Shear Thickening in Dense Anisotropic Colloids by Tunable Frictional Contacts

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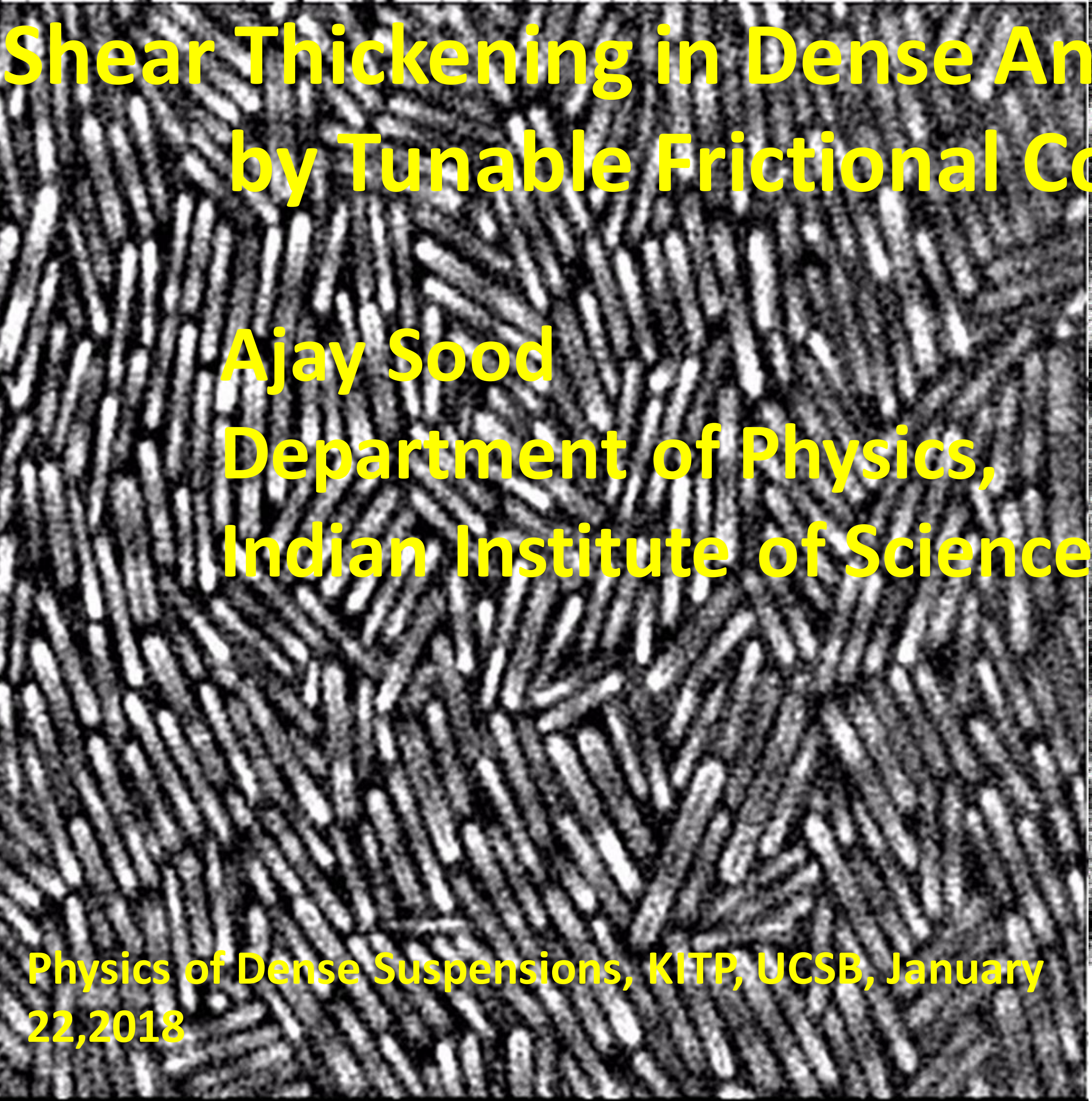
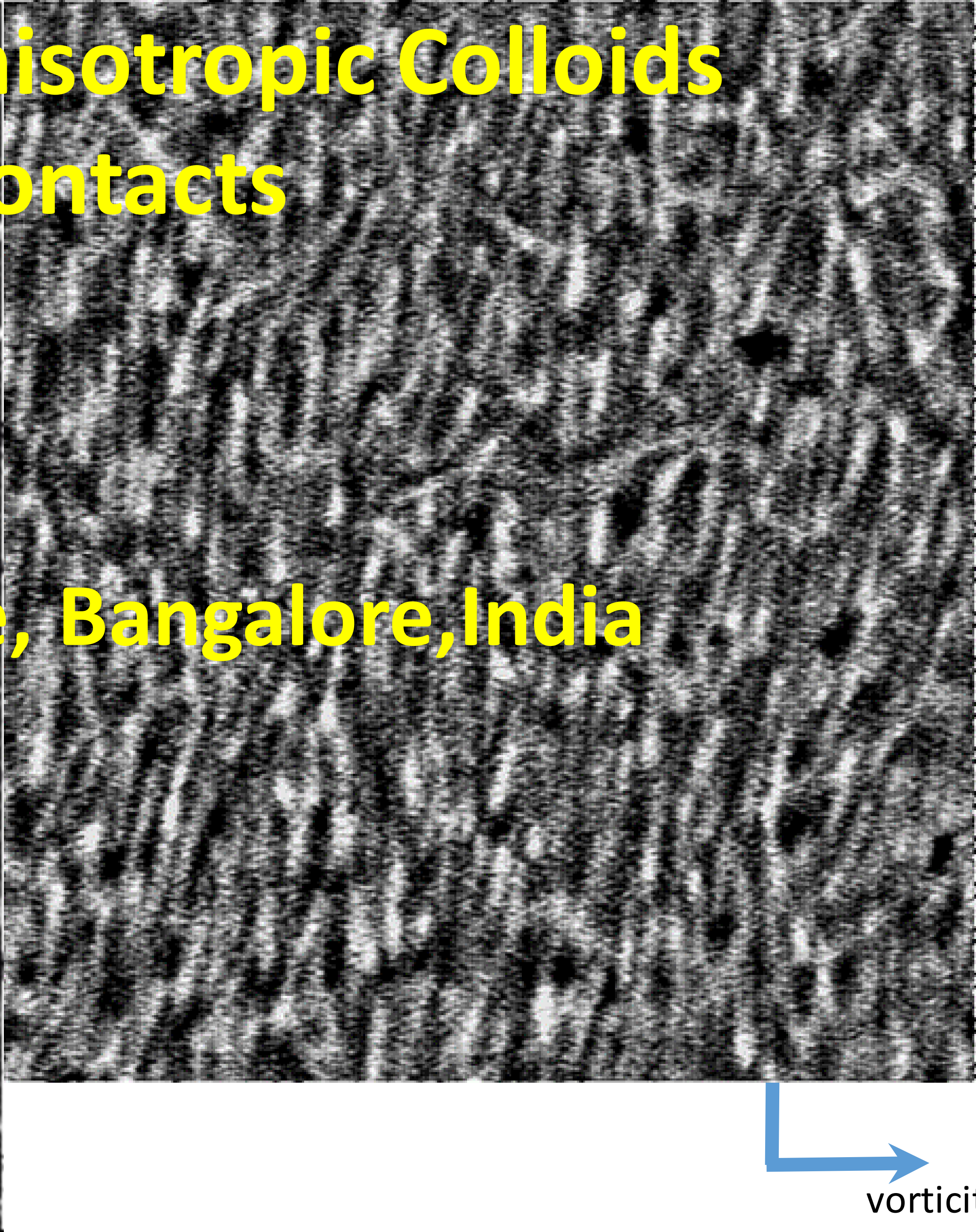
Department of Physics,
Indian Institute of Science, Bangalore,India

