nematohydrodynamics  
 & elasticity  $\Rightarrow$  **complications!**

shear-induced ordering  
 $\Rightarrow$  **shear-thinning**

shear-induced growth  
 $\Rightarrow$  **shear-thickening**



$\Rightarrow$  flow behaviour shared  
 with dense suspensions?

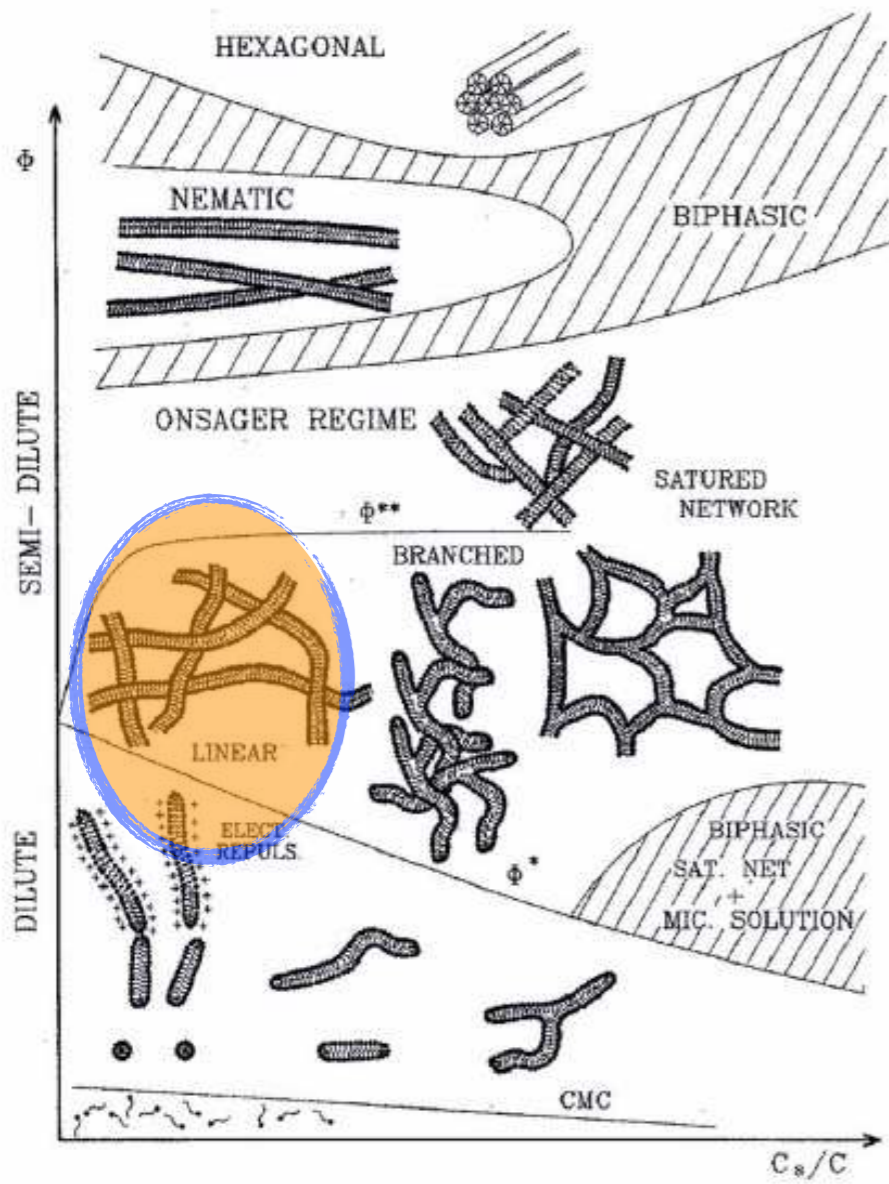
see also Cates & Fielding, *Adv. Phys.* 55, 799-879 (2006)  
 Manneville, *Rheol. Acta* 47, 301-318 (2008) & Olmsted, *ibid.* 283-300  
 Lerouge & Berret, in *Polymer Characterization*, 1-71 (2009)



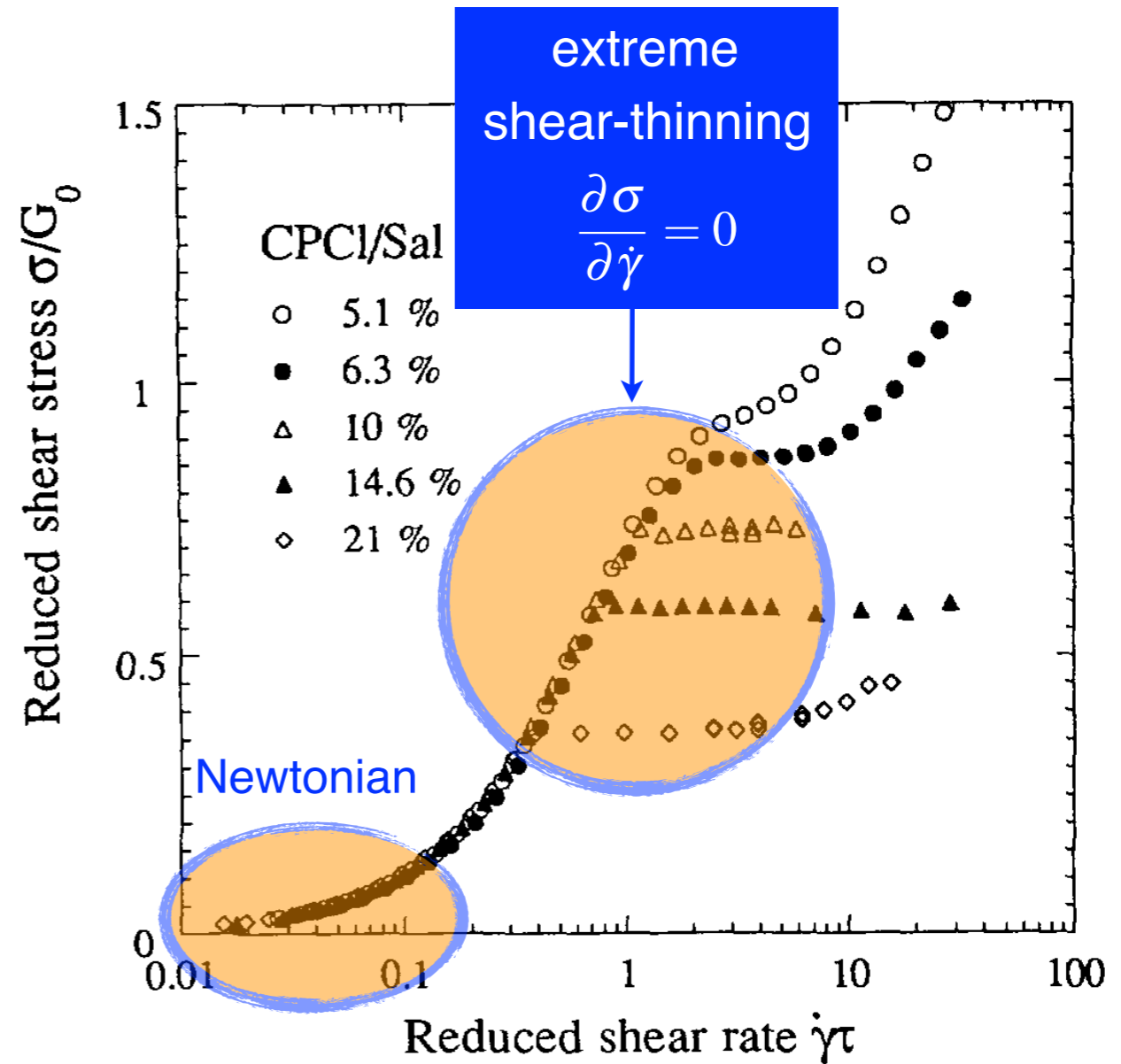
# Shear banding in (semidilute) wormlike micelles



a semidilute “suspension” of semi-flexible, breakable cylindrical aggregates with radius  $\approx 1$  nm & length up to  $\approx 1$   $\mu$ m



Candau & Lequeux, *Rheol. Acta* 12, 357-373 (1994)

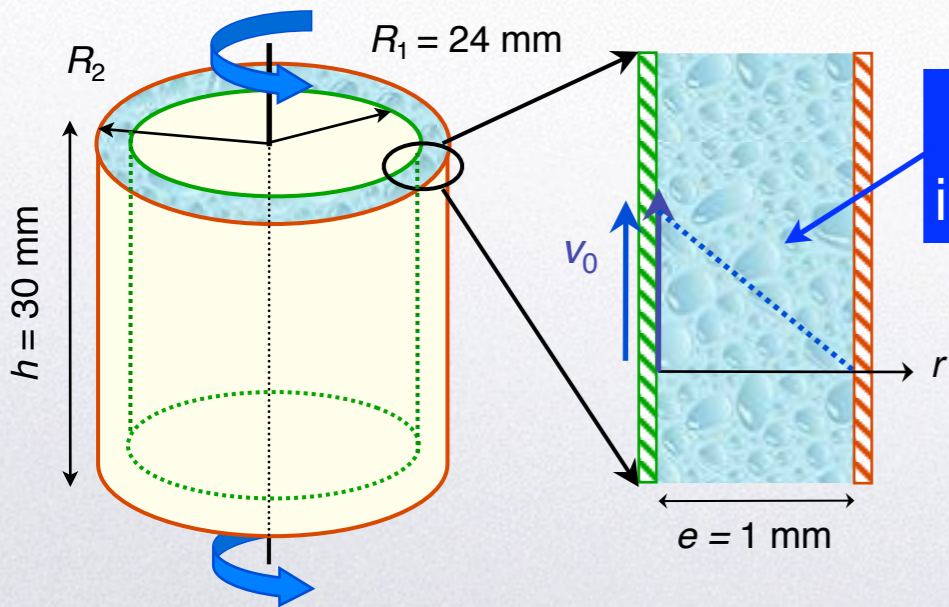
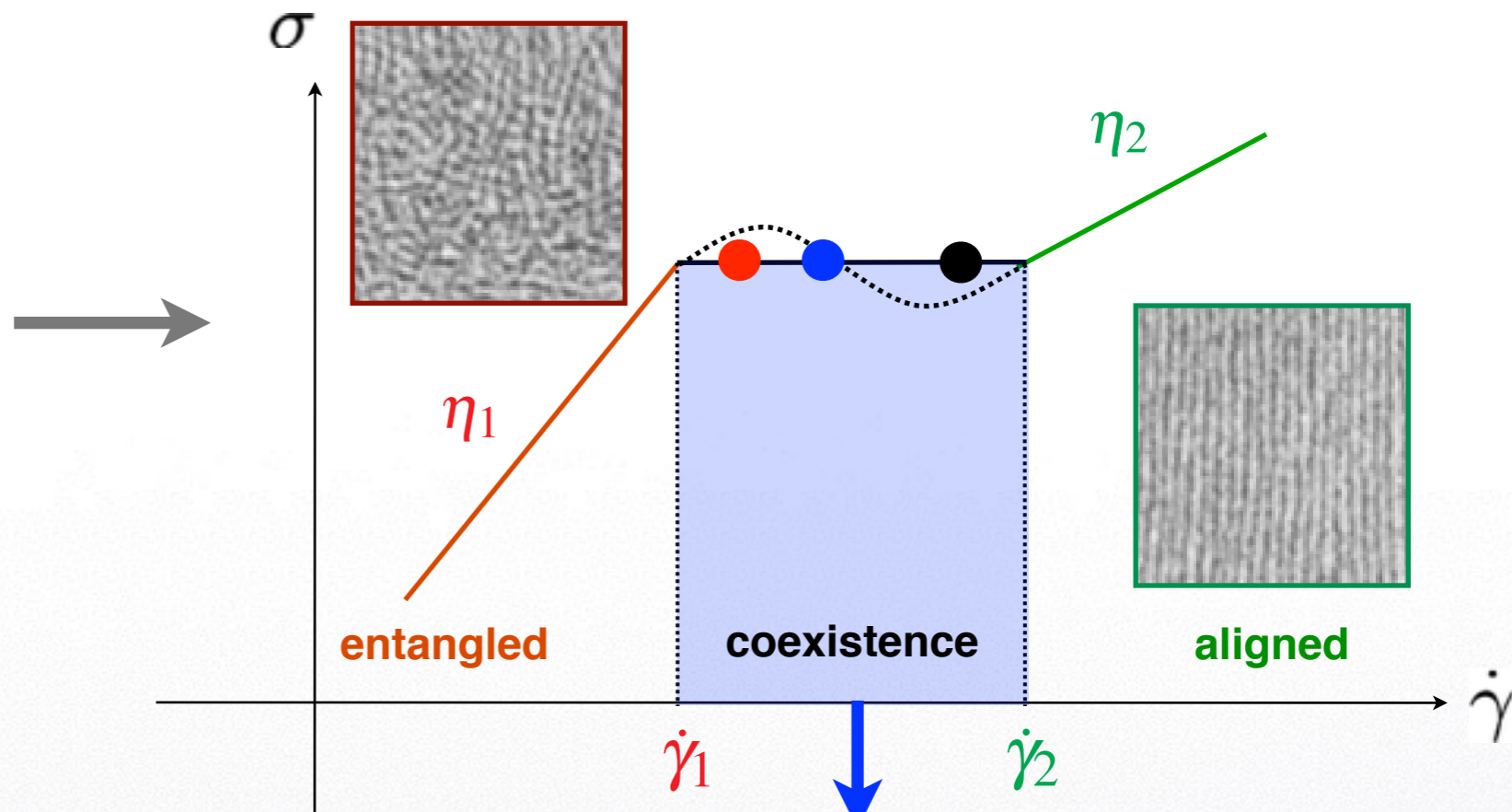
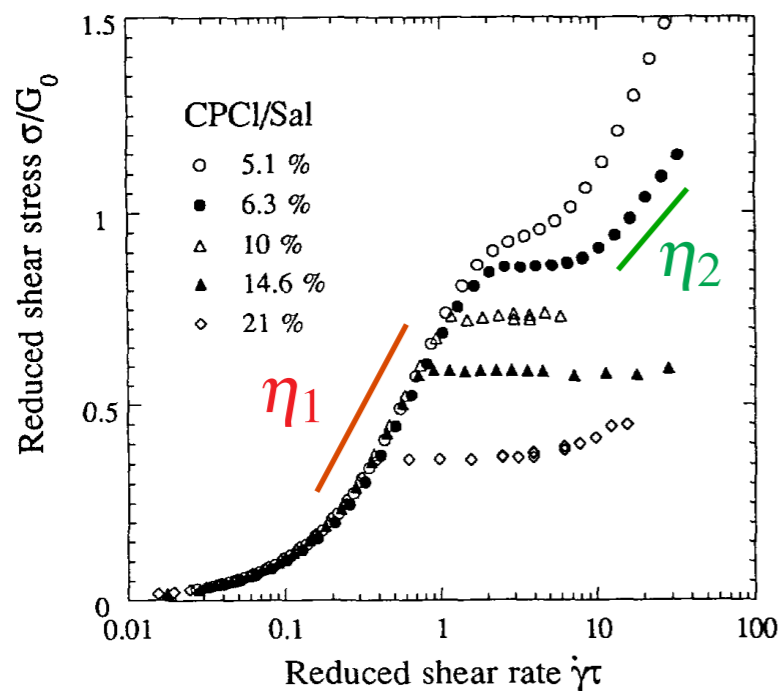


Berret et al., *J. Phys II France* 4, 1261-1279 (1994)

analogy with a first-order phase transition

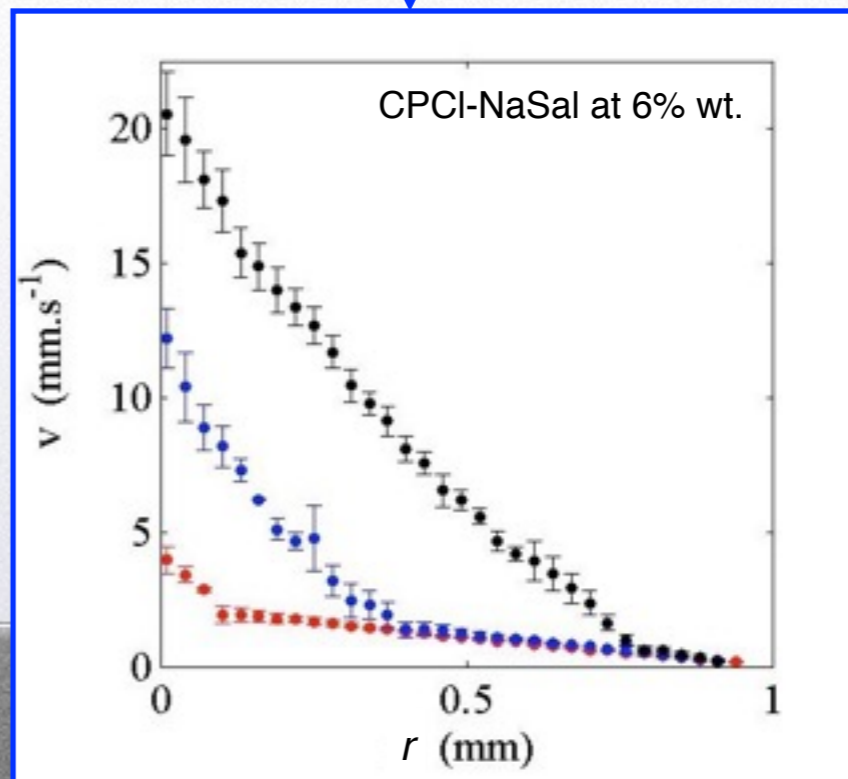


# Shear banding in (semidilute) wormlike micelles



velocity profile in Couette geometry

coexistence of two shear bands along the gradient direction



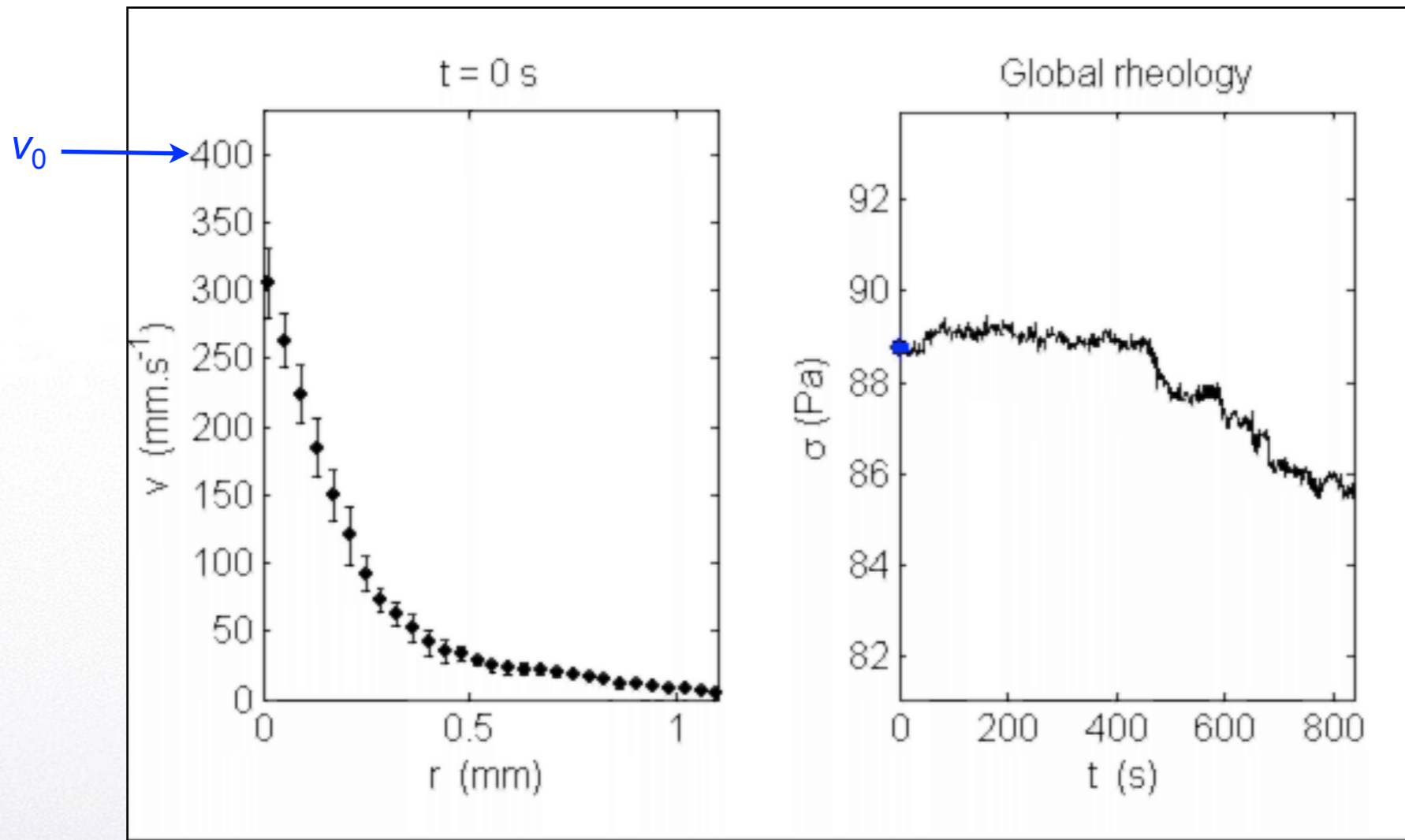


# Unsteady shear bands



$\dot{\gamma} = 400 \text{ s}^{-1}$  during 900 s

CTAB-D<sub>2</sub>O at 20% wt.



Bécu *et al.*, *PRL* **93**, 018301 (2004) & *PRE* **76**, 011503 (2007)

Lettinga & Manneville, *PRL* **103**, 248302 (2009)

- fluctuations of interface position and of wall slip velocity
- intermittent nucleation of a high-shear band at the stator

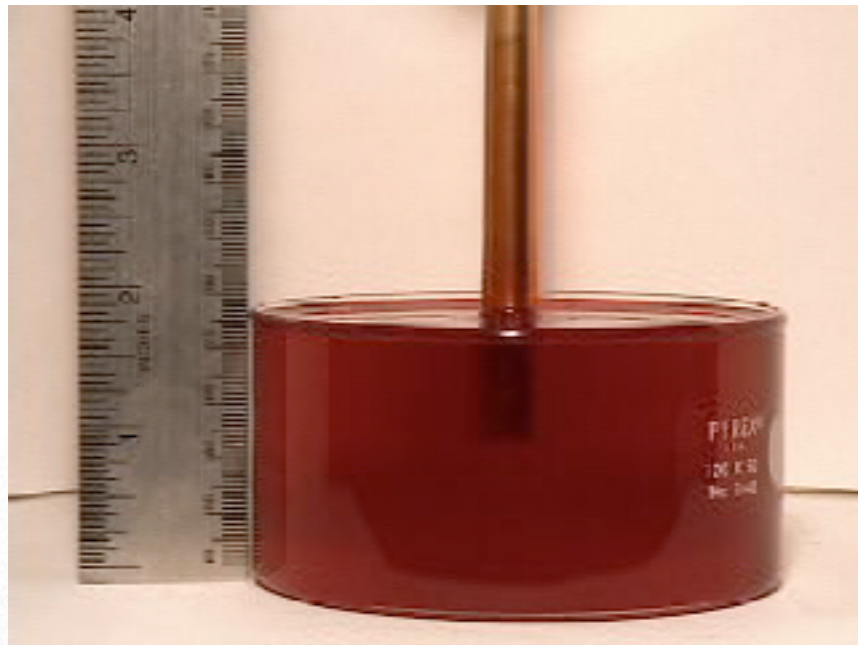
⇒ unstable, three-dimensional flow?