Physics of Dense Suspensions, KITP, UCSB, January 22,2018





Prof Rajesh Ganapathy
JNCASR, Bangalore,India

Srishti Arora

Dr Vikram Rathee

Now at
Georgetown Washington Univ

Plan of my talk ….

1. Continuous and Discontinuous Shear Thickening in *Colloidal Silica Rods*

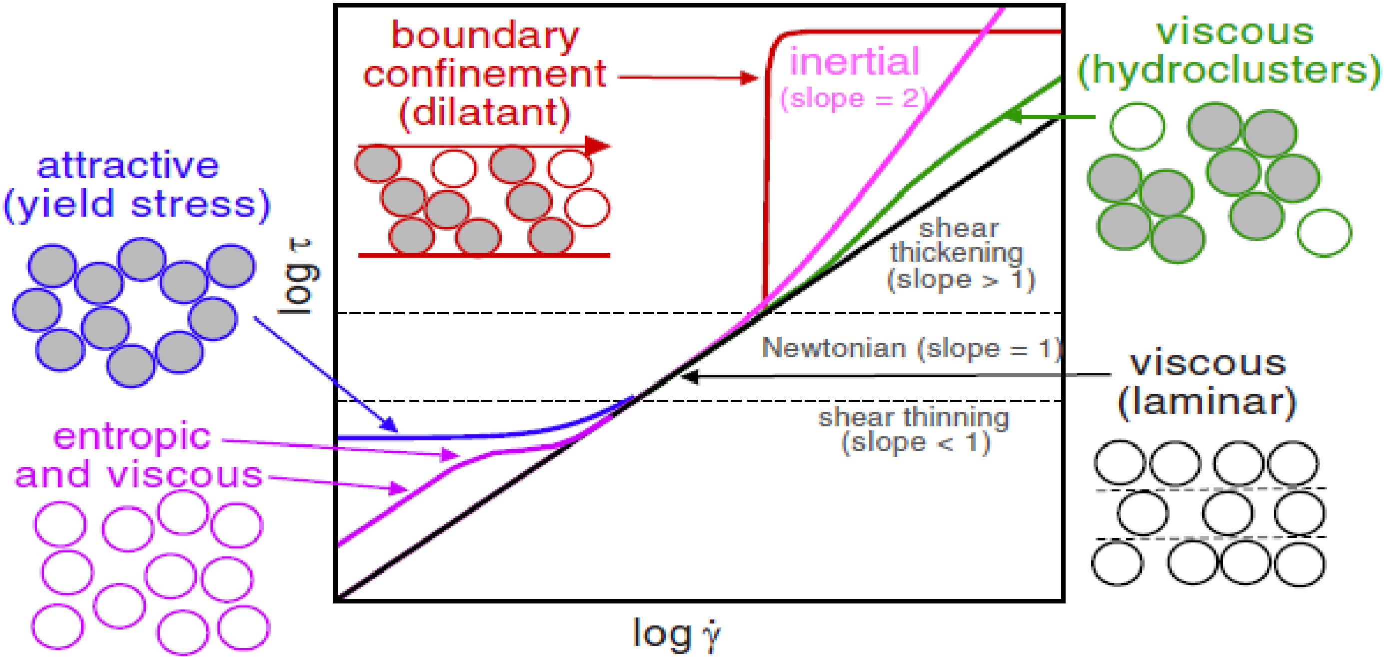
2. Tuning frictional coefficient between silica rods by Temperature tunable polymer brushes.

3. Role of confinement and waiting time at each stress to get shear jamming.

4. Revisit shear thickening in CNT suspensions showing unusual ST at 0.5 to 10 Wt %.
   Rheology of Fractal objects .; Fluctuations of stress at fixed shear rate and vice versa
   Possibly a Shear Jammed state.

Flow behavior of dense suspensions show

- Shear thinning
- Shear thickening
  - Continuous shear thickening (CST)
  - Discontinuous shear thickening (DST)
- Shear jamming



Brown E and Jaeger H M 2011 Through thick and thin *Science* 333 1230

E Brown and H Jaeger , Reports on Prog in Phys. (2014)

Many excellent Reviews in last few years covering this area:

- H A Barnes , J Rheology (1989)
- Wagner and Brady , Physics Today (1990)
- Mewis and Wagner , Colloidal Suspension Rheology (2012)
- E Brown and H Jaeger , RMP (2014)
- Morton Denn , Jeff Morris and D Bonn , Soft Matter (2018)

Shear Thickening

- Continuous Shear Thickening at intermediate concentrations.
- DST at large solid concentrations.
- ST is seen for both Brownian and Non –Brownian suspensions.

Three mechanisms

1. Hydroclustering: Particles are pushed into clusters under shear leading to increased lubrication drag forces between particles
2. Order-disorder transition
3. Dilatency: Volume of particulate packing increases under shear pushing against the boundaries and hence results in additional stresses from solid-solid friction.

DST: Between τ_{min} and τ_{max} below critical volume fraction $\phi_c(\mu)$.

$\boldsymbol{\phi} > \boldsymbol{\phi_c}$: Jamming transition. System has a yield stress
$\phi_c \sim$ 0.64 for RCP of spherical particles
$\sim$ 0.55 for RLP of spherical particles

DST: Generally believed to be associated with particle-particle frictional contacts. Hydrodynamic clustering gives CST.

$\eta \sim \tau^{\beta}$: β < 1 for CST
β = 1 for DST

Normal stress Σ_{ij}

i = 1: flow ($\boldsymbol{v}$)

i = 2: gradient ($\nabla\boldsymbol{v}$)

i = 3: vorticity ($\boldsymbol{v} \times \boldsymbol{\nabla}\boldsymbol{v}$)

$$N_1 = \Sigma_{11} - \Sigma_{22}$$
$$N_2 = \Sigma_{22} - \Sigma_{33}$$

Cone plate geometry (CP): N_1

Parallel plate geometry (PP): $N_1 - N_2$

$N_1 < 0$: Hydrodynamic effects are dominant

$N_1 > 0$: Frictional contacts are dominant

PHYSICAL REVIEW E **84**, 031408 (2011)

Shear thickening and jamming in densely packed suspensions of different particle shapes