# Normal forces in viscoelastic fluids

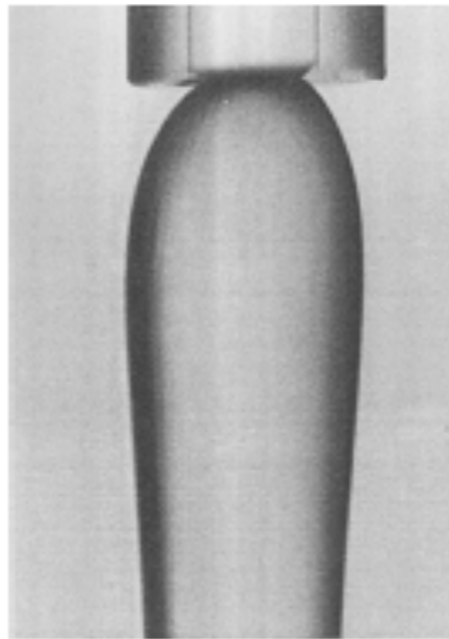


Weissenberg effect (1946)

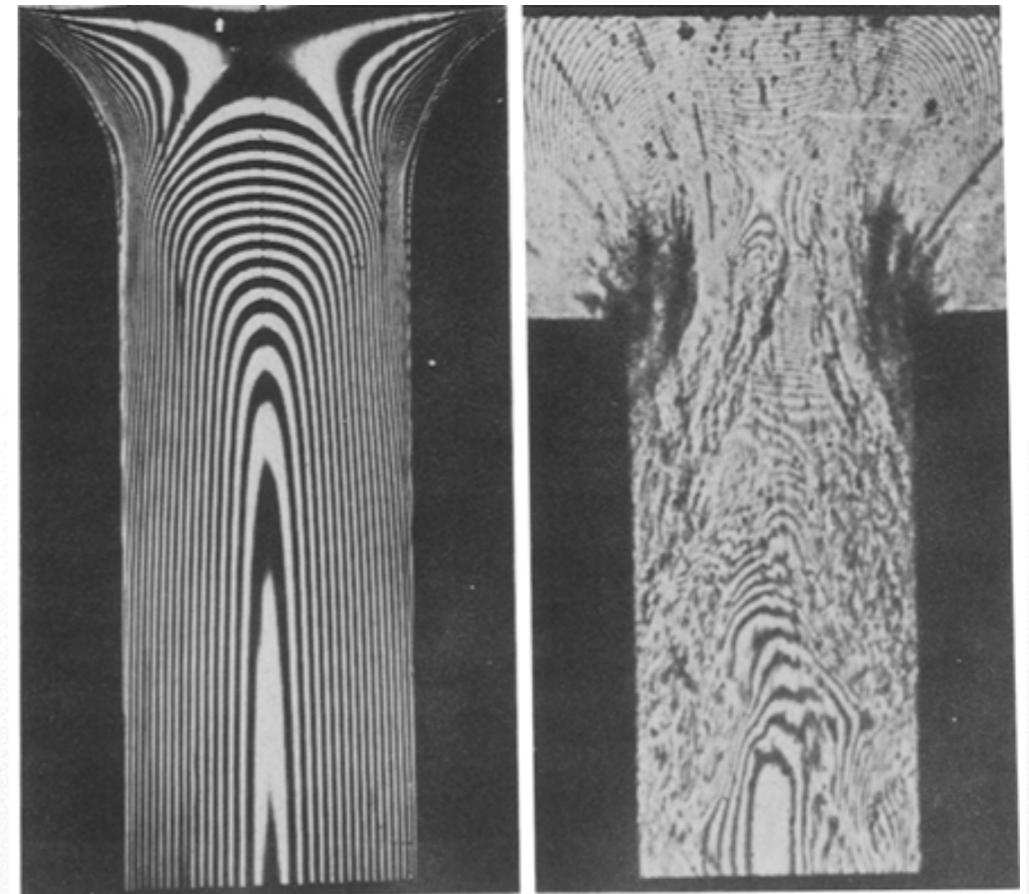


G. McKinley, MIT

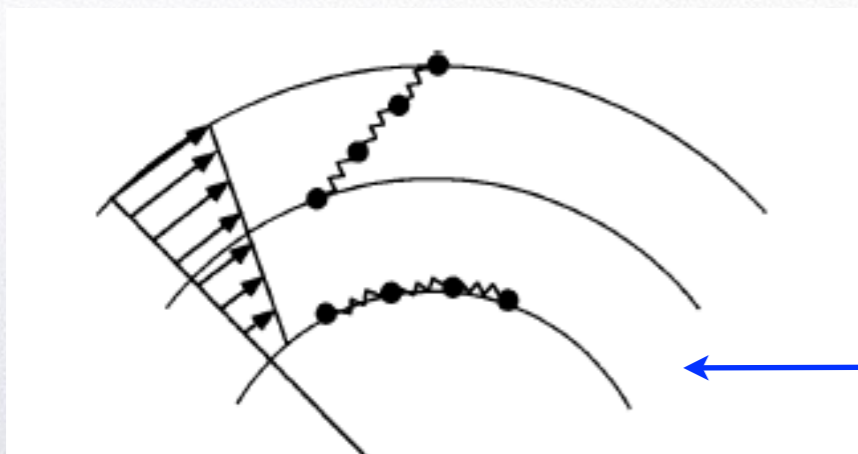
die swell



polymer flow birefringence



Vinogradov, *Rheol. Acta* 12, 357-373 (1973)



Pakdel & McKinley, *PRL* 77, 2459-2463 (1996)

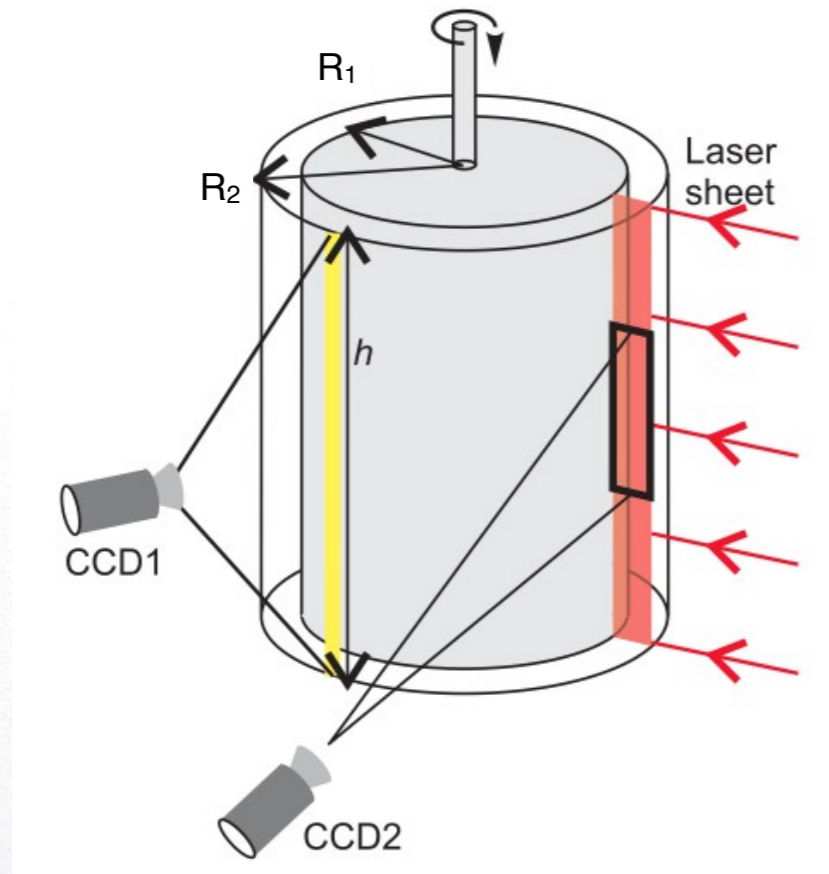
in a cylindrical geometry  
curved streamlines  $\Rightarrow$  inward forces

possibility of elasticity-driven instabilities  
in the absence of inertia

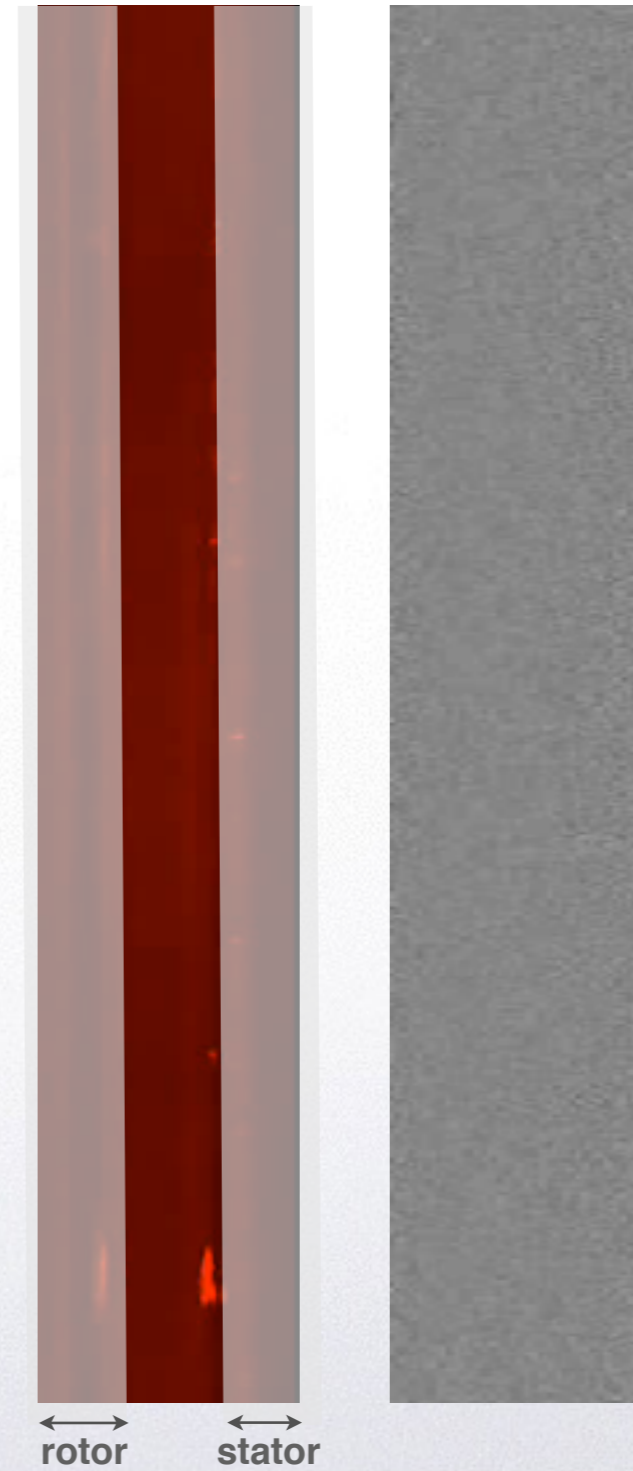




# Rheo-optical study of shear banding

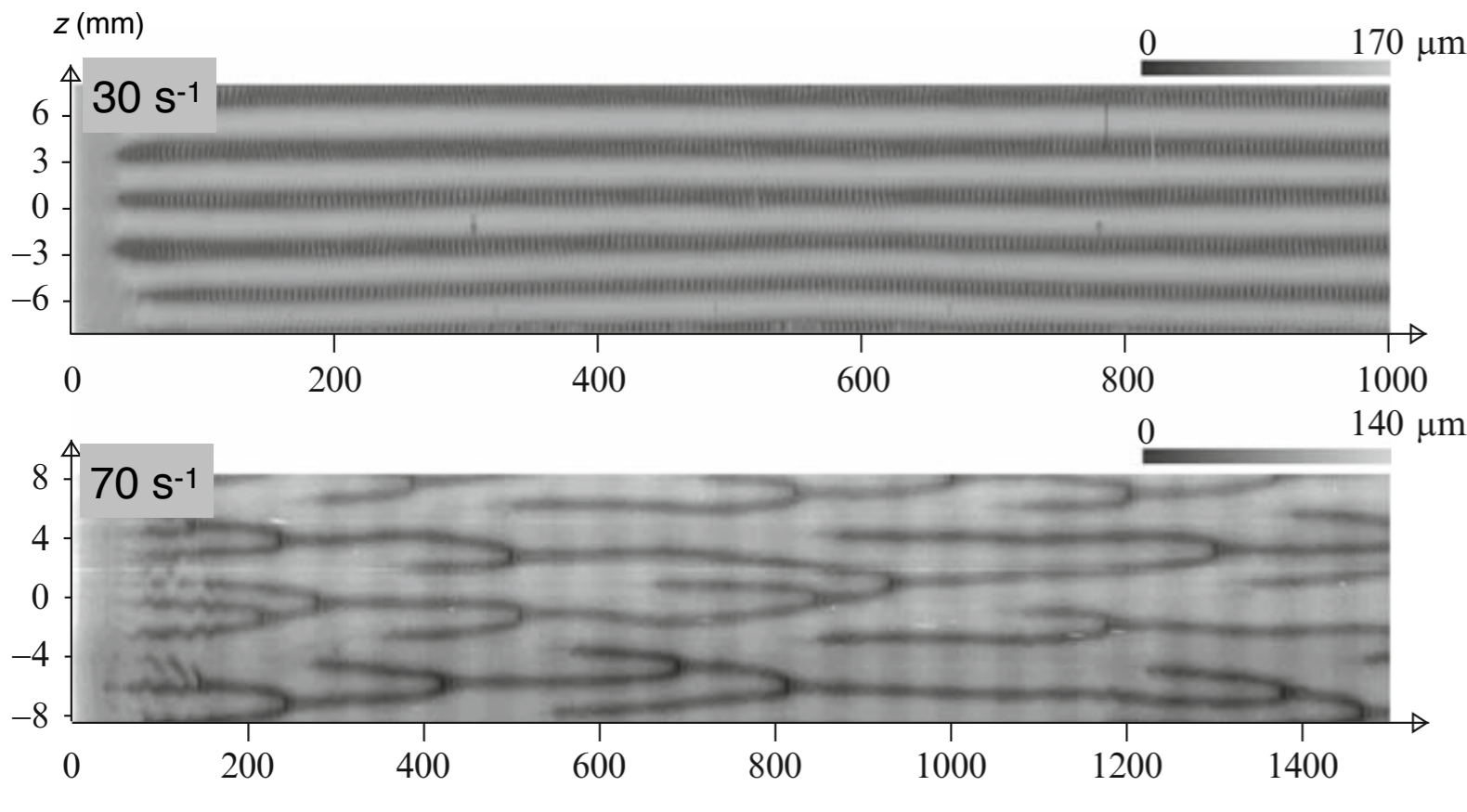


CTAB- $\text{NaNO}_3$  at  $30 \text{ s}^{-1}$



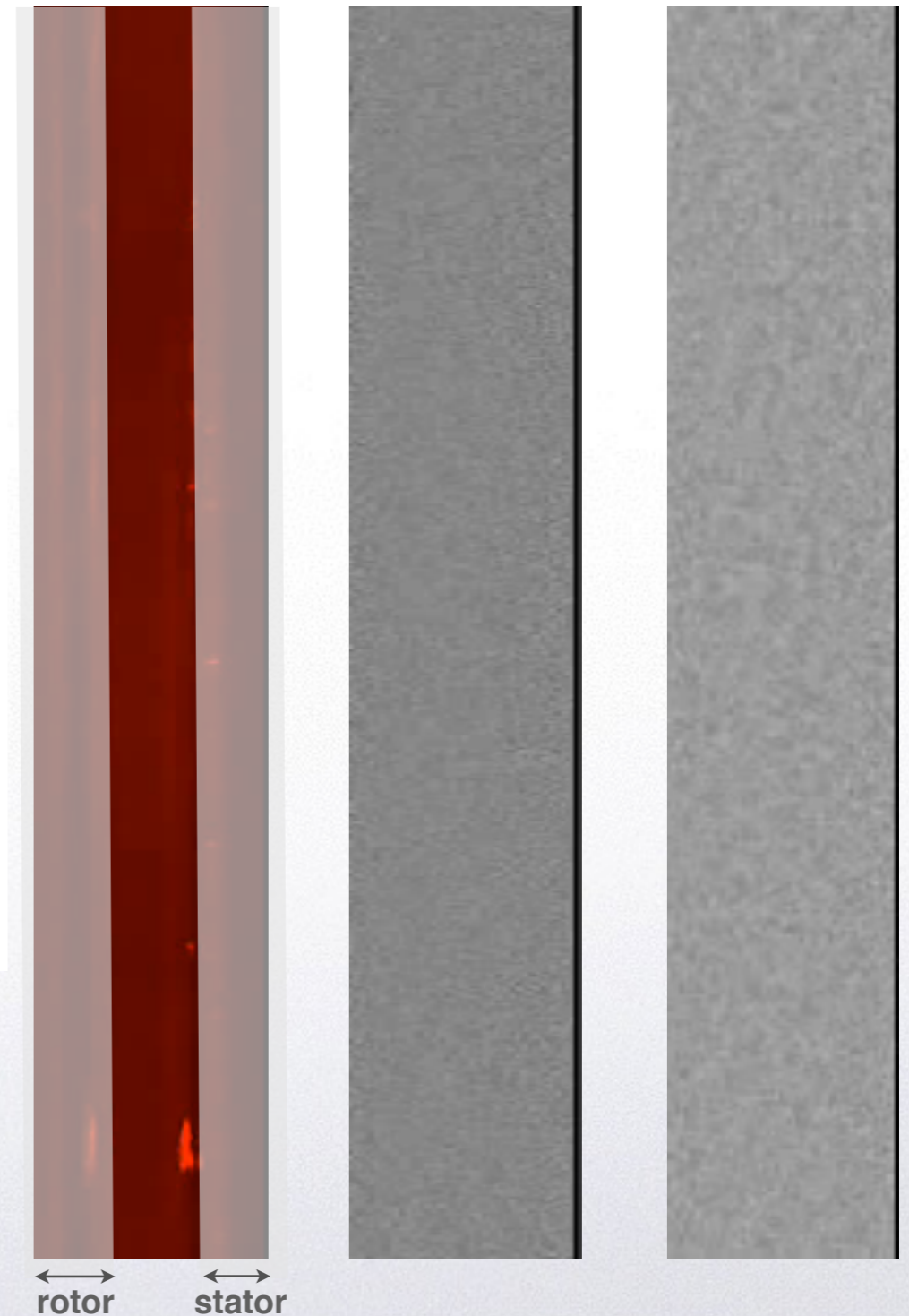


# Rheo-optical study of shear banding



CTAB-NaNO<sub>3</sub> at 30 s<sup>-1</sup>

at 70 s<sup>-1</sup>



- instability of the interface between shear bands
- pairs of counter-rotating vortices
- creation-annihilation dynamics  $\Rightarrow$  chaotic?

Lerouge *et al.*, *PRL* **96**, 088301 (2006)

Lerouge *et al.*, *Soft Matter* **4**, 1808-1819 (2008)

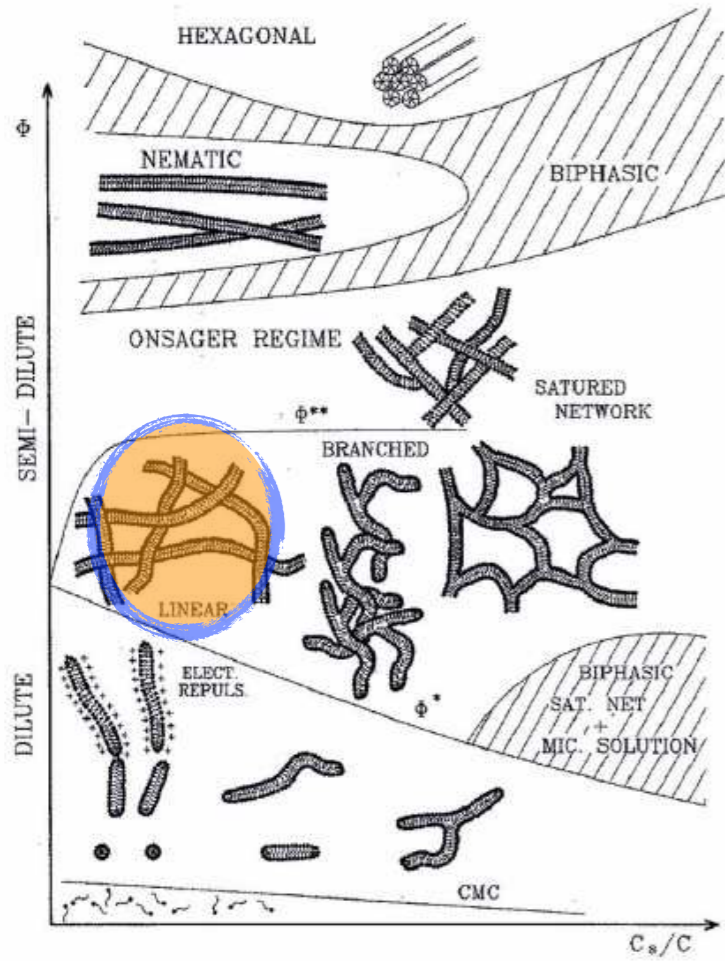
Fardin *et al.*, *PRL* **103**, 028302 (2009)

how to quantify these unstable dynamics?

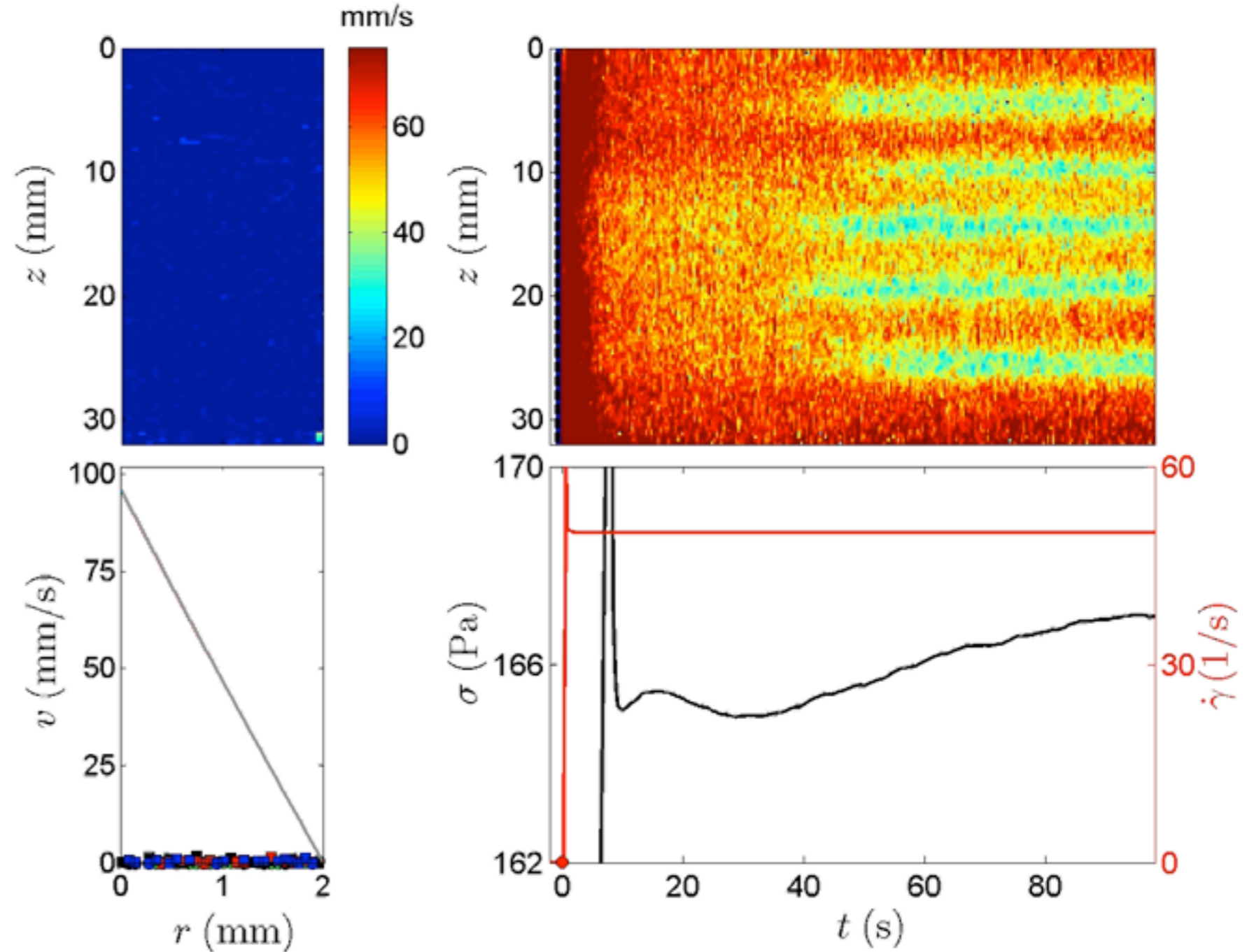


# Rheo-ultrasonic imaging of elastic instability

CTAB (0.3 M) - NaNO<sub>3</sub> (0.4 M)



Transition to a shear-banded vortex flow at  $\dot{\gamma}=50 \text{ s}^{-1}$ :  $t=-0.8 \text{ s}$



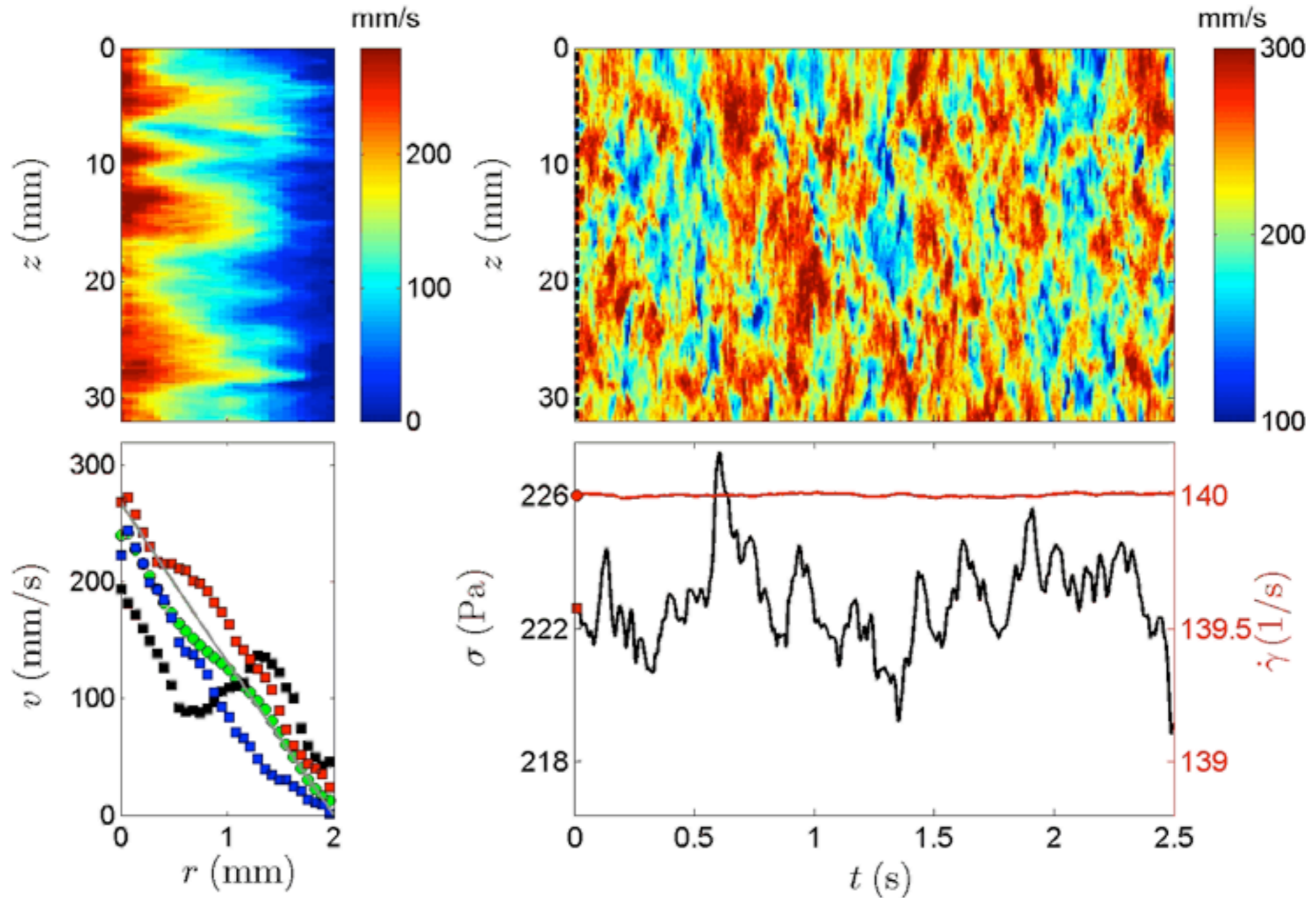
Perge *et al.*, *Eur. Phys. J E* 37, 23 (2014) & *Soft Matter* 10, 1450 (2014)

Fardin *et al.*, *Phys. Rev. E* 89, 011001(R) (2014)



# Rheo-ultrasonic imaging of elastic turbulence

Elastic turbulence at  $\dot{\gamma}=140 \text{ s}^{-1}$ :  $t=0.01 \text{ s}$



Perge *et al.*, *Eur. Phys. J E* **37**, 23 (2014) & *Soft Matter* **10**, 1450 (2014)

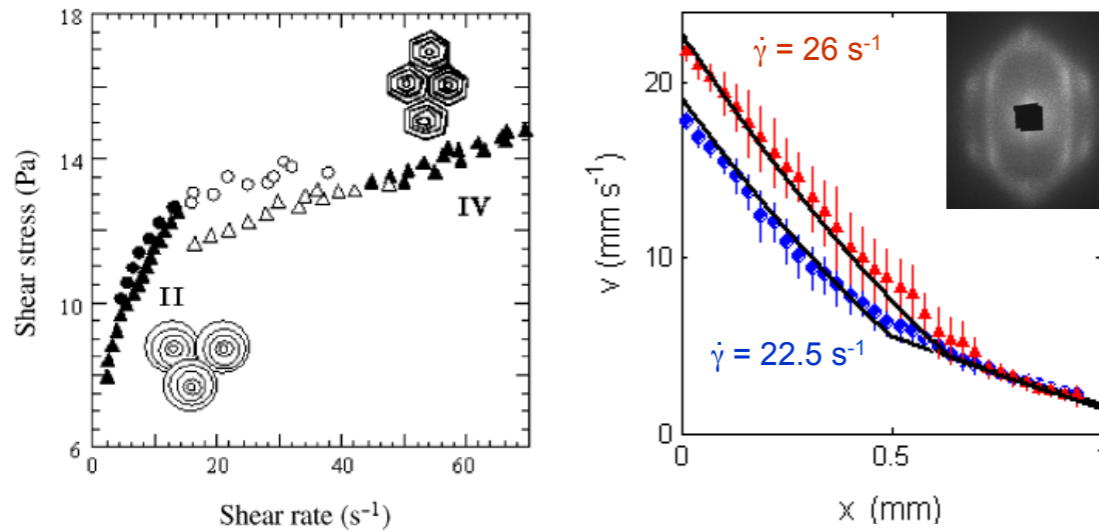
Fardin *et al.*, *Phys. Rev. E* **89**, 011001(R) (2014)



# Similar phenomenology in...

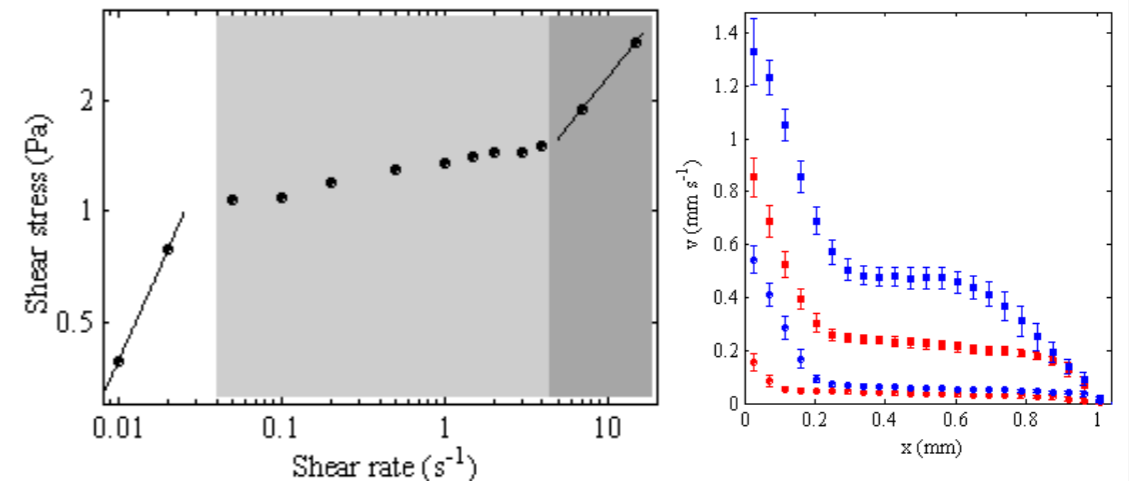


## surfactant multilamellar vesicles



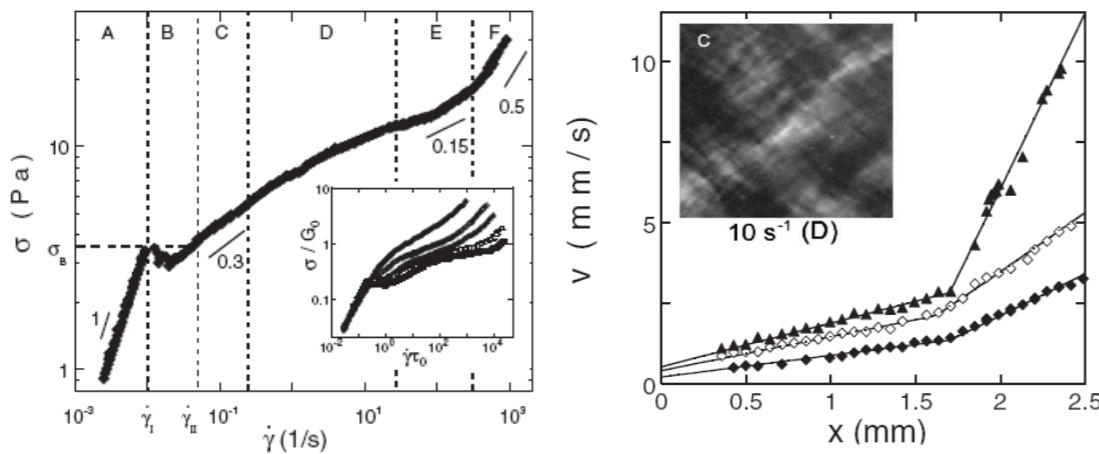
Salmon *et al.*, *PRE* **68**, 051503 (2003)

## triblock copolymer micelles



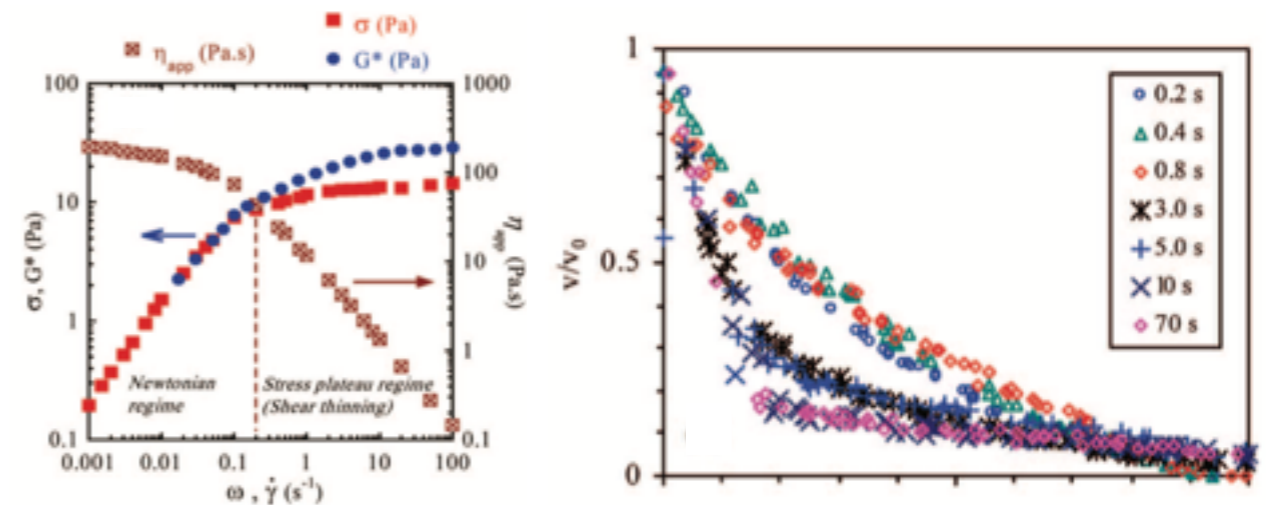
Manneville *et al.*, *PRE* **75**, 061502 (2007)

## EHUT supramolecular polymers



van der Gucht *et al.*, *PRL* **75**, 108301 (2006)

## entangled DNA solutions



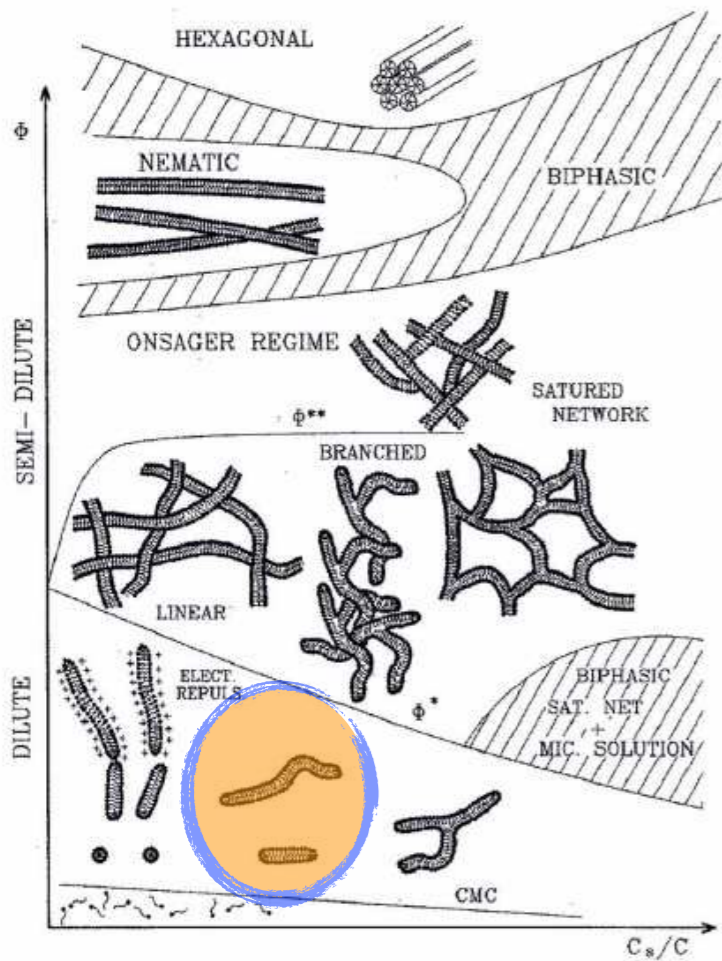
Boukany *et al.*, *Macromol.* **41**, 2644-2650 (2008)

gradient banding is widespread  
in shear-thinning transitions

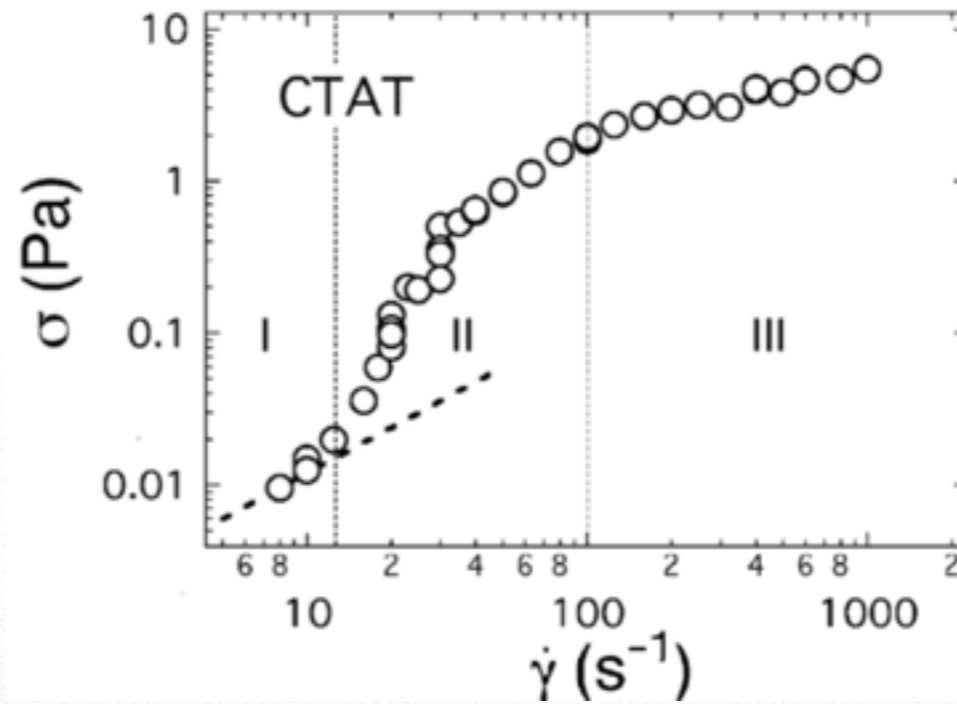
+ complications  
due to elasticity!



# Shear-thickening in (dilute) wormlike micelles ← | →

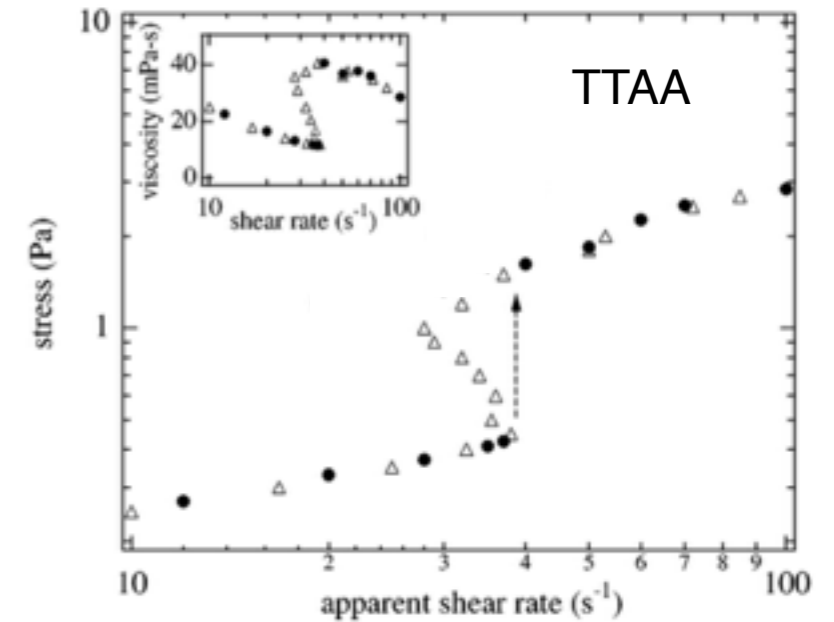


continuous transition



Gamez-Corrales *et al.*, *Langmuir* 79, 6755-6763 (1999)

discontinuous transition

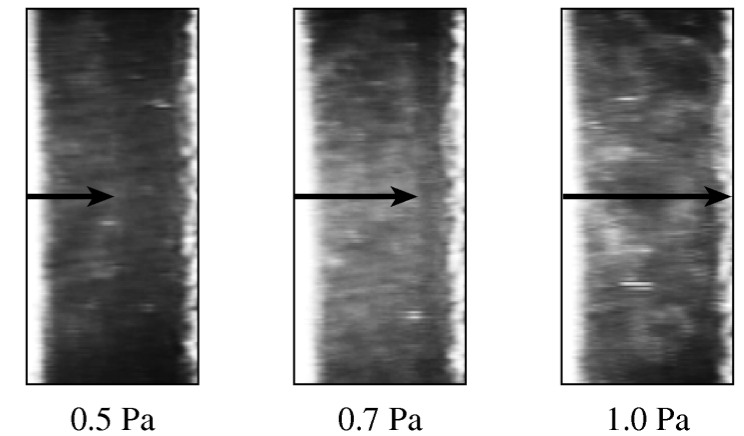


Boltenhagen *et al.*, *PRL* 79, 2359 (1997)

Hu *et al.*, *J. Rheol.* 42, 1185 (1998)

⇒ growth of gel-like shear-induced structures (SIS)

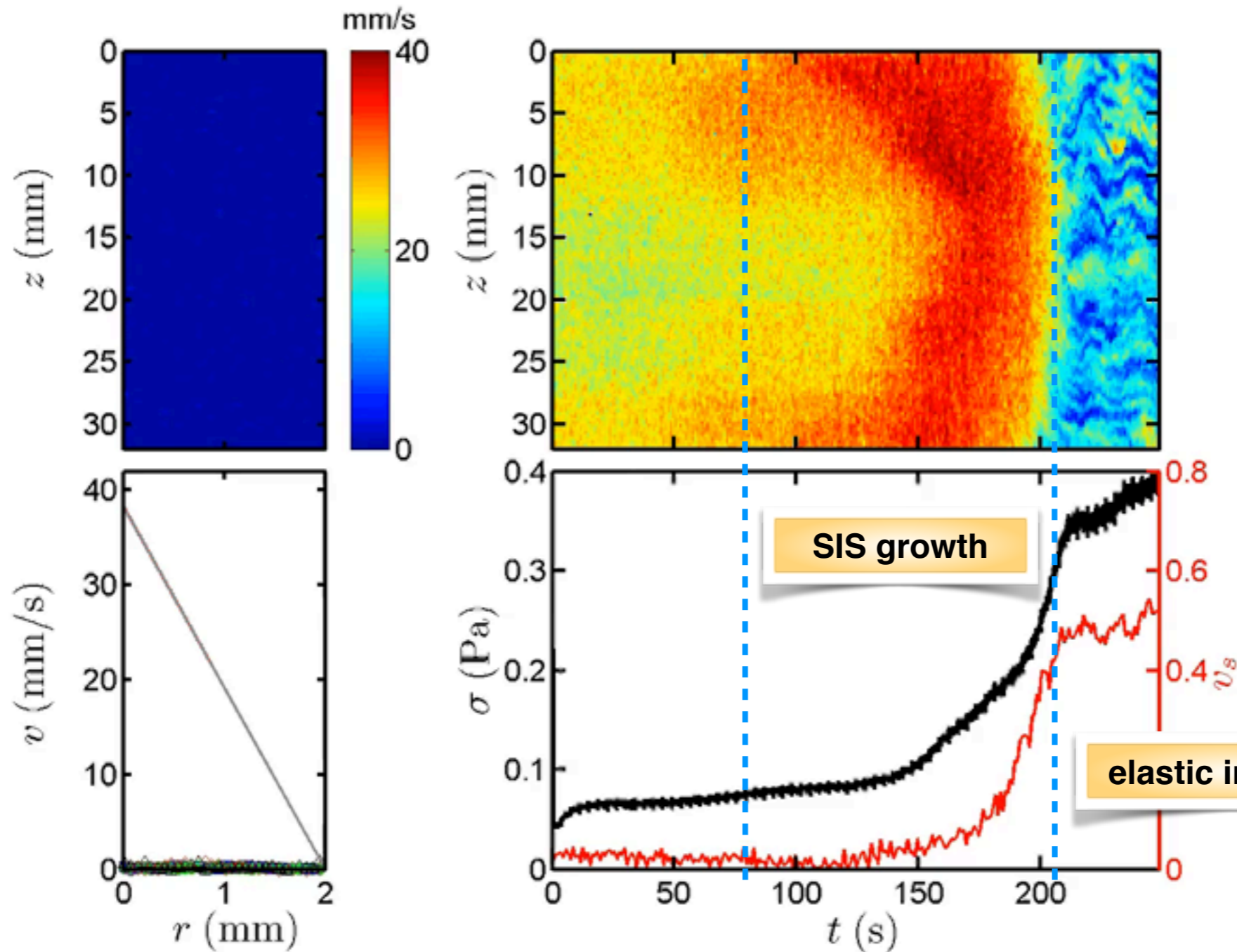
⇒ phase coexistence under imposed stress



# 🏠 Dynamics of shear-thickening wormlike micelles ← | →

SIS without TVF at  $T=20^\circ\text{C}$   $\dot{\gamma}=20\text{ s}^{-1}$ ;  $t=-0.5\text{ s}$

CTAT  
0.16% wt.