Eric Brown,[1,*] Hanjun Zhang,[2,†] Nicole A. Forman,[2,3] Benjamin W. Maynor,[3] Douglas E. Betts,[2]
Joseph M. DeSimone,[2,3] and Heinrich M. Jaeger[1]

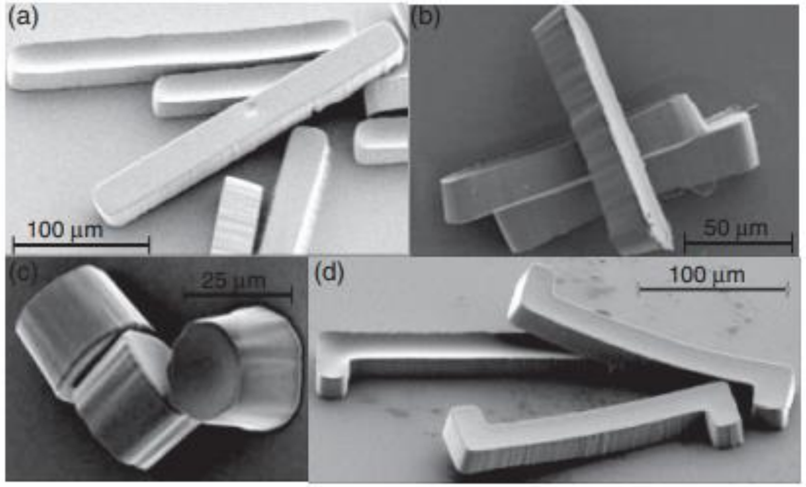


FIG. 1. Scanning electron microscope images of dry PEG particles. (a) Aspect ratio $\Gamma = 9$ rods. (b) $\Gamma = 6$ rods. (c) $\Gamma = 1$ rods. (d) $\Gamma = 9$ hooked rods.

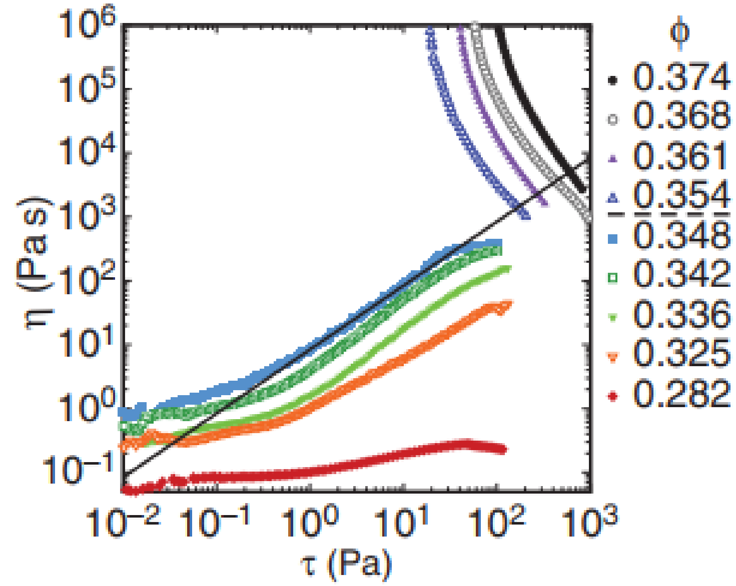
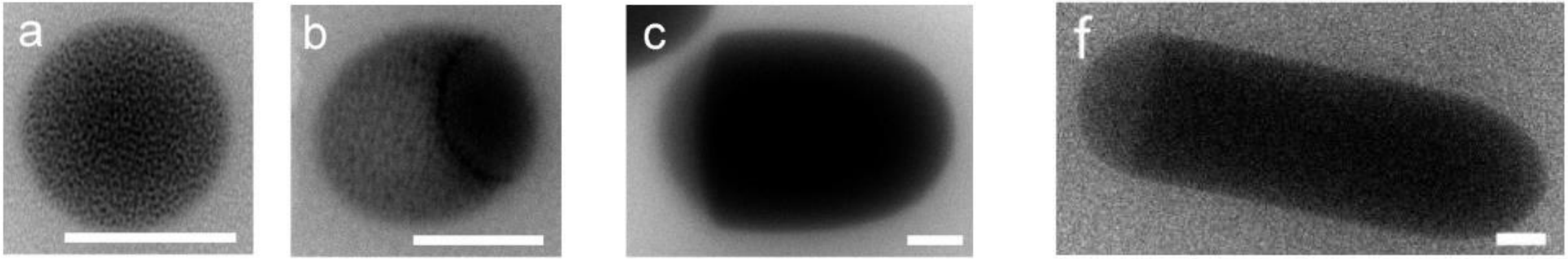


FIG. 2. (Color online) Viscosity vs shear