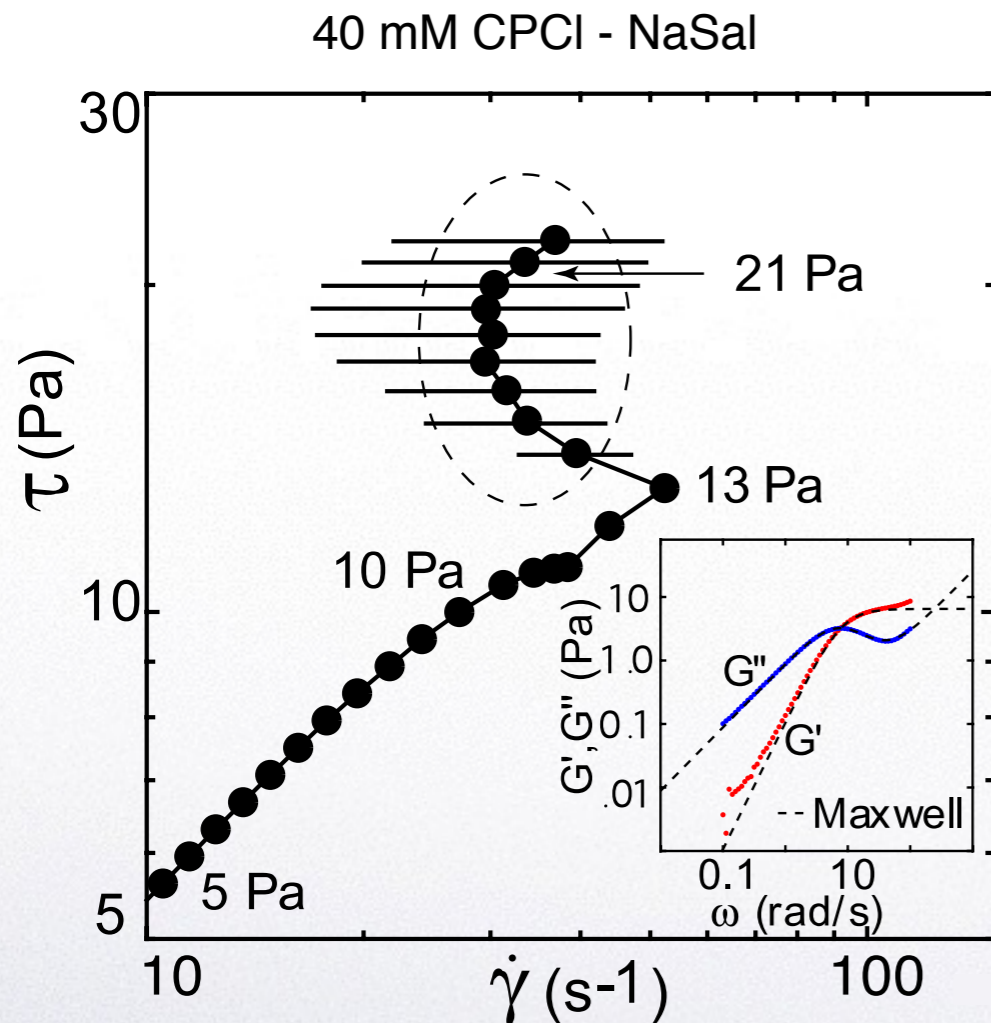
⇒ long induction phase and subsequent elastic instability of the SIS



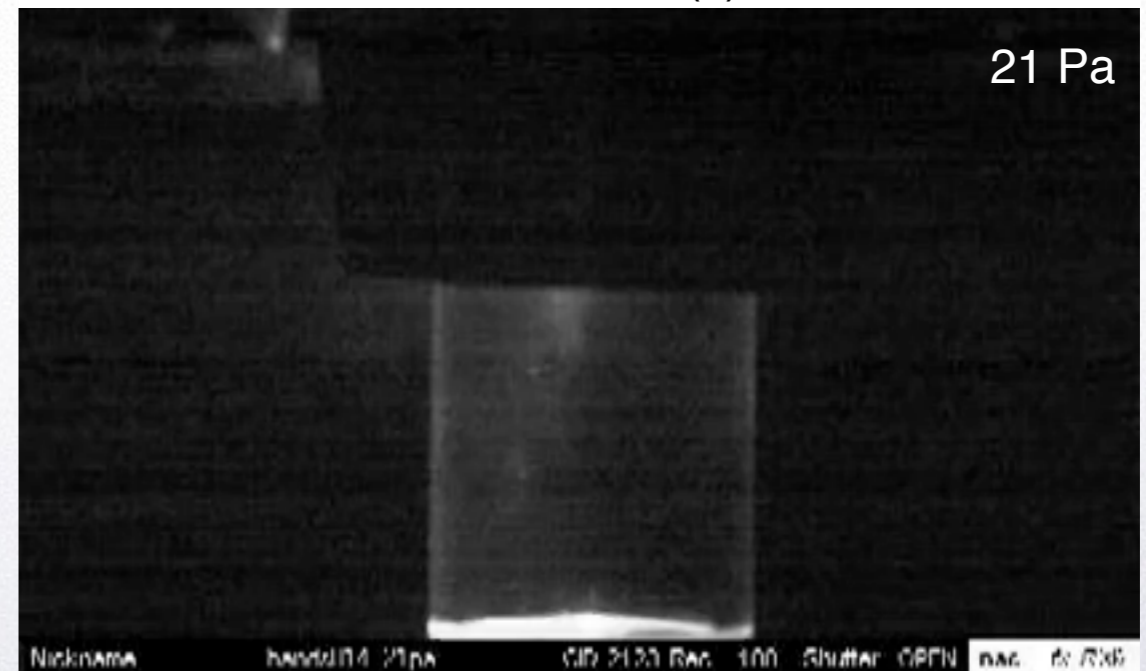
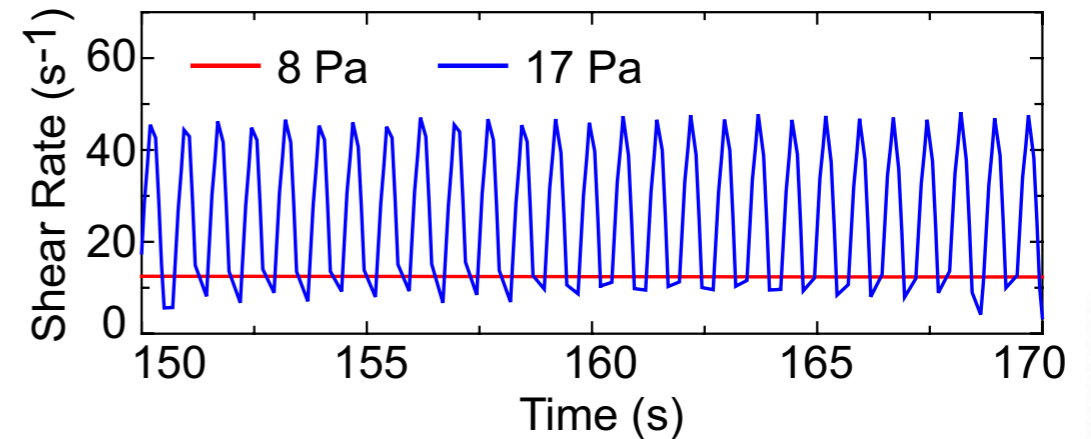
# Vorticity banding in wormlike micelles



shear-thinning followed by shear-thickening !



Herle *et al.*, *PRL* **99**, 158302 (2007) &  
*Eur. Phys. J. E* **26**, 3-12 (2008)

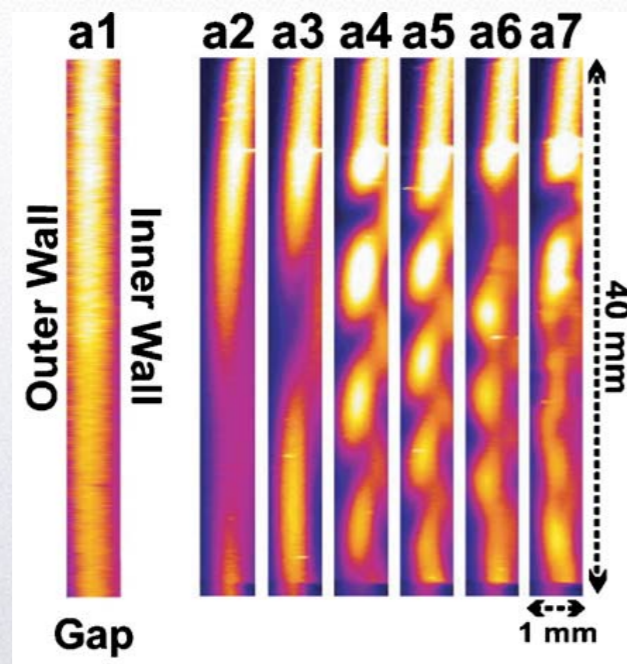
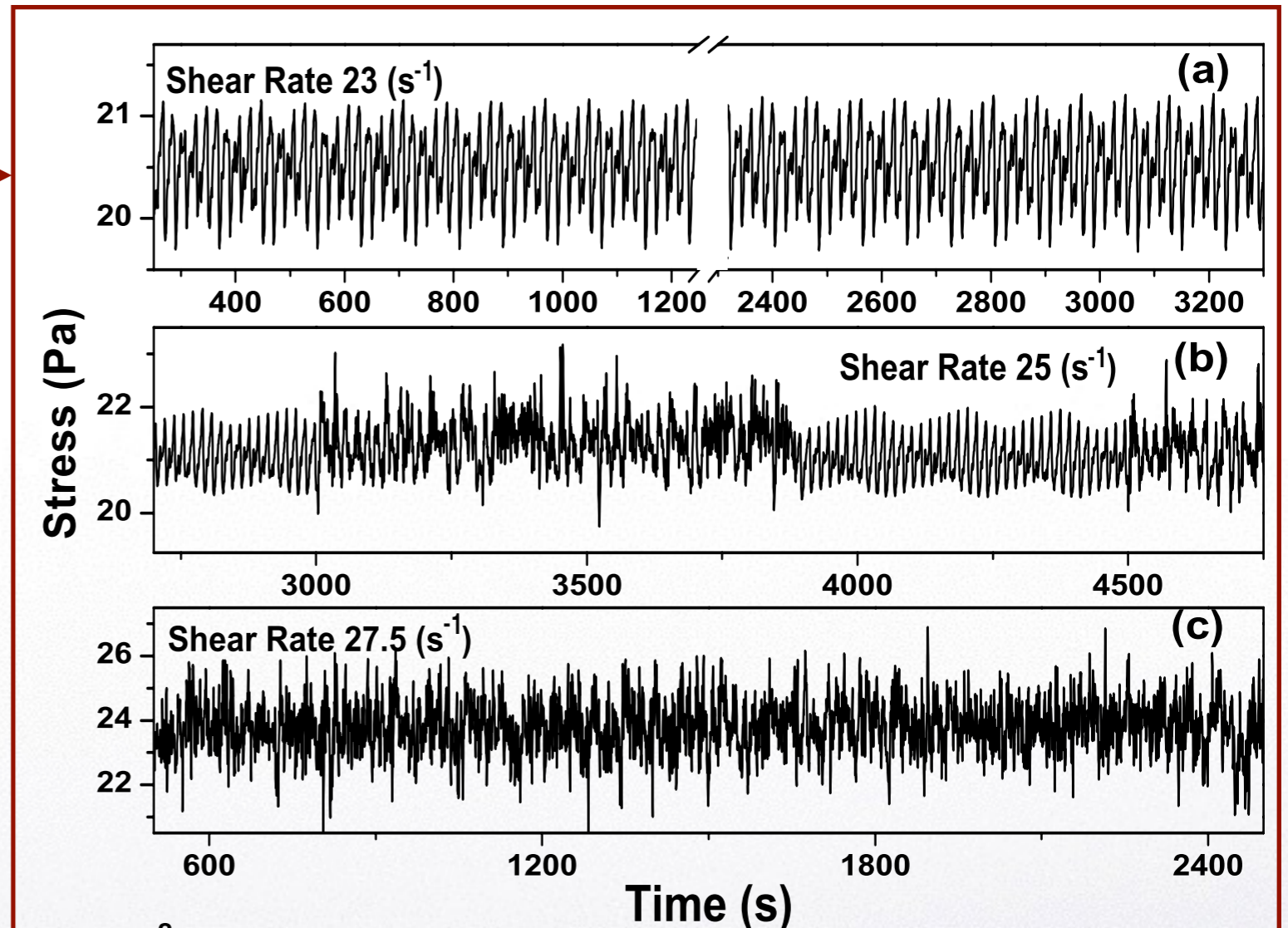
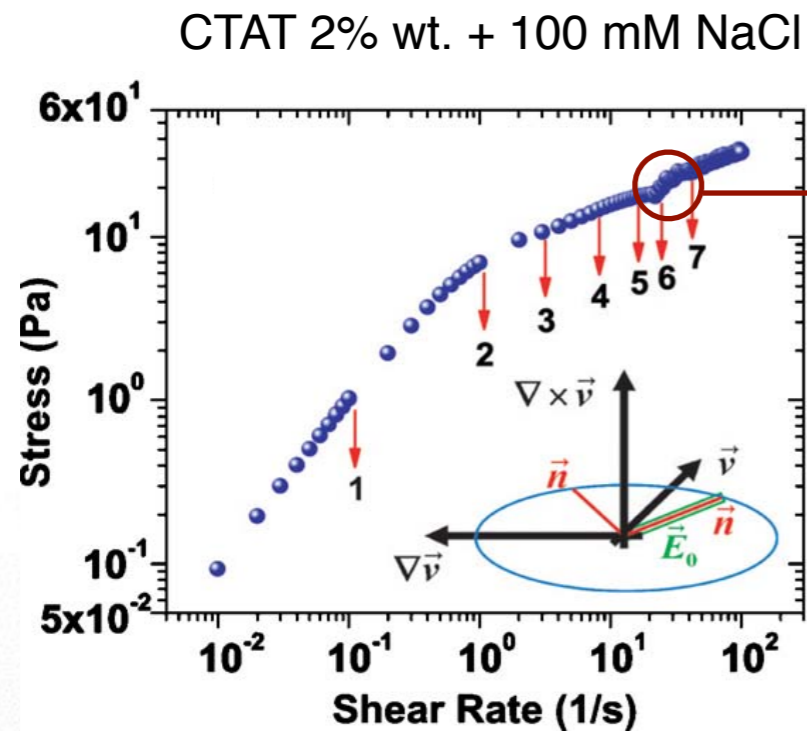


periodic oscillations of the shear rate & alternating vorticity bands  
⇒ interplay between alignment/concentration & viscoelasticity





# Rheochaos in wormlike micelles



Ganapathy & Sood, *PRL* 96, 108301 (2006) & *PRE* 78, 021504 (2008)

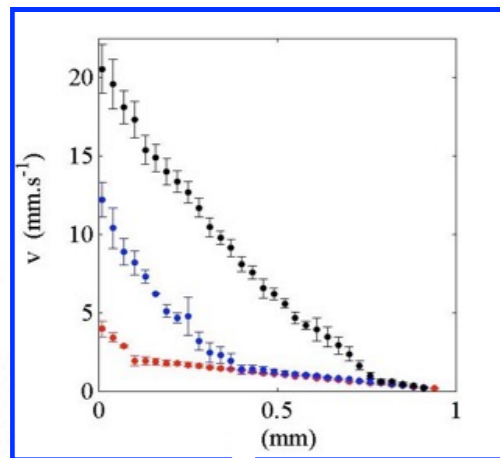
⇒ evidence for type-II intermittency (via quasiperiodicity)  
⇒ flow-concentration coupling and/or elastic instability?



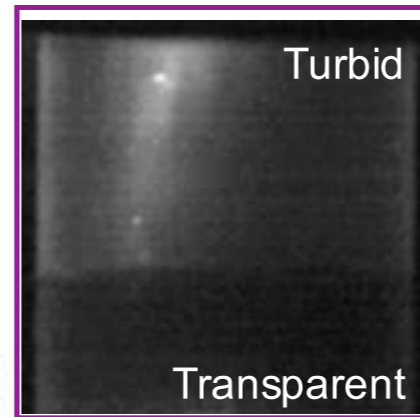
# Wormlike micelles summary



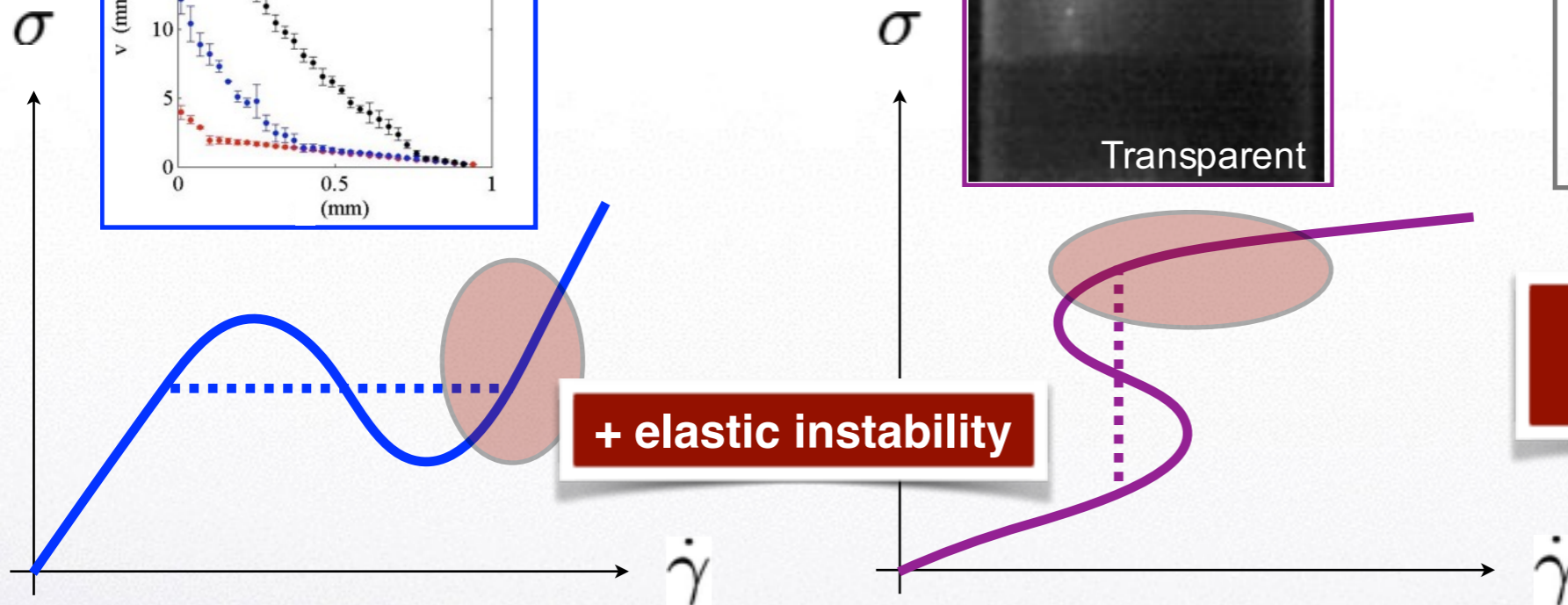
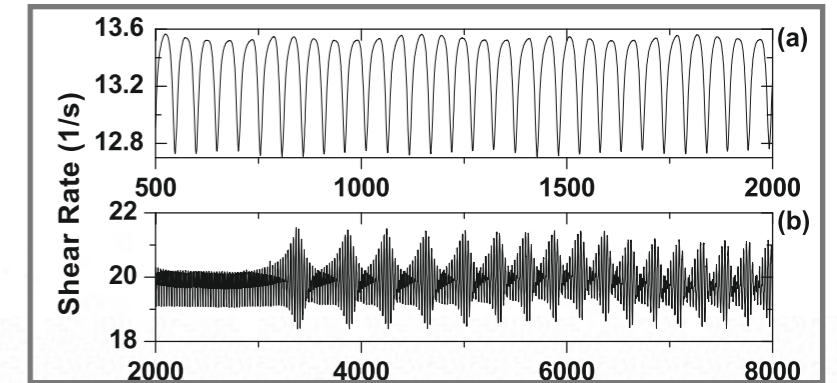
shear-thinning  
⇒ gradient banding



shear-thickening  
⇒ vorticity banding

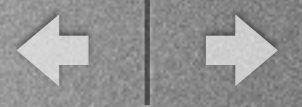


... or both?



+ flow-concentration coupling  
+ nematohydrodynamics

surfactant wormlike micelles show a wide range of heterogeneous flows & dynamical behaviours (that are interesting to keep in mind for dense suspensions)



## I. Surfactant solutions

*from gradient banding to elastic turbulence to vorticity banding*

## II. Yielding in soft glassy (“squishy”) materials

*from steady shear localization to critical-like fluidization dynamics*

T. Divoux, M.-A. Fardin, SM & S. Lerouge, *Ann. Rev. Fluid Mech.* **48**, 81–103 (2016)

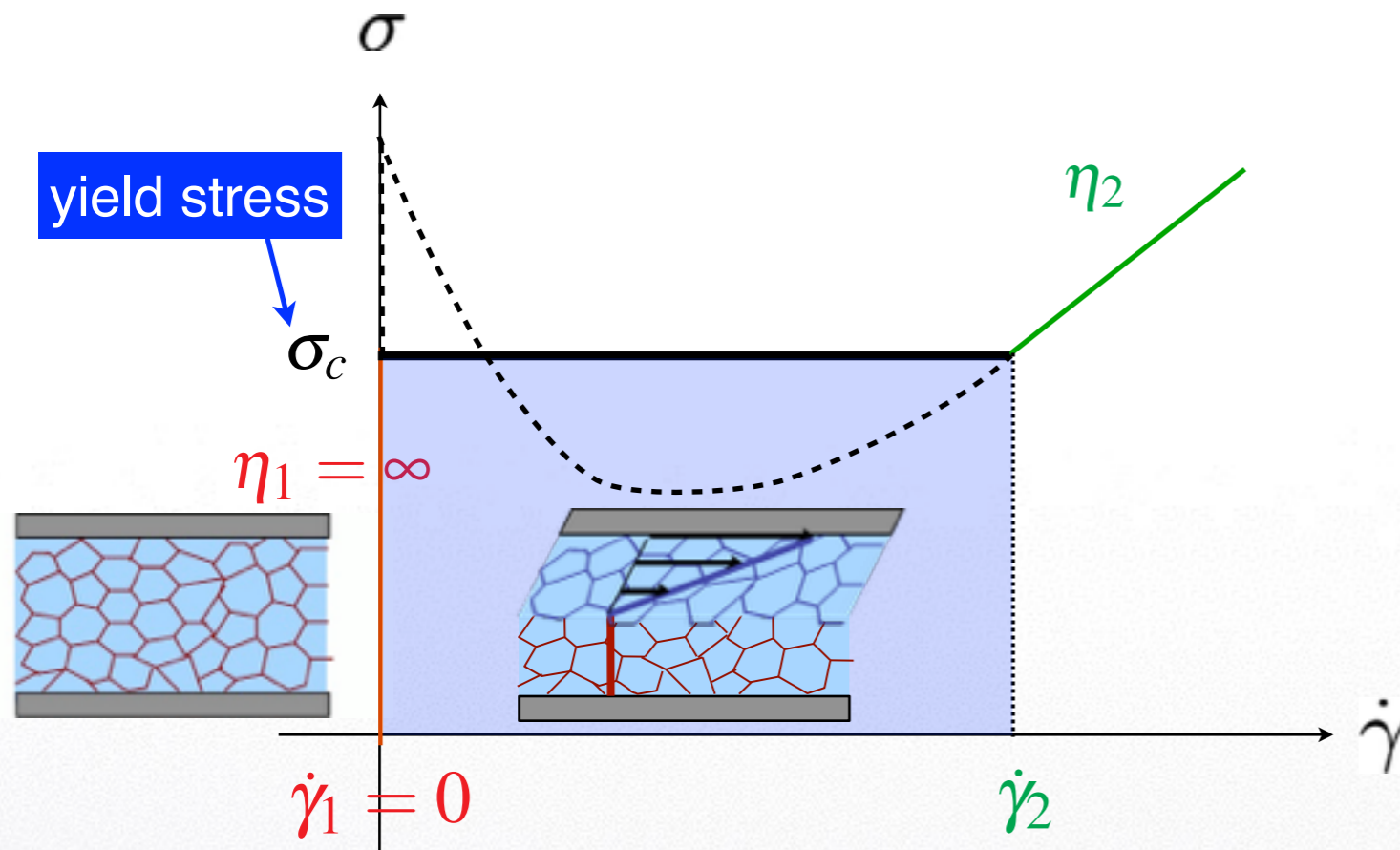
D. Bonn, M. Denn, L. Berthier, T. Divoux & SM, *Rev. Mod. Phys.* **89**, 035005 (2017)

## III. What about dense suspensions?

*similarities and differences with other complex fluids*

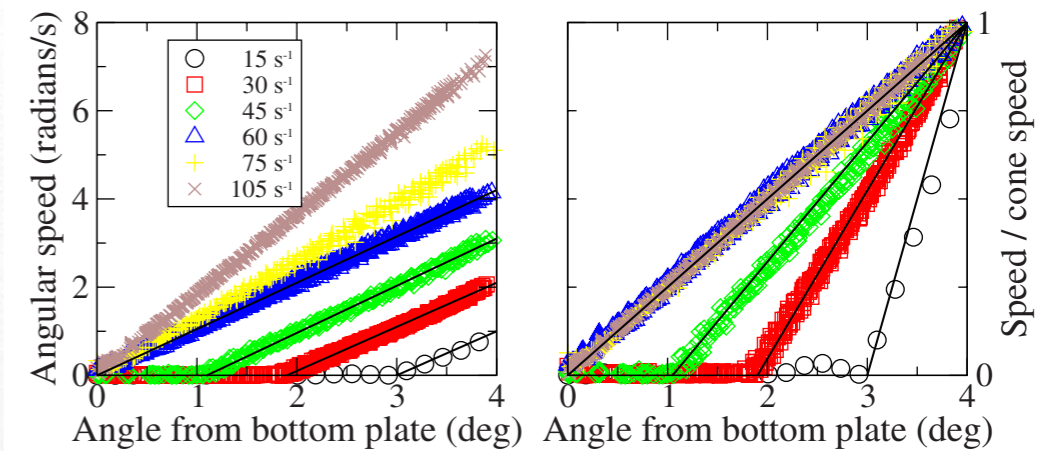
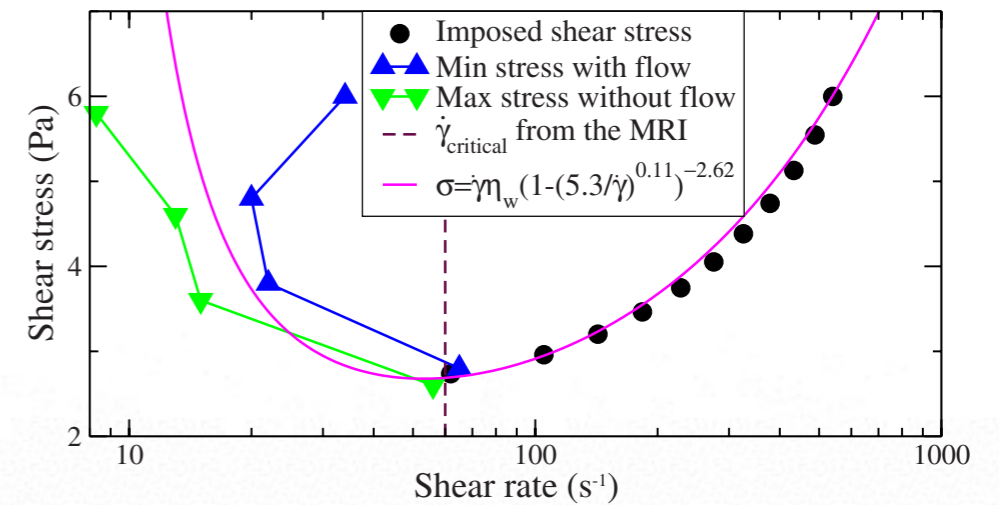


# Shear banding in yield stress fluids



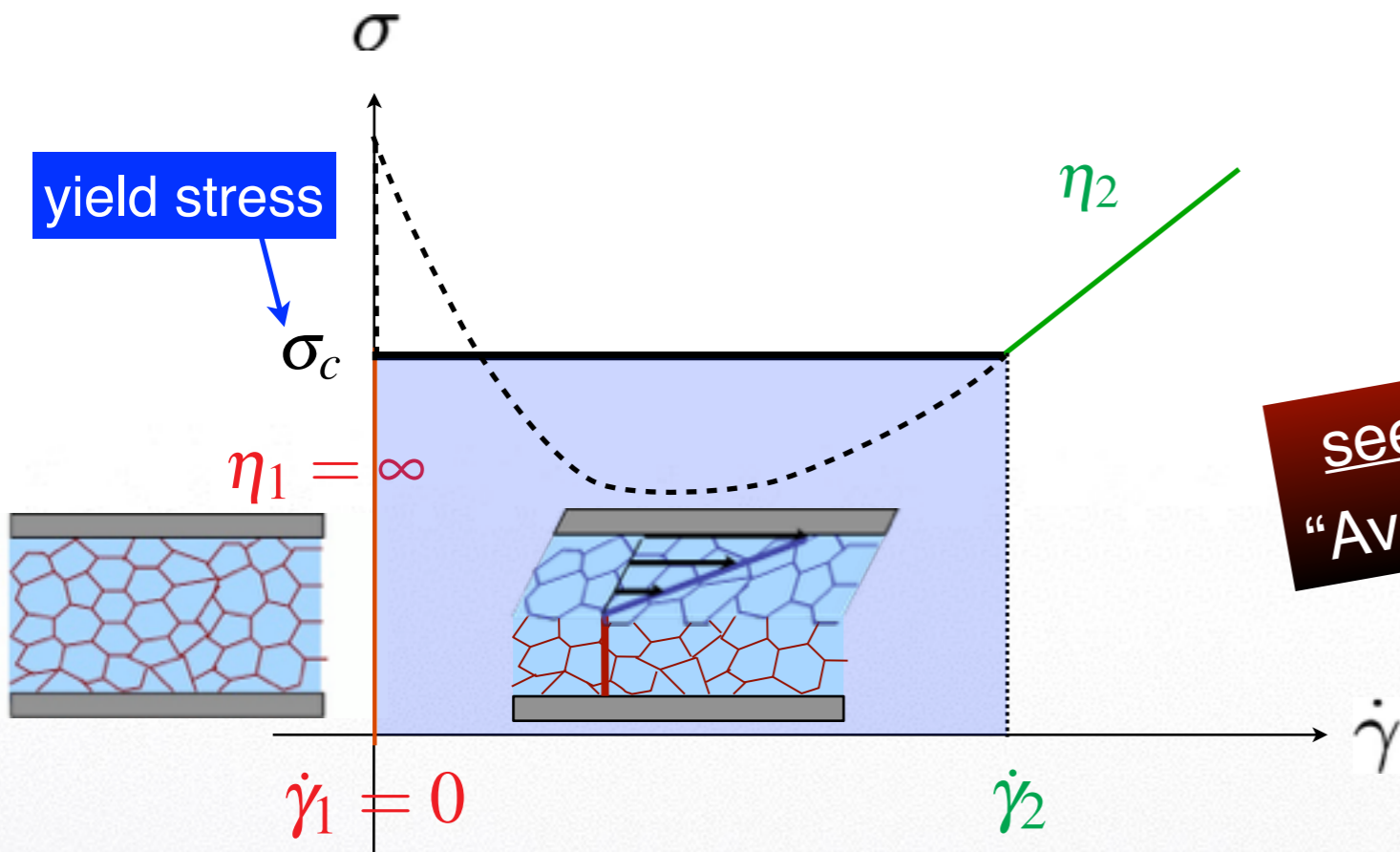
- “1<sup>st</sup> order” shear-induced solid-liquid transition
- coexistence = shear localization in a fluidized region

Iudox colloidal gel  
Møller *et al.*, *PRE* 77, 041507 (2008)



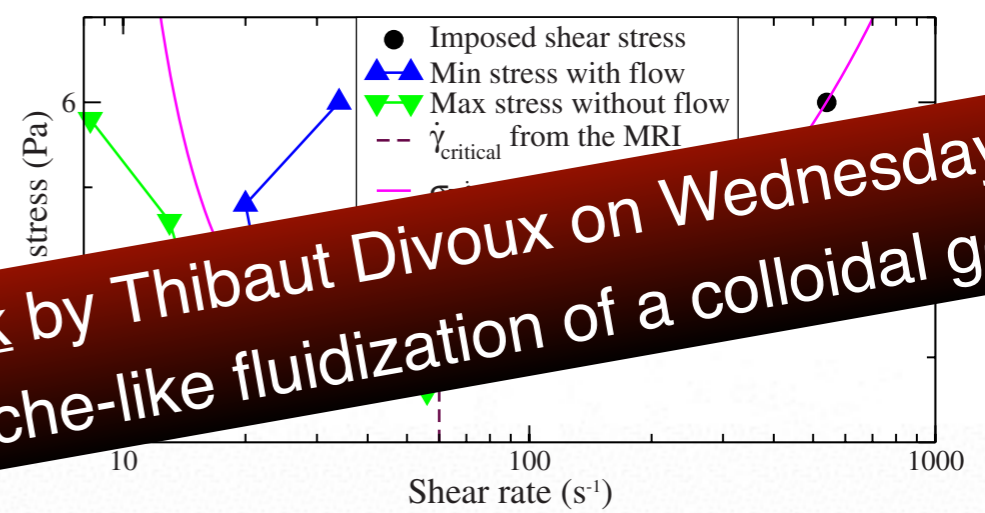


# Shear banding in yield stress fluids

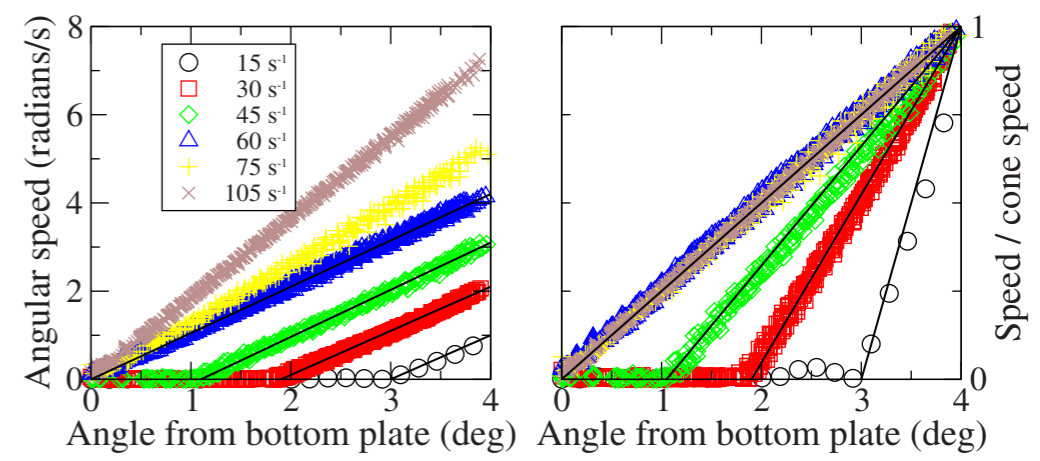


Iudox colloidal gel  
Møller *et al.*, *PRE* 77, 041507 (2008)

see talk by Thibaut Divoux on Wednesday  
"Avalanche-like fluidization of a colloidal gel"



- "1<sup>st</sup> order" shear-induced solid-liquid transition
- coexistence = shear localization in a fluidized region



Seen in :  
colloidal gels



pastes



and clay suspensions



⇒ interplay between aging and shear rejuvenation

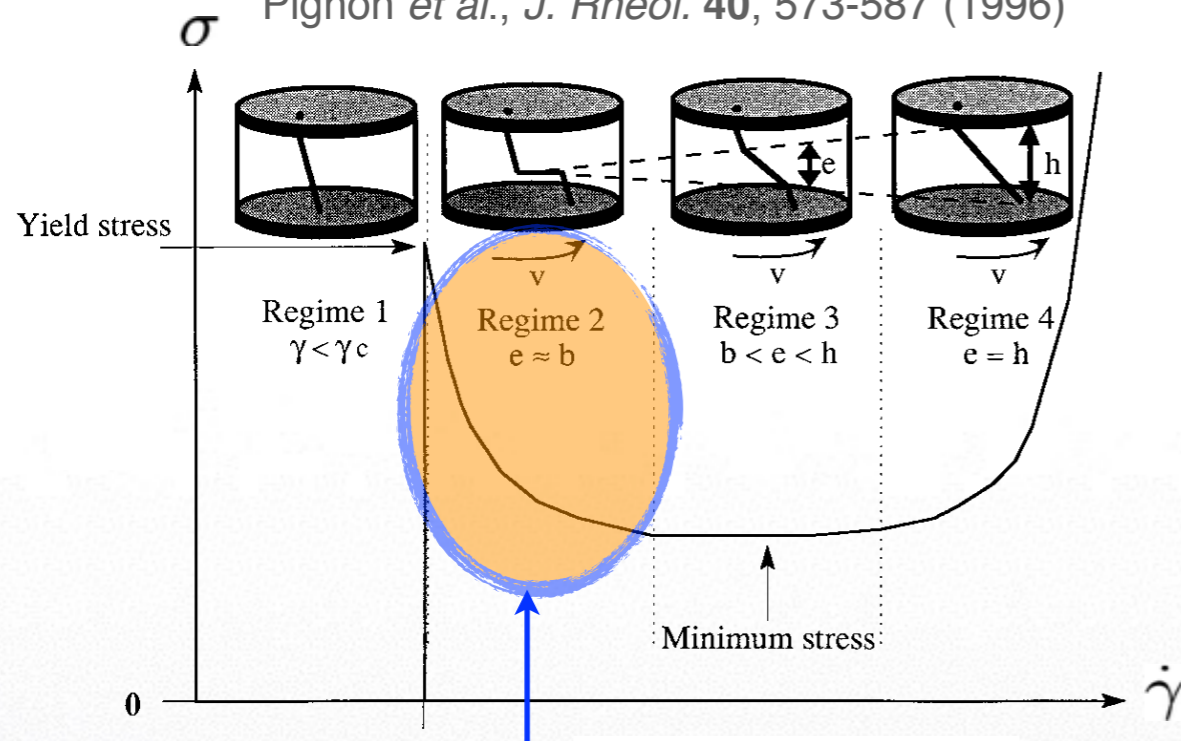


# Other instability modes



## laponite suspensions

Pignon *et al.*, *J. Rheol.* **40**, 573-587 (1996)

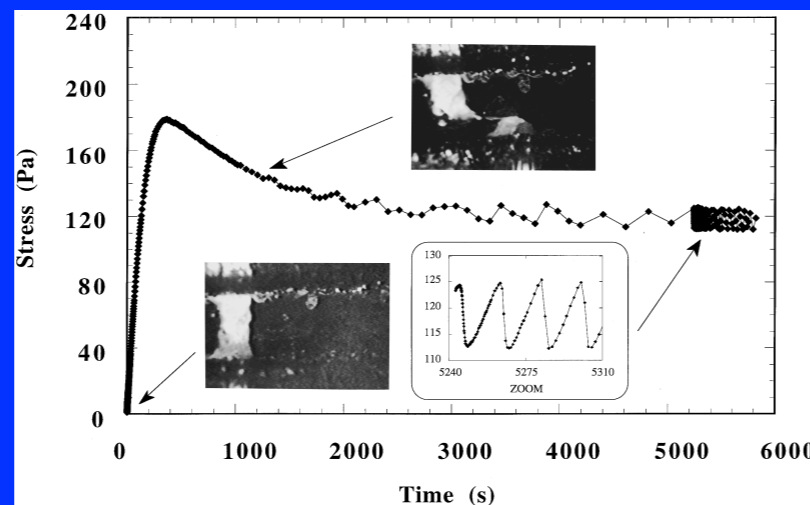
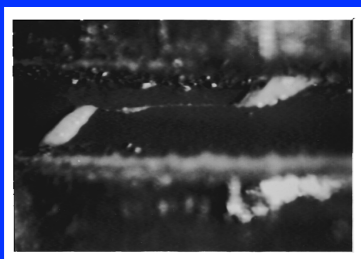
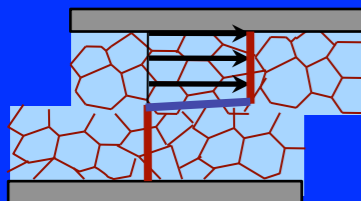


## casein gels

Leocmach *et al.*, *PRL* **113**, 038303 (2014)



## no steady flow: fractures and stick-slip

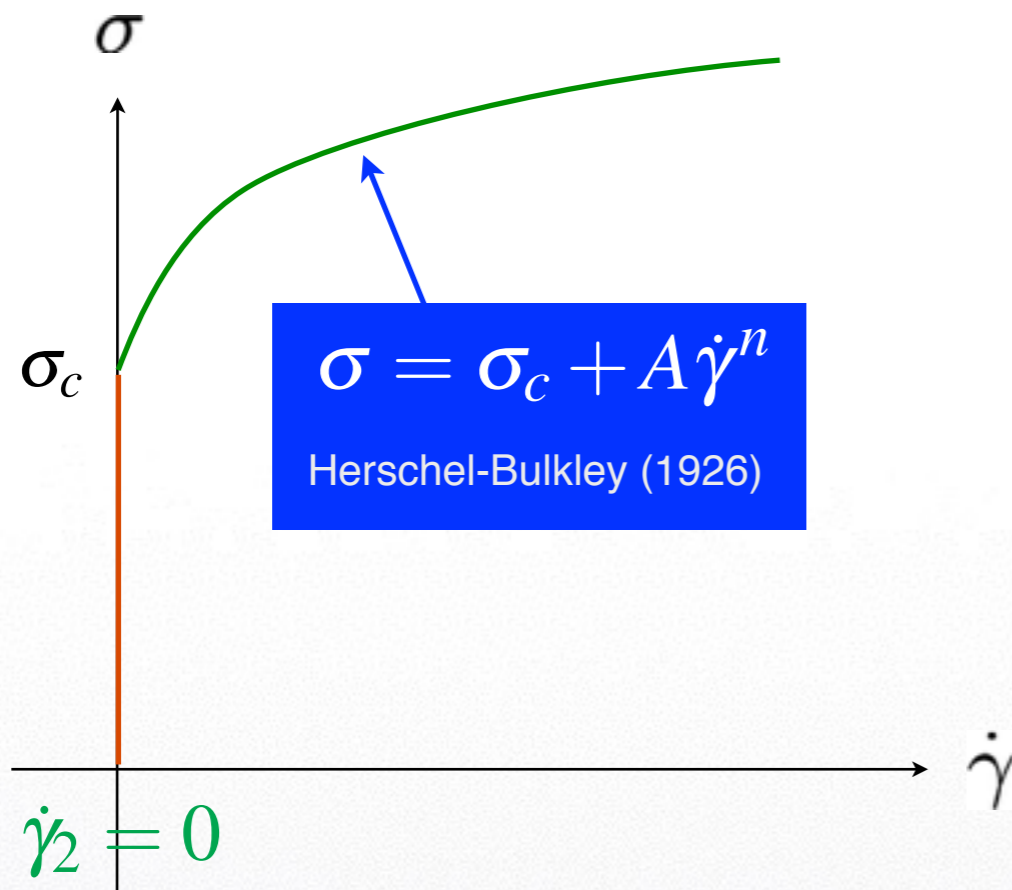


- irreversible fluidization
- fracture growth
- well-defined wavelength
- macroscopic phase separation

⇒ does homogeneous, continuous yielding exist at all?

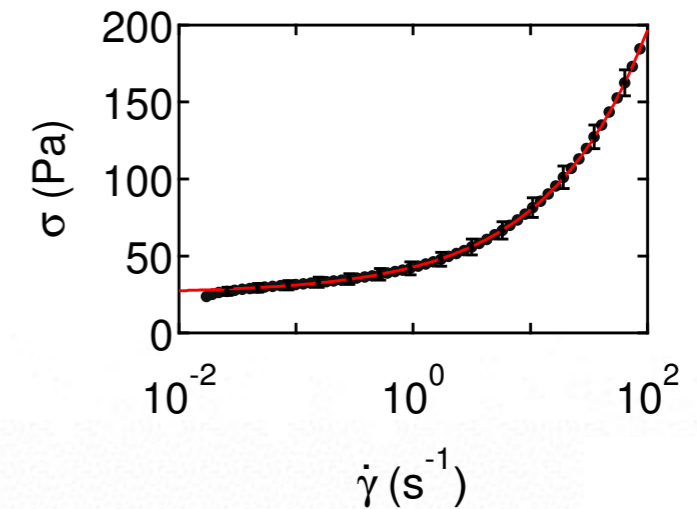


# Simple yield stress fluids

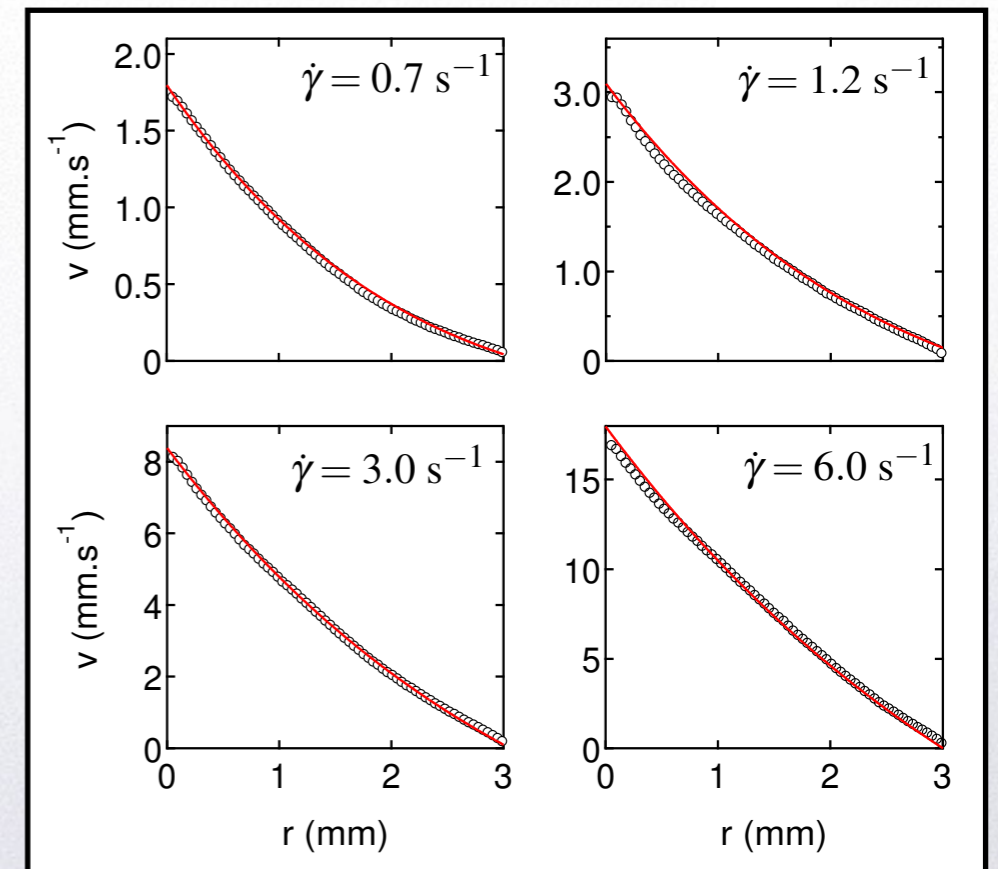


carbopol microgel (ETD 2050)

Divoux *et al.*, *Soft Matter* **8**, 4151-4164 (2012)



- “2<sup>nd</sup> order” shear-induced solid-liquid transition
- homogeneously sheared flow



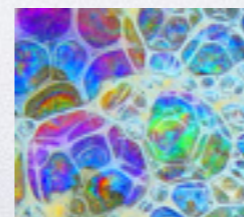
Seen in :  
emulsions



microgels



and foams



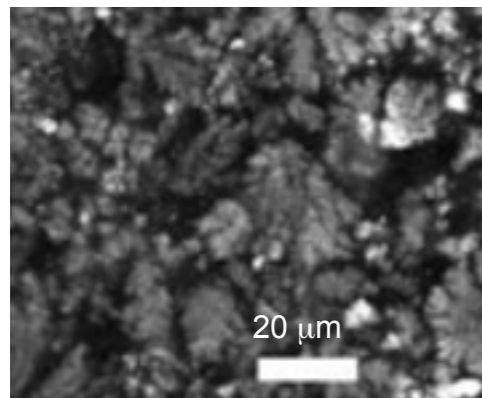
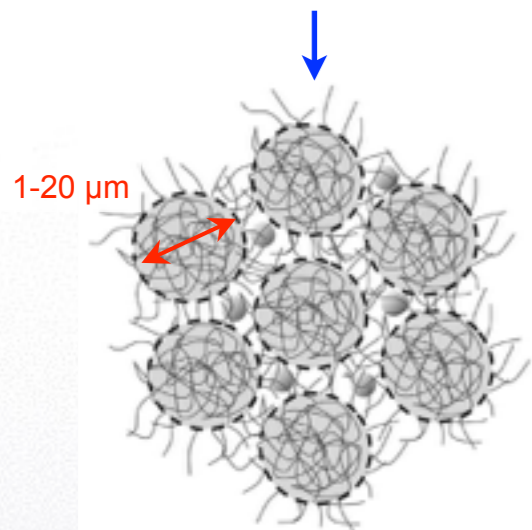
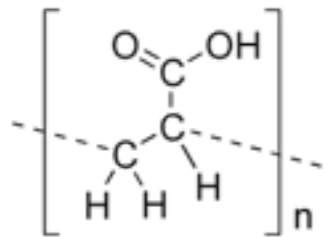
⇒ focus on fluidization dynamics in simple YSF



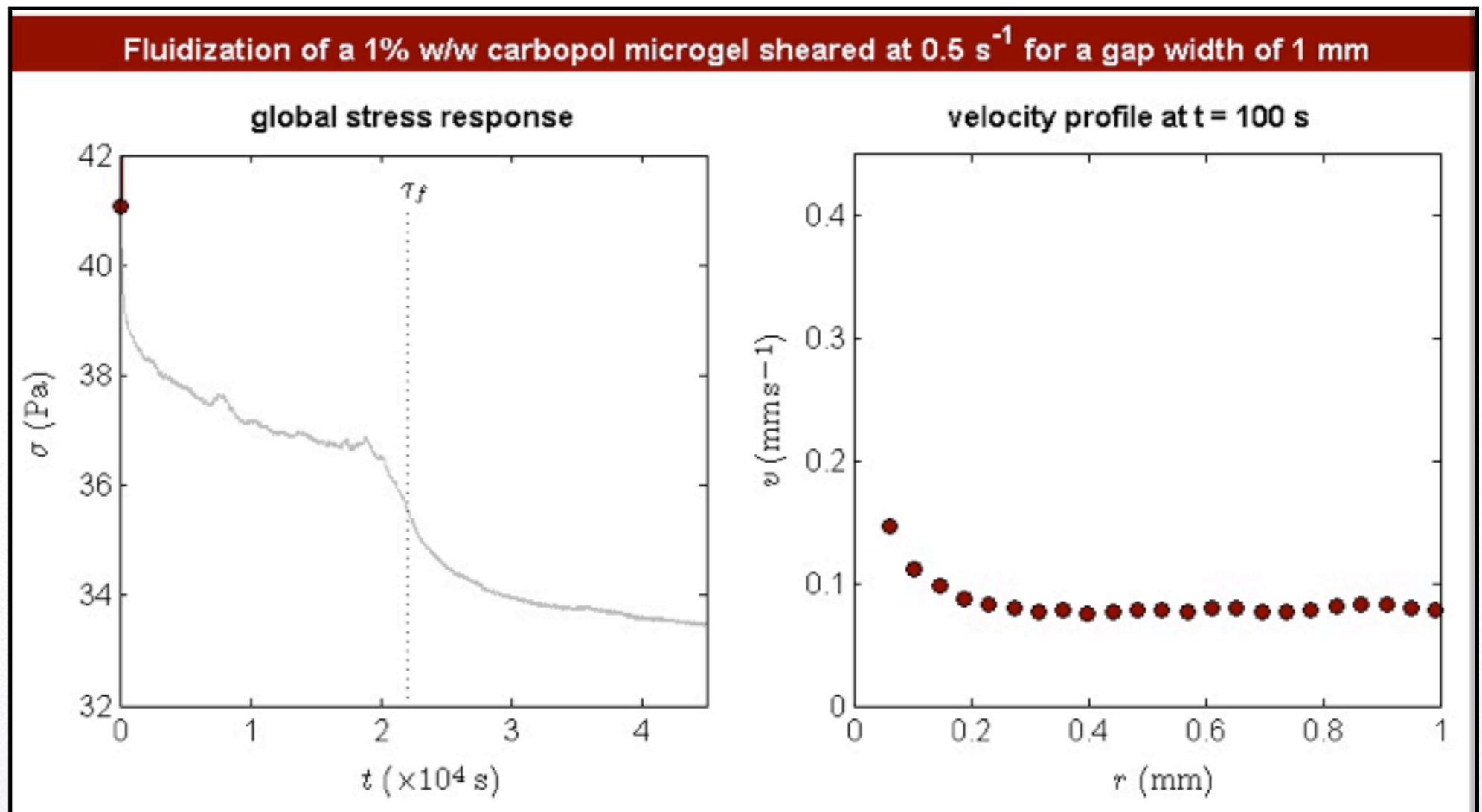
# Slow fluidization dynamics in carbopol



poly(acrylic acid) polymer



Gutowski *et al.*, *Rheol. Acta* 51, 441-450 (2012)



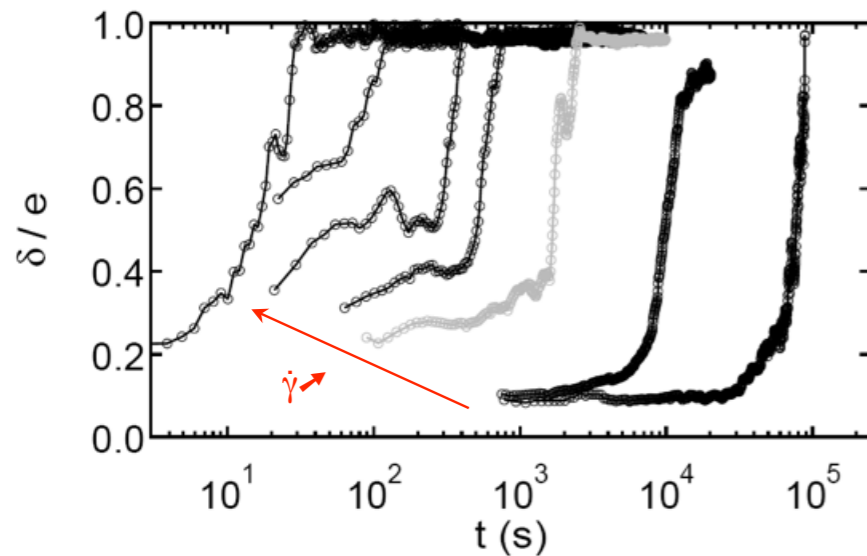
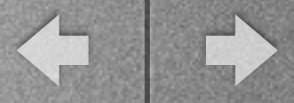
Divoux *et al.*, *PRL* 104, 208301 (2010) & *Soft Matter* 8, 4151-4164 (2012)

- ⇒ long-lasting transient shear-banding
- ⇒ fluctuations and “sudden” fluidization at  $\tau_f$
- ⇒ rheological signature : “kink” around  $\tau_f$

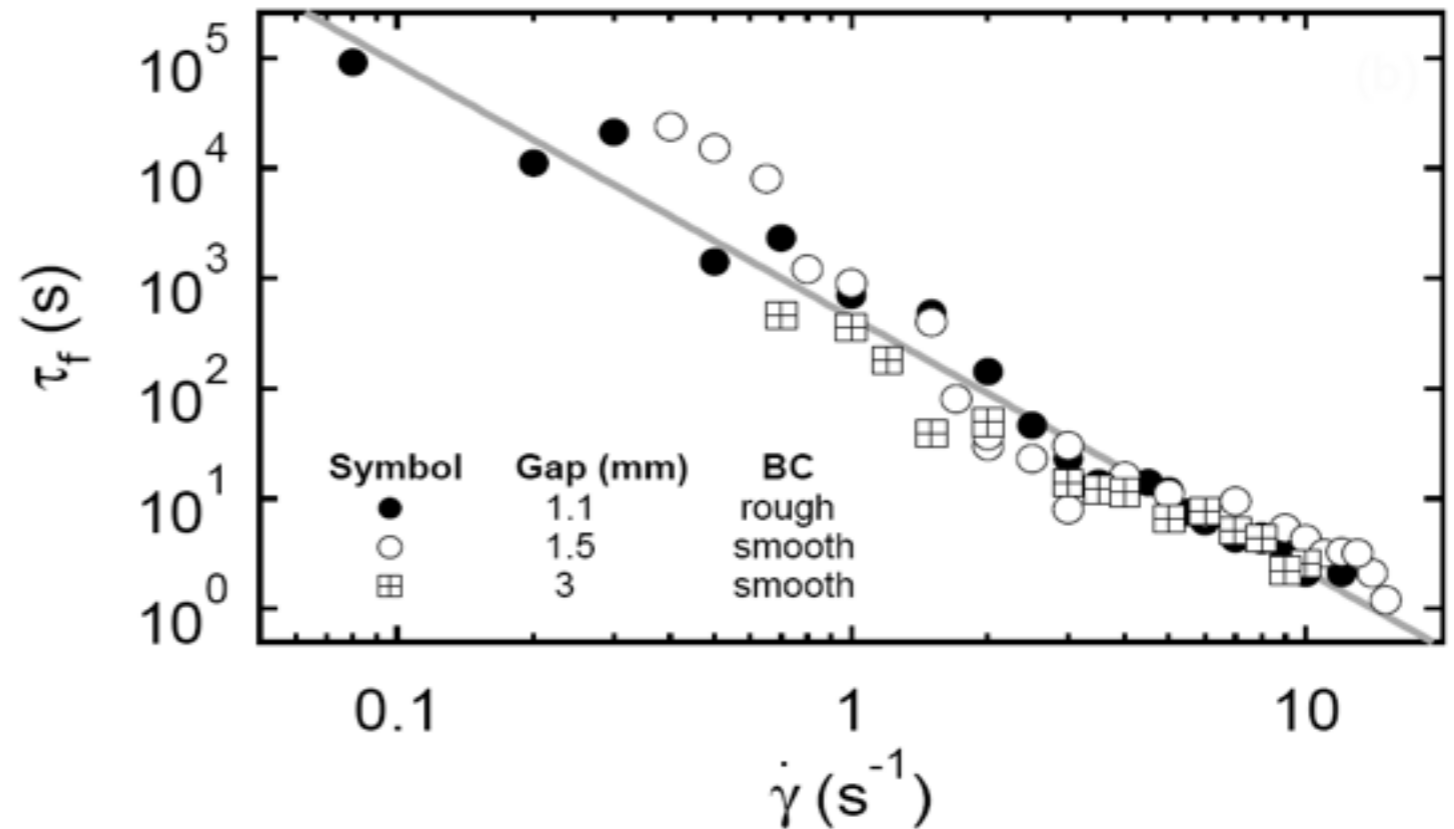




# Shear-rate controlled experiments



$$\delta(\tau_f) = 0.9e$$



$$\tau_f \sim \dot{\gamma}^{-\alpha}$$

with

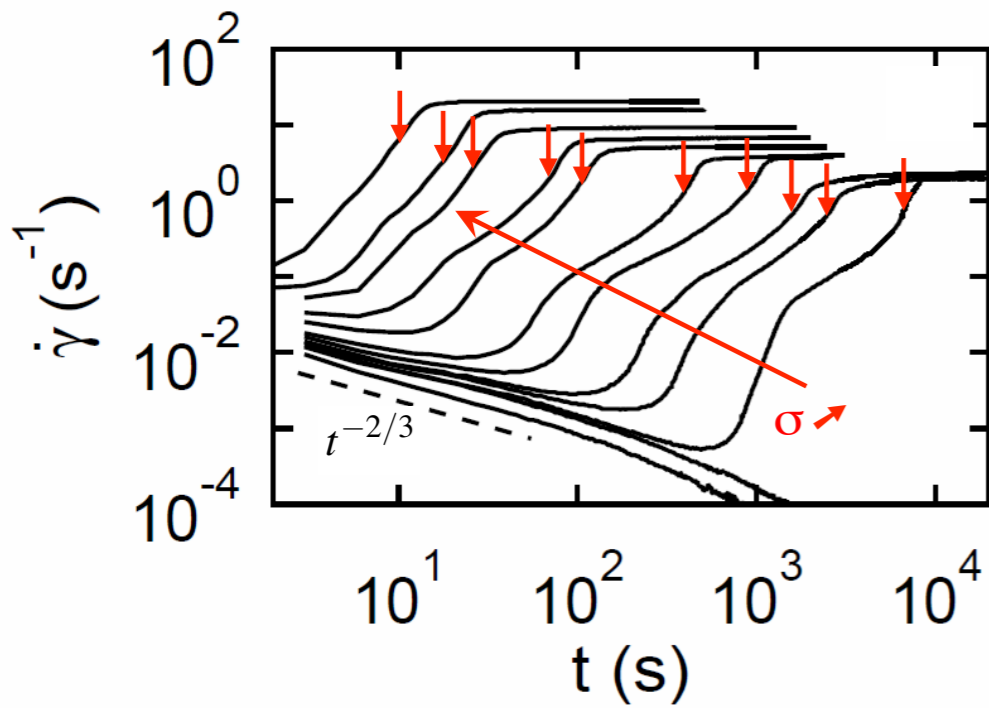
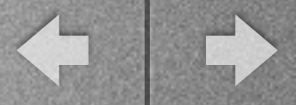
$$\alpha = 2.3 \pm 0.1$$

- independent of gap width and wall roughness
- dependent on carbopol batch (preparation, concentration)

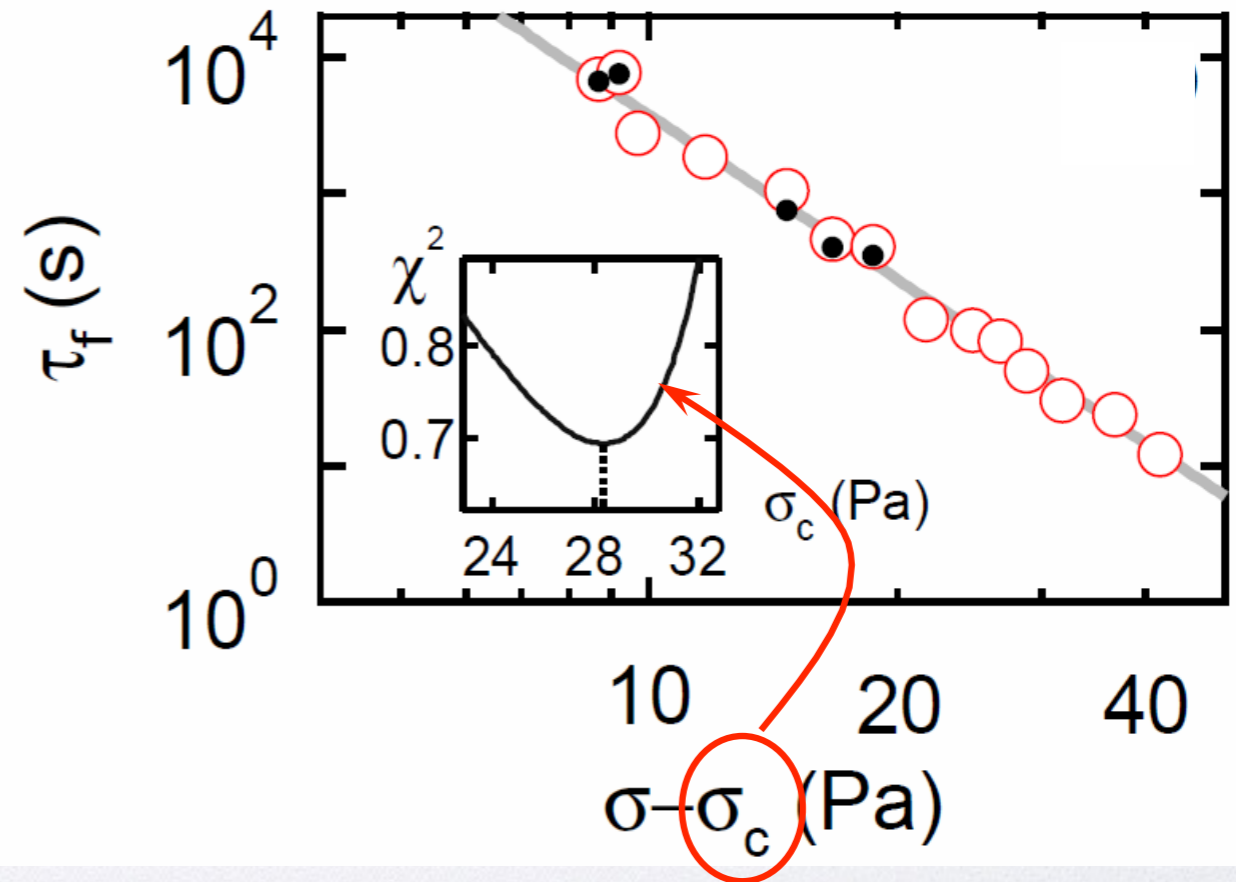
⇒ what about imposing the shear stress (creep)?



# Stress-controlled experiments



$\tau_f$  : second inflexion point



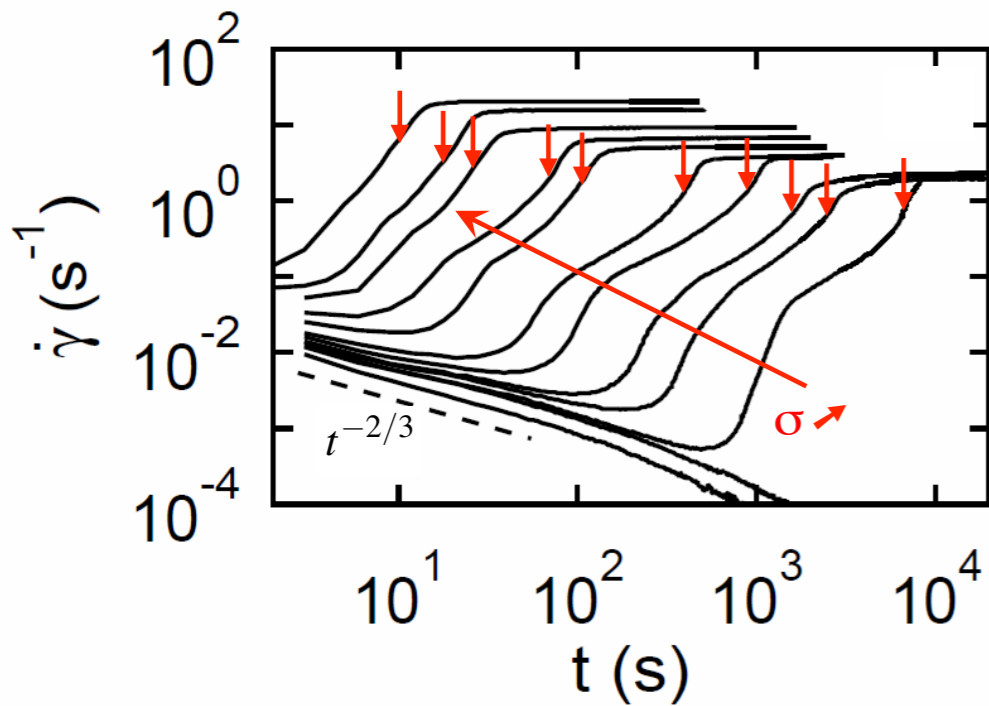
$$\tau_f \sim (\sigma - \sigma_c)^{-\beta}$$

with

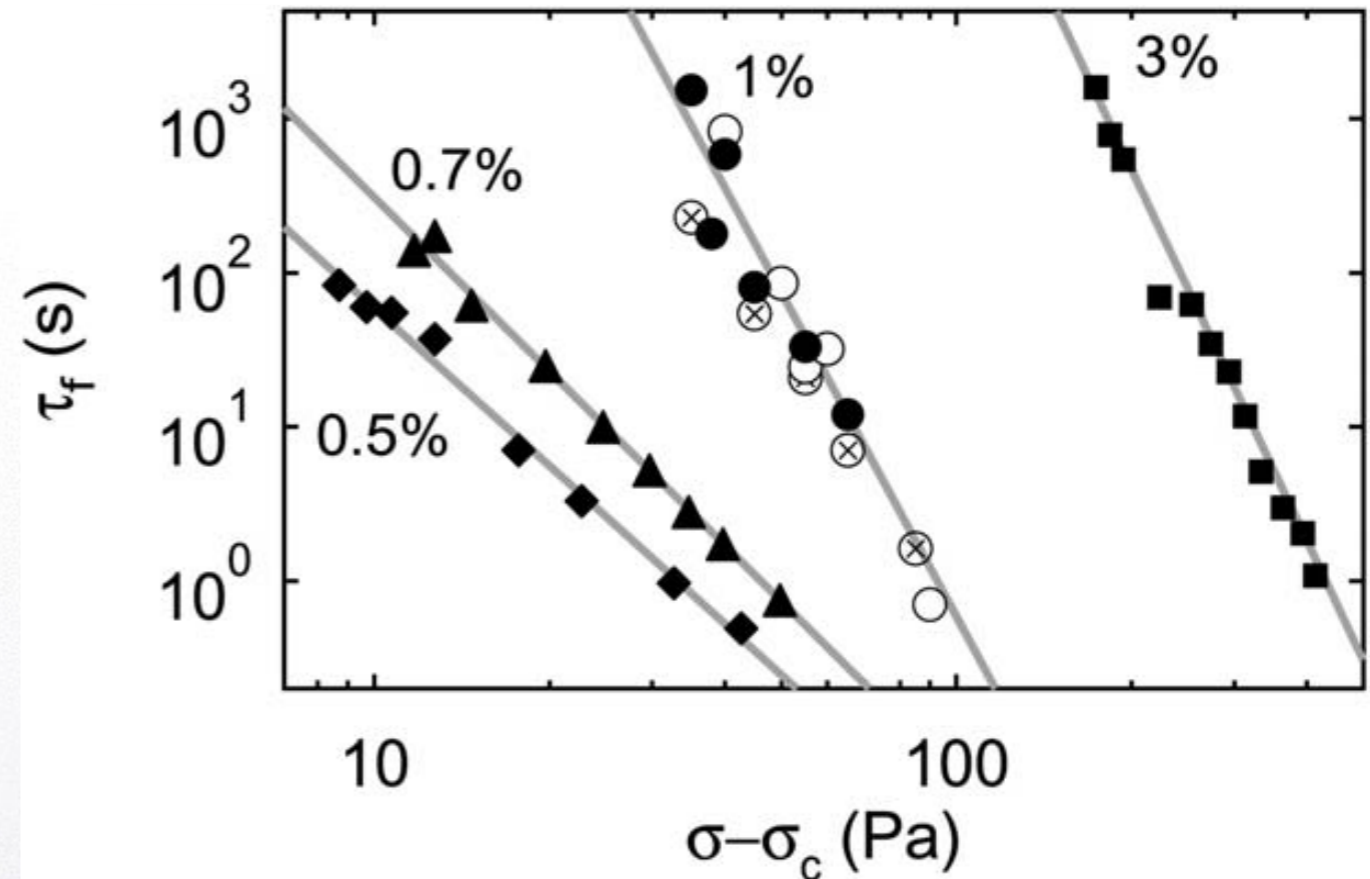
$$\beta = 4.0 \pm 0.1$$



# Stress-controlled experiments



$\tau_f$  : second inflexion point



$$\tau_f \sim (\sigma - \sigma_c)^{-\beta}$$

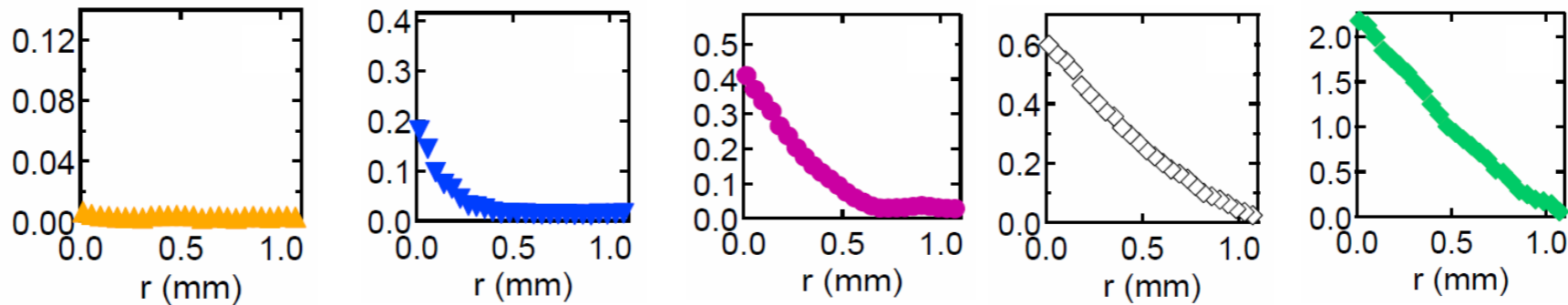
with

$$\beta = 4.0 \pm 0.1$$

- independent of gap width and wall roughness
- dependent on carbopol batch (preparation, concentration)
- estimate of  $\sigma_c$  consistent with steady-state flow curve



# Link between transients and steady-state



$$\tau_f^{(\dot{\gamma})} = a/\dot{\gamma}^\alpha$$

let us assume

$$\tau_f^{(\sigma)} = \lambda \tau_f^{(\dot{\gamma})} \Rightarrow$$

$$\sigma = \sigma_c + A\dot{\gamma}^n$$

$$n = \alpha/\beta$$

$$\tau_f^{(\sigma)} = b/(\sigma - \sigma_c)^\beta$$

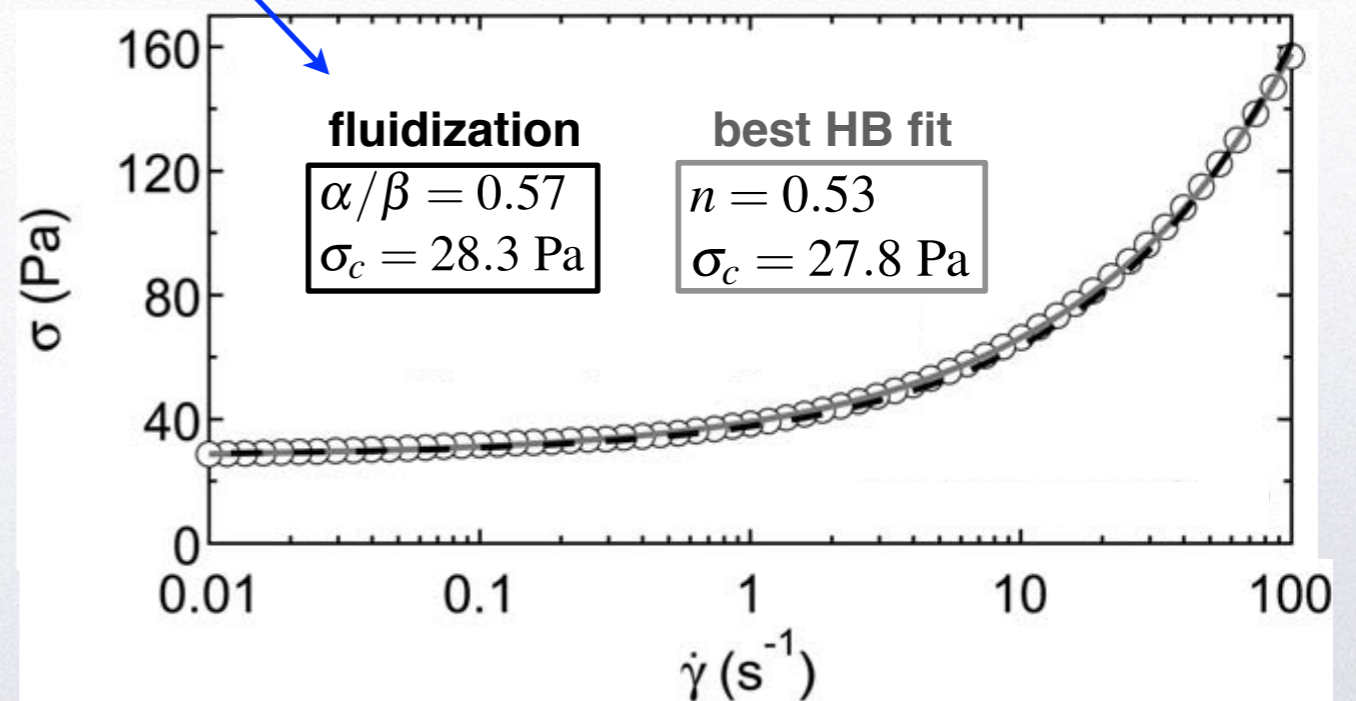
$$A = (b/\lambda a)^{1/\beta}$$

one free parameter:  $\lambda \approx 10$

transient shear-banding  
with  
critical-like dynamics

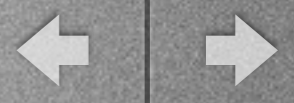


Herschel-Bulkley rheology  
in  
steady state

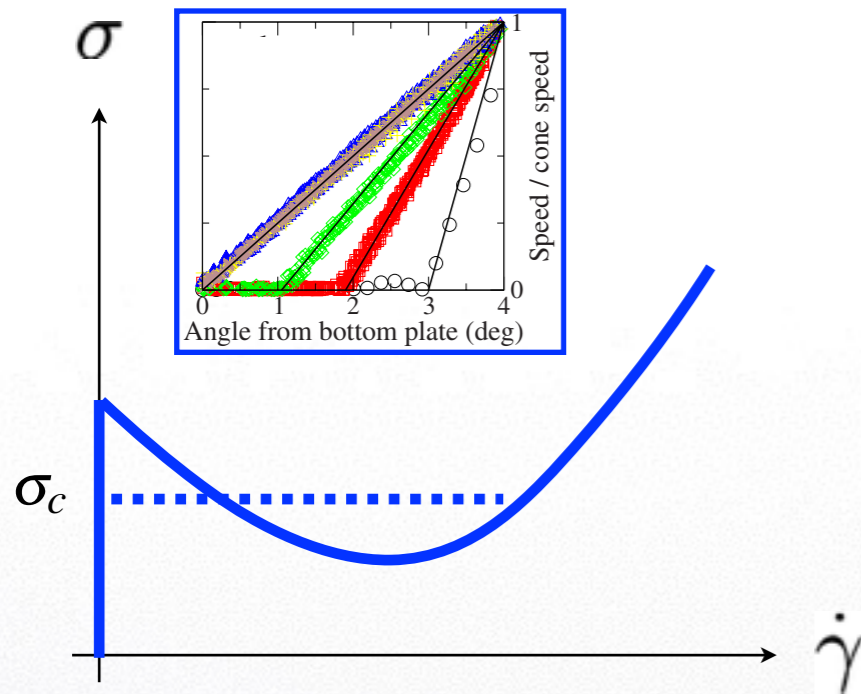




# “Squishy” materials summary



heterogeneous flow

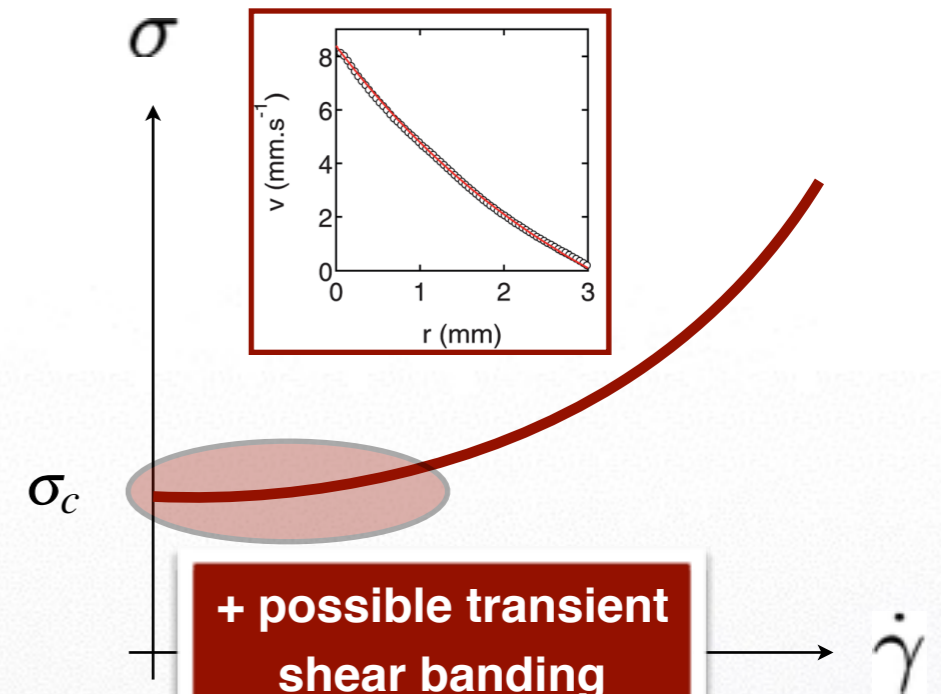


how to tune the system to go from a simple to “thixotropic” yield stress fluid?

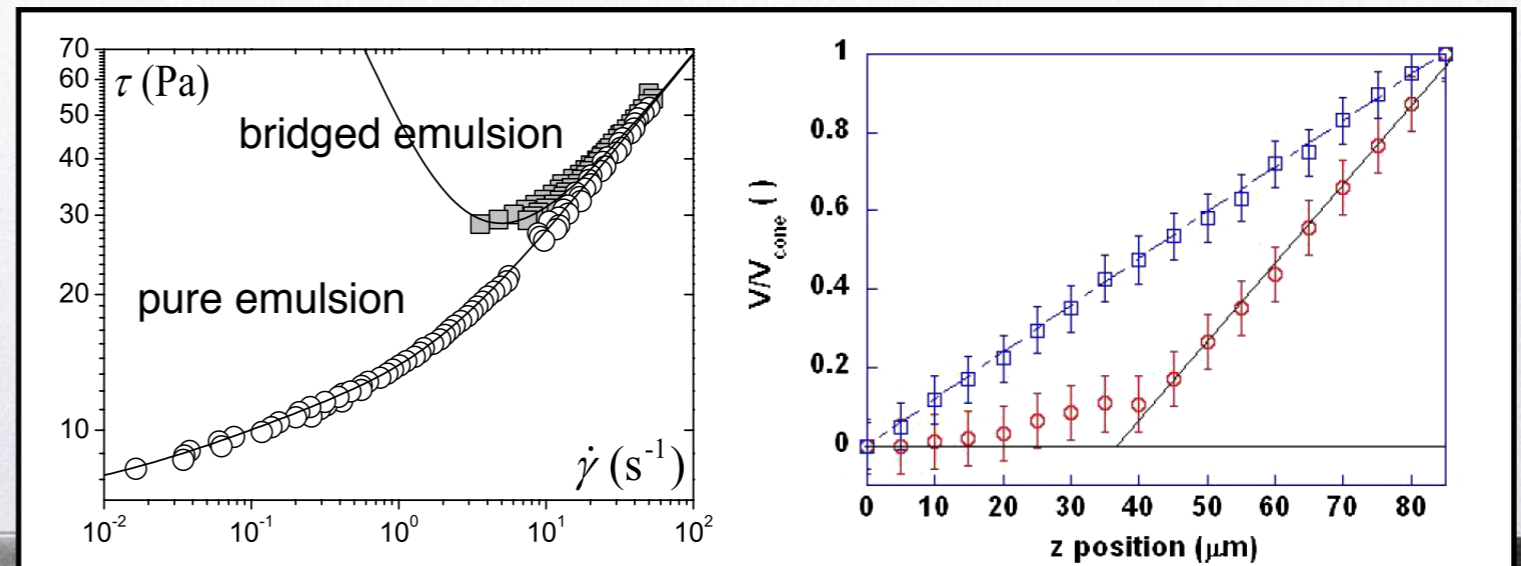
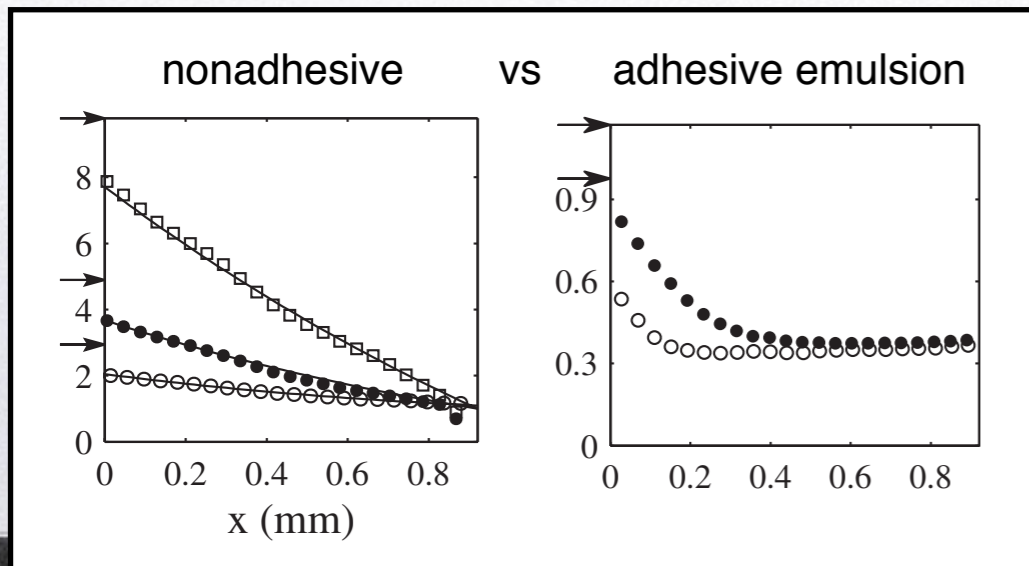


by playing with interactions

homogeneous flow



+ possible transient shear banding





## I. Surfactant solutions

*from gradient banding to elastic turbulence to vorticity banding*

## II. Yielding in soft glassy (“squishy”) materials

*from steady shear localization to critical-like fluidization dynamics*

T. Divoux, M.-A. Fardin, SM & S. Lerouge, *Ann. Rev. Fluid Mech.* **48**, 81–103 (2016)

D. Bonn, M. Denn, L. Berthier, T. Divoux & SM, *Rev. Mod. Phys.* **89**, 035005 (2017)

## III. What about dense suspensions?

*similarities and differences with other complex fluids*



# What is a “dense suspension”?



## Suspension (chemistry)

From Wikipedia, the free encyclopedia

In **chemistry**, a **suspension** is a **heterogeneous mixture** that contains **solid** particles sufficiently large for **sedimentation**. The particles may be **visible** to the **naked eye**, **usually must be larger than 1 micrometer**, and will eventually settle. A suspension is a heterogeneous mixture in which the **solute** particles do not **dissolve**, but get suspended throughout the bulk of the **solvent**, left floating around freely in the medium.<sup>[1]</sup>

suspensions involve  
non-Brownian  
particles (?)

“dense” = concentrated enough to  
lead to non-Newtonian behaviour (?)

## Dispersion (chemistry)

From Wikipedia, the free encyclopedia

A **dispersion** is a system in which particles are dispersed in a continuous **phase** of a different composition (or state). See also **emulsion**. A dispersion is classified in a number of different ways, including how large the particles are in relation to the particles of the continuous phase, whether or not **precipitation** occurs, and the presence of **Brownian motion**.

### IUPAC definition

Material comprising more than one phase where at least one of the phases consists of finely divided phase domains, often in the *colloidal* size range, dispersed throughout a *continuous phase*.<sup>[1]</sup>

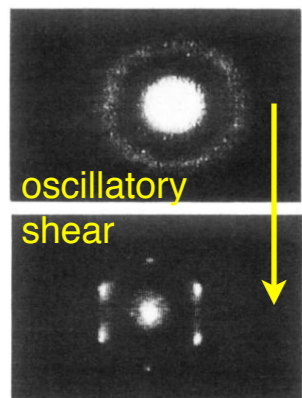
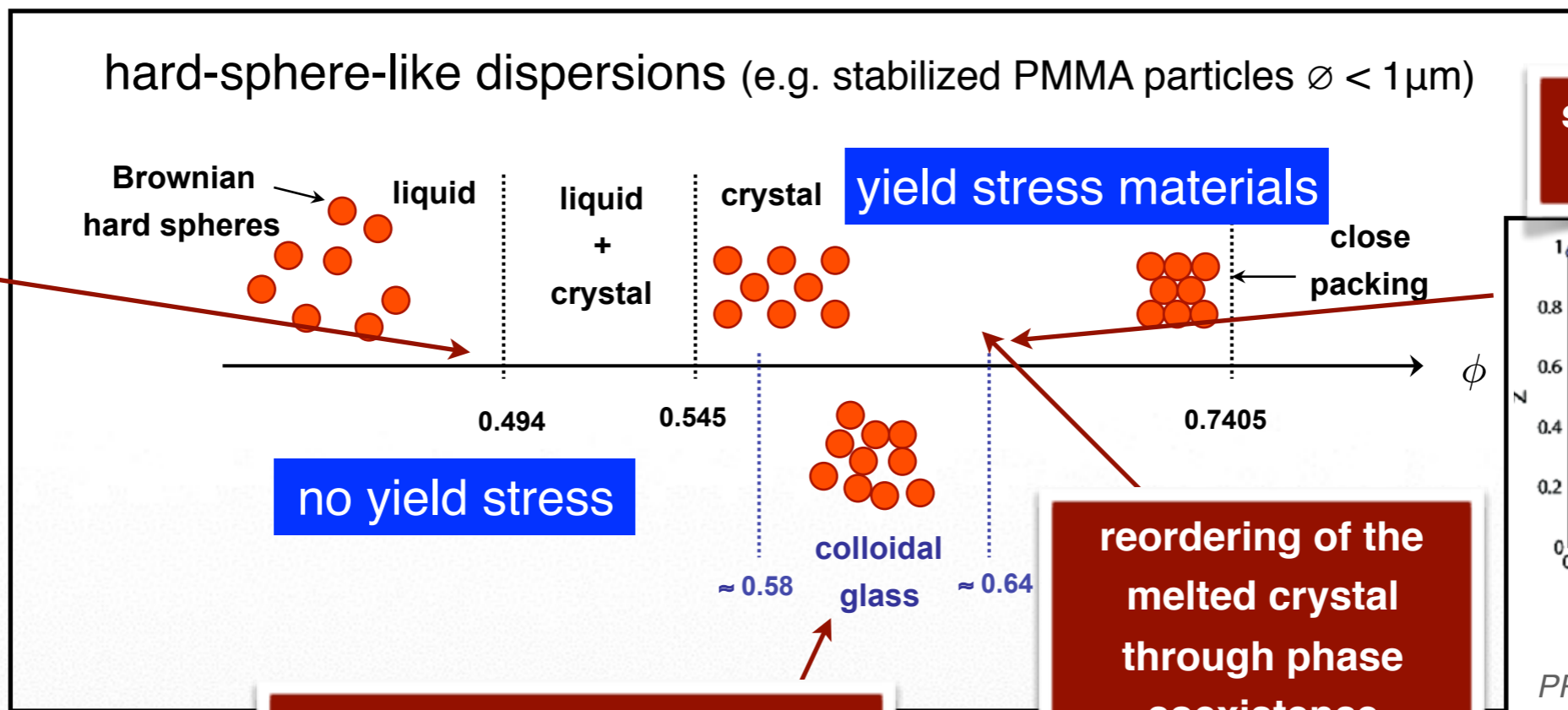
*Note 1:* Modification of definition in ref.<sup>[2]</sup>

There are three main types of dispersions:

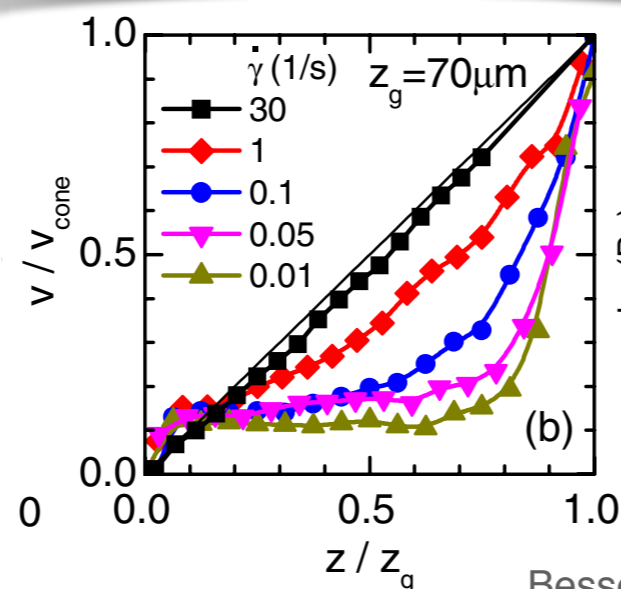
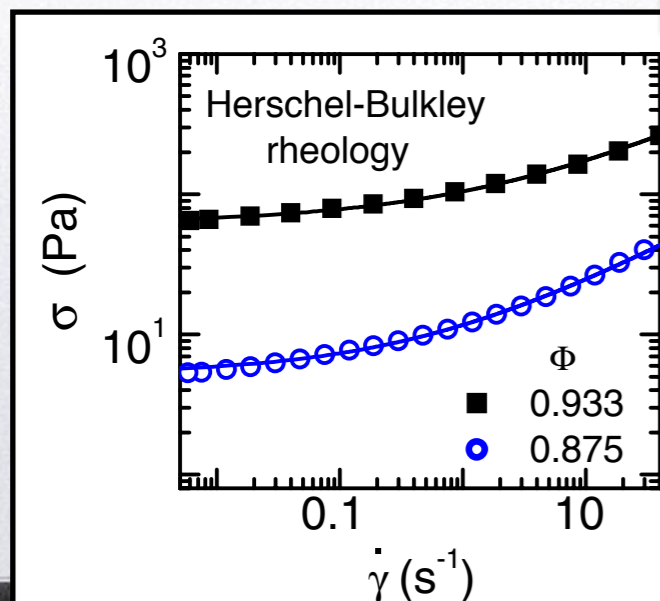
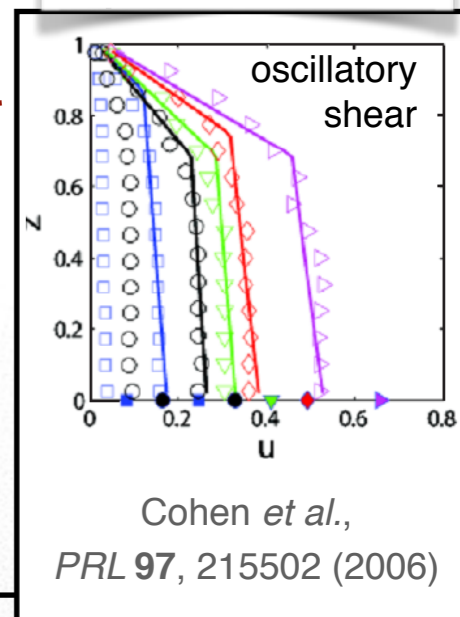
- Coarse dispersion (**suspension**)
- Colloid
- Solution



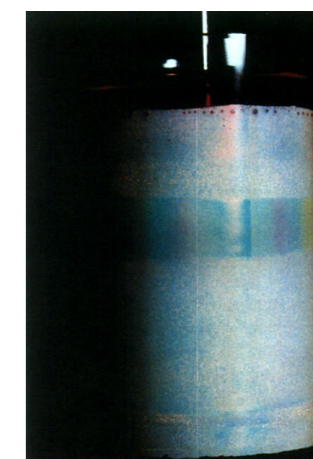
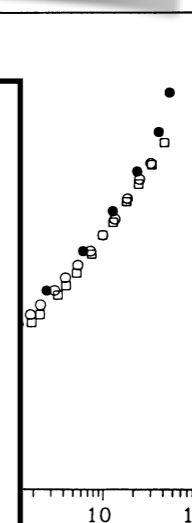
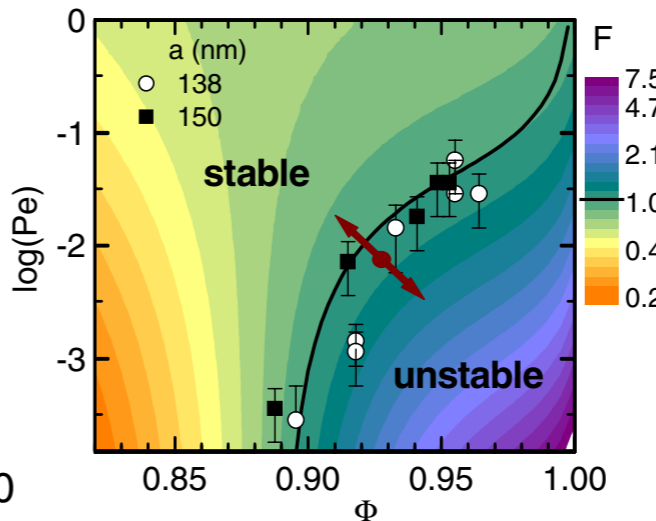
# The flow of dense colloidal "dispersions"



Ackerson & Pusey, *PRL* **61**, 1033-1036 (1988)



Besseling *et al.*, *PRL* **105**, 268301 (2010)



Chen *et al.*, *PRL* **69**, 688-691 (1992)

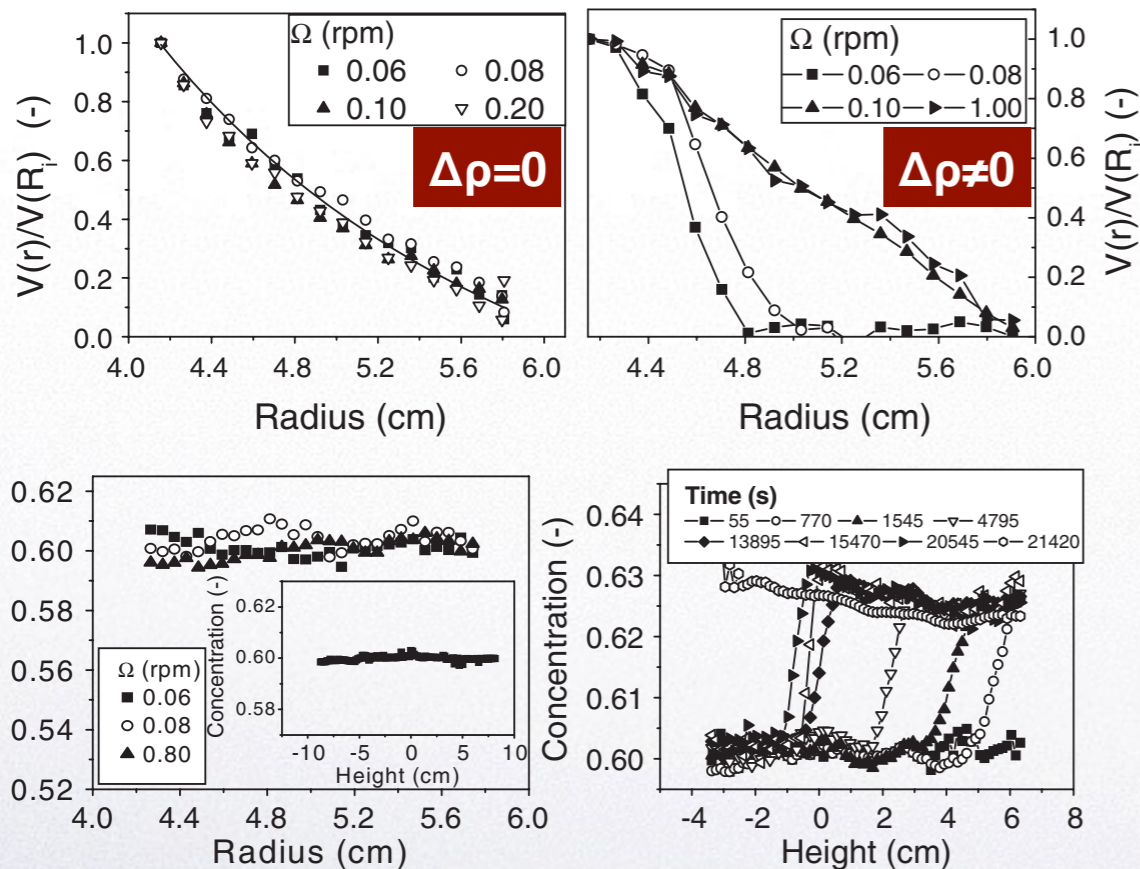


# What about dense non-Brownian “suspensions”?

no Brownian motion  
 ⇒ no yield stress

shear-thickening  
 is ubiquitous in dense suspensions

PS spheres  $\phi = 0.40$

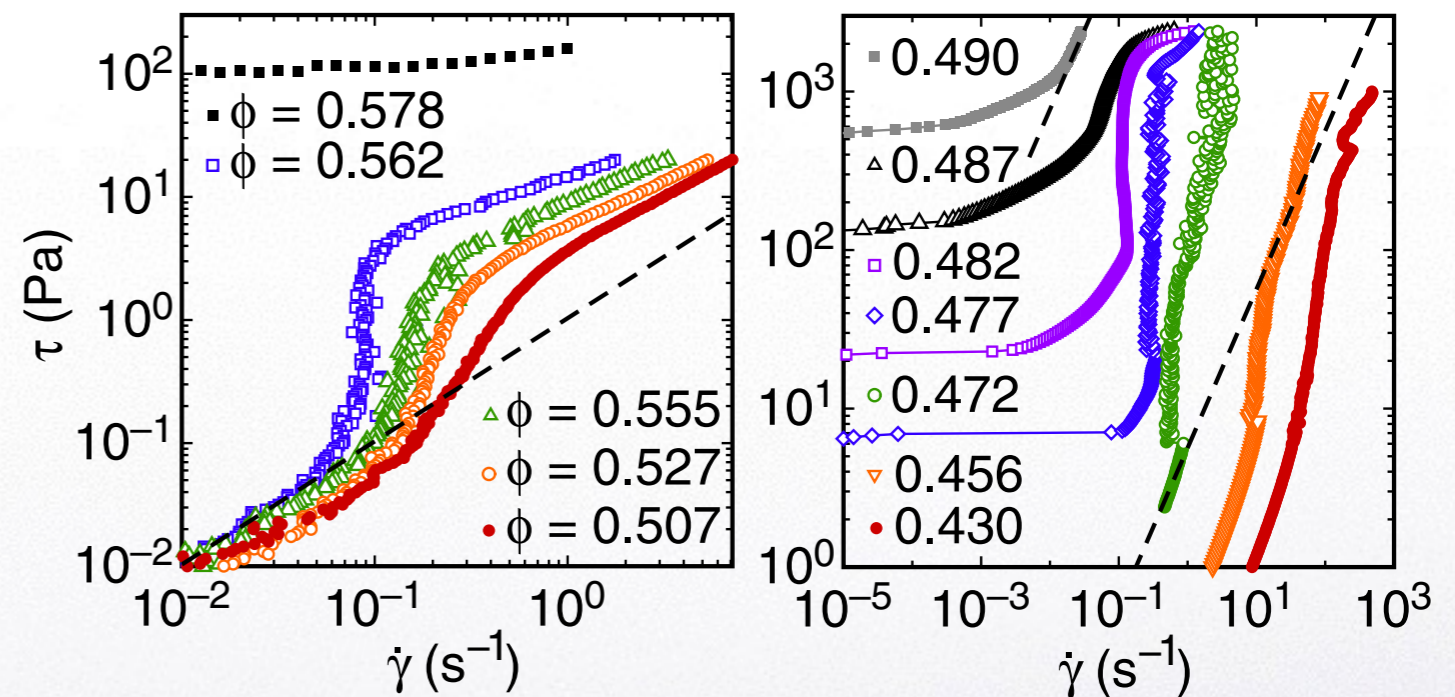


Fall *et al.*, *PRL* **103**, 178301 (2009)

yield stress due to sedimentation

glass spheres  $\phi = 0.578-0.562$

cornstarch



Brown & Jaeger, *PRL* **103**, 086001 (2009)

continuous transition vs discontinuous transition

see also Brown & Jaeger, *Rep. Prog. Phys.* **77**, 046602 (2014)

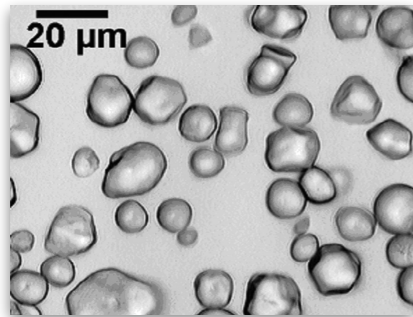
Denn *et al.* *Soft Matter* **14**, 170-184 (2018)



# Heterogeneous flows in shear-thickening

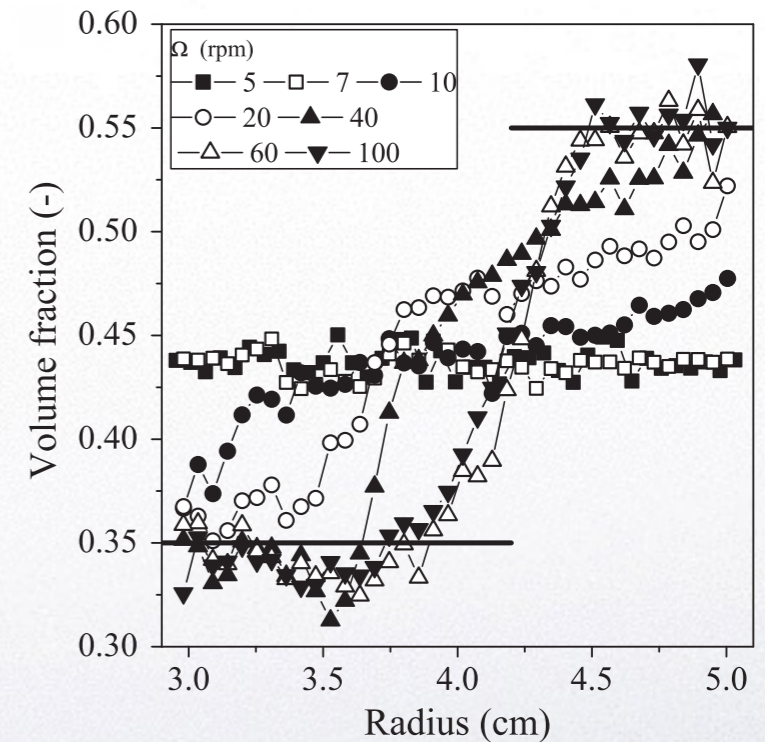
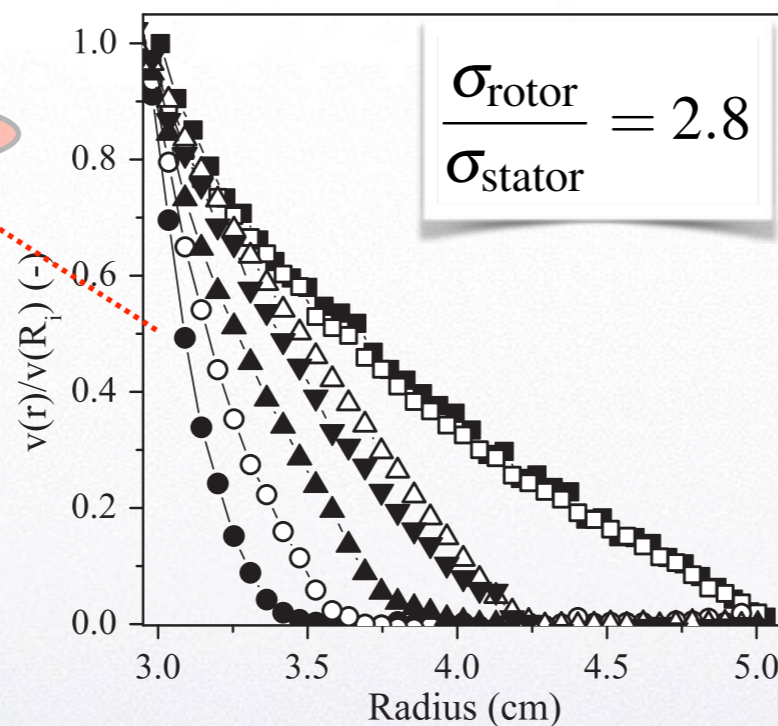
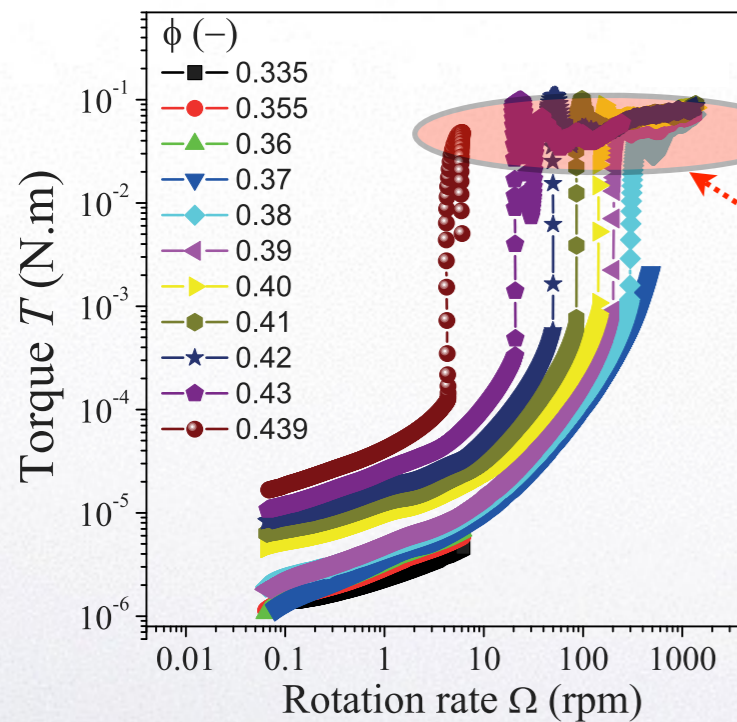


cornstarch



shear banding in DST  
associated with migration  
(in wide-gap Couette geometry)

Fall *et al.*, *PRL* 114, 098301 (2015)



⇒ is migration inherent to the flow of dense suspensions?

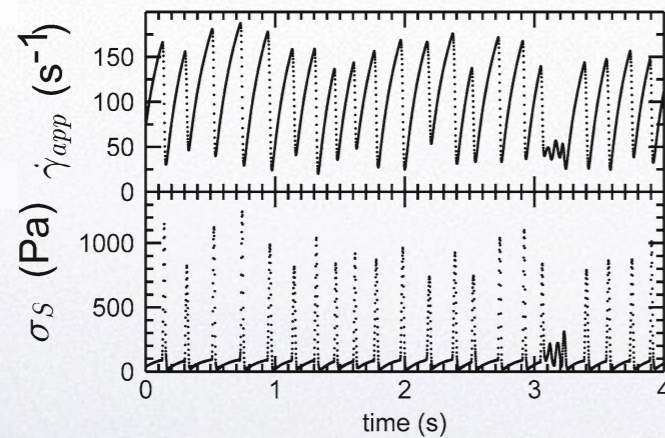
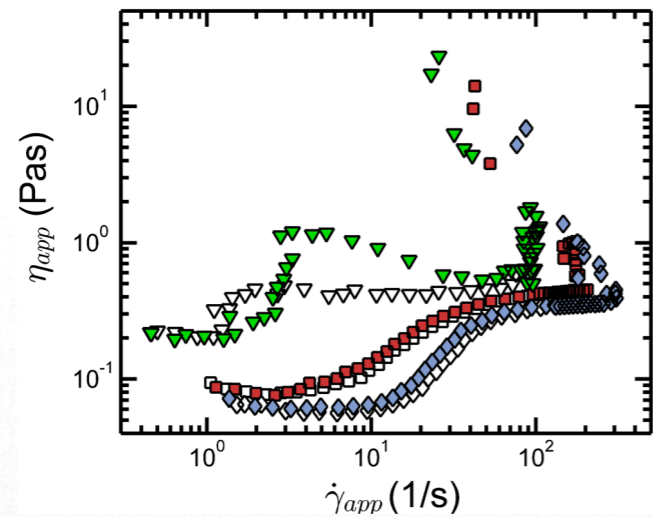
see talk by Guillaume Ovarlez  
on Monday



# Stick-slip-like oscillations in shear-thickening

PS particles  $\varnothing$  5.8  $\mu\text{m}$

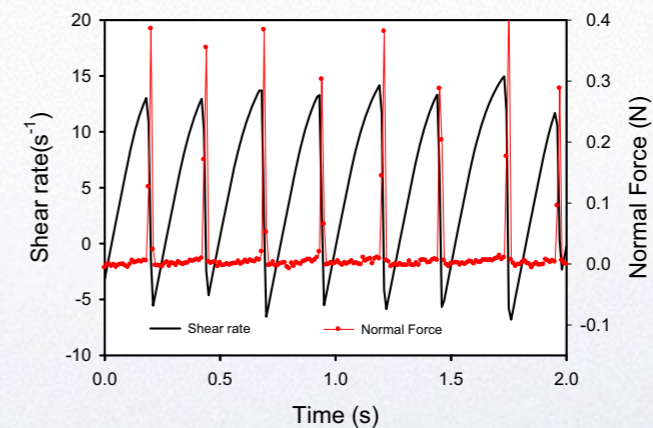
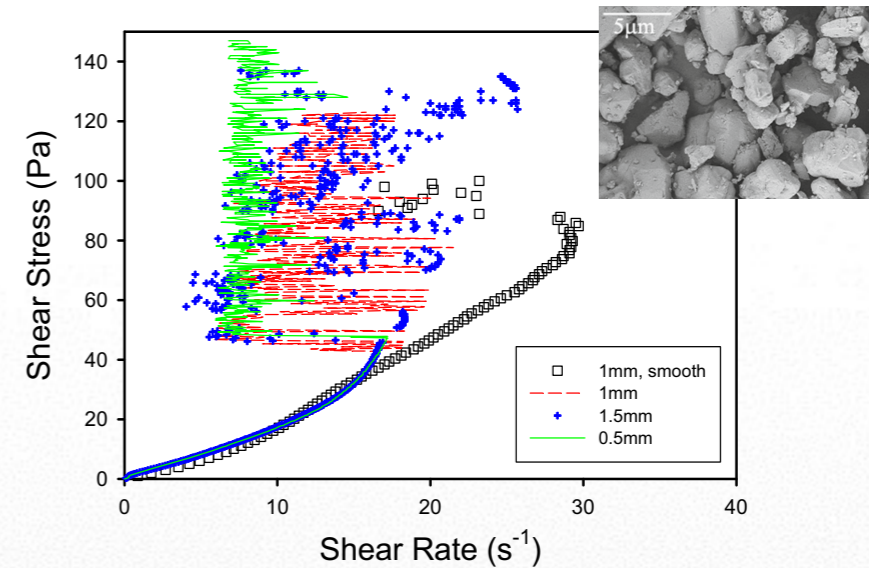
Larsen *et al.*, *Rheol. Acta* **53**, 333-347 (2014)



competition between dilatancy  
and wall slip through  
flow-concentration coupling

calcium carbonate  $\varnothing$  5.5  $\mu\text{m}$

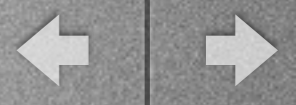
Bossis *et al.*, *Rheol. Acta* **56**, 415-430 (2017)



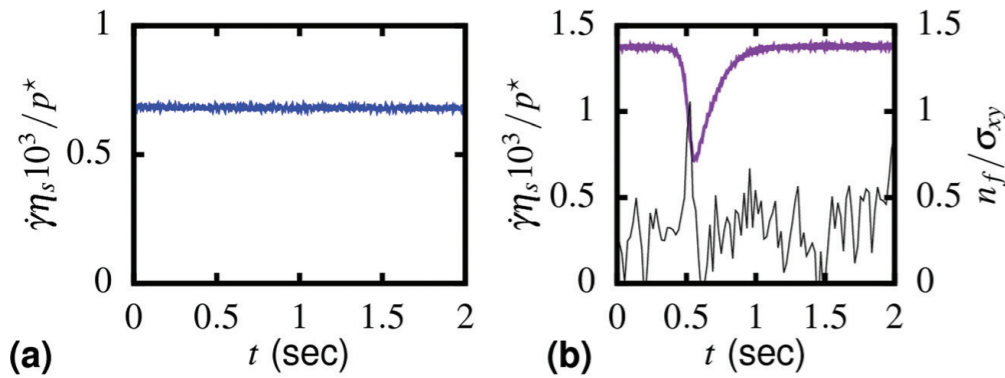
coupling between elasticity of  
the frictional particle network  
and instrument inertia



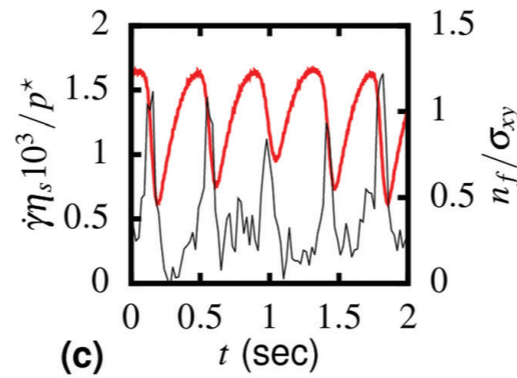
# Unstable dynamics during shear-thickening



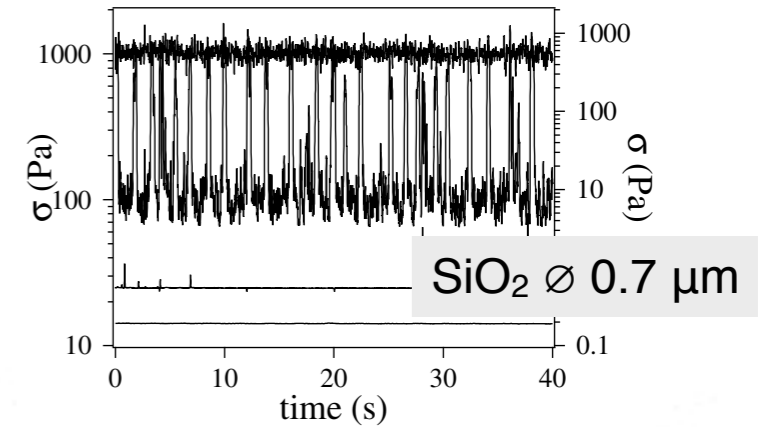
cornstarch



rheochaos?

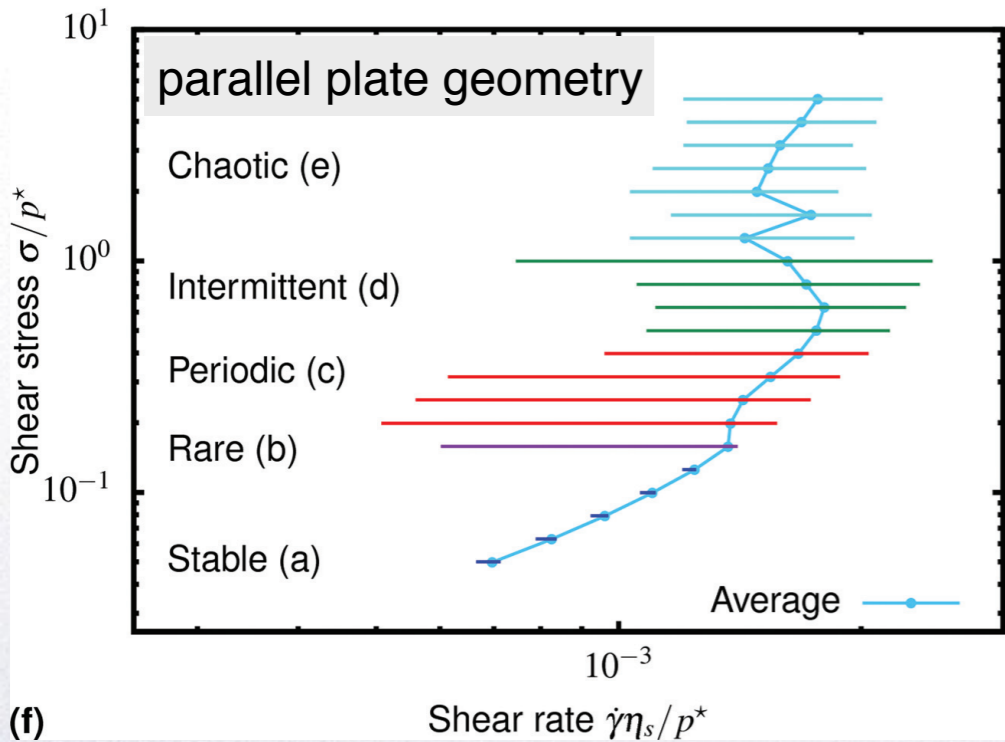


giant stress fluctuations

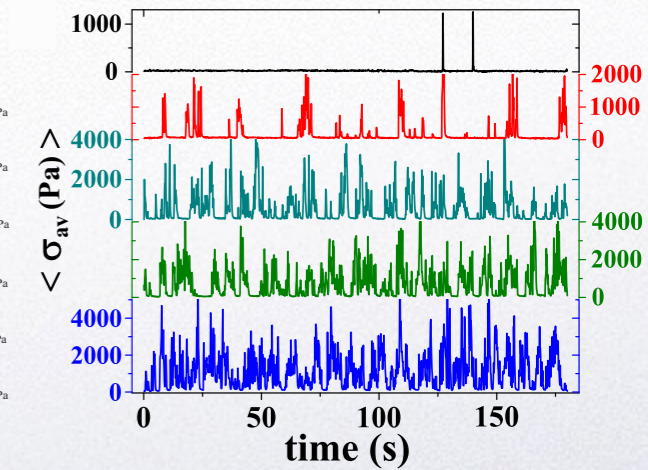
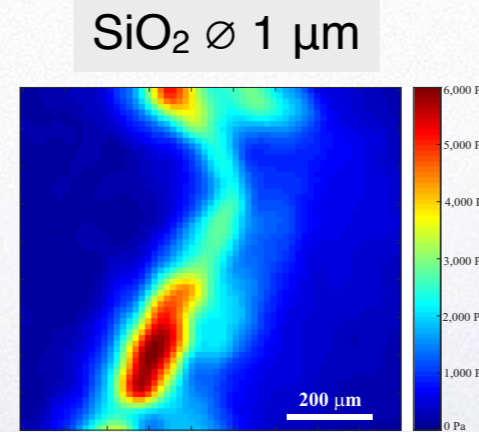
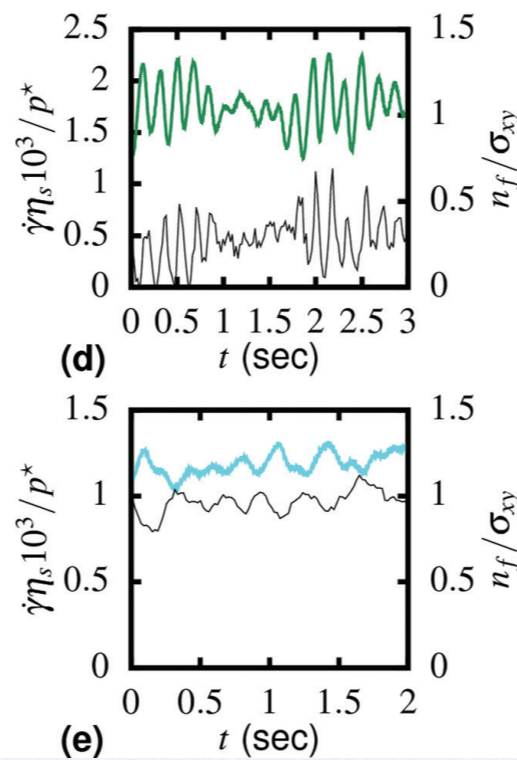


Lootens *et al.*, *PRL* **90**, 178301 (2003)

localized stress fluctuations



Hermes *et al.*, *J. Rheol.* **60**, 905-916 (2016)



Rathee *et al.*, *PNAS* **114**, 8740-8745 (2017)

$\Rightarrow$  is unsteadiness inherent to the flow of dense suspensions?

see my talk  
on Wednesday



# More questions about dense suspensions



⇒ do dense suspensions show vorticity banding?

so far, no experimental evidence for steady vorticity bands

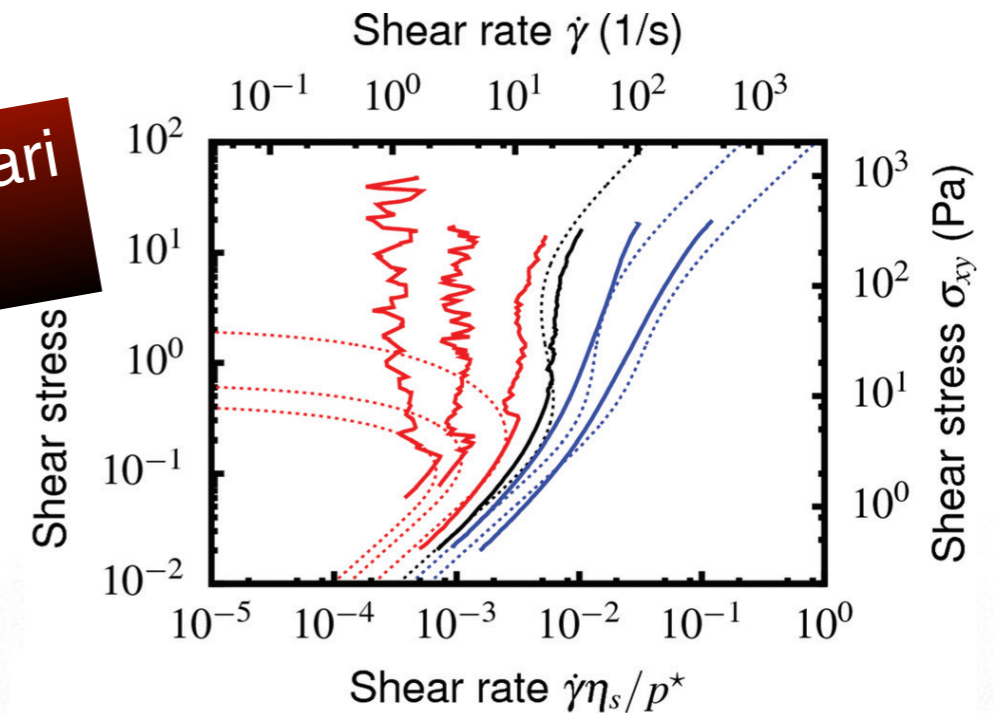
Pan *et al.*, *PRE* **92**, 032202 (2015)

see talk by Romain Mari on Tuesday

⇒ can “full jamming” be observed in experiments?

Cates *et al.*, *J. Phys.: Condens. Matter* **17**, S2517 (2005)

Wyart & Cates, *PRL* **112**, 098302 (2014)



⇒ back to colloids: role of attractive interactions? link with yield stress?

non-glassy hard-sphere colloids also show shear-thickening

Frith *et al.*, *J. Rheol.* **40**, 531-548 (1996)

but shear-thickening is lost when a yield stress builds up due to attraction

Gopalakrishnan & Zukoski *et al.*, *J. Rheol.* **48**, 1321-1344 (2004)

Pednekar *et al.*, *Soft Matter* **13**, 1773-1779 (2017)

⇒ role of particle-particle interactions and particle-surface interactions?

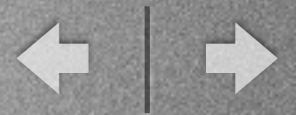
need for microscopic friction measurements

Clavaud *et al.*, *PNAS* **114**, 5147-5152 (2017)

Comtet *et al.*, *Nat. Comm.* **8**, 15633 (2017)



# Acknowledgements



Thomas Gibaud



Brice Saint-Michel



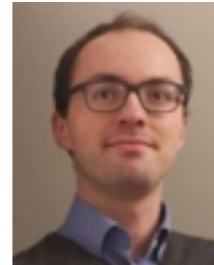
Marc-Antoine Fardin



Thibaut Divoux



Christophe Perge



Thomas Gallot



Mathieu Leocmach

Lydiane Bécu  
(U. Metz)



Jean-Baptiste Salmon  
(Solvay-CNRS)



Annie Colin  
(ESPCI)



David Tamarit  
(res. eng. 2009)



Bernard Pouligny  
(CRPP)

Sandra Lerouge  
(U. Paris 7)

Catherine Barentin  
(iLM, U. Lyon 1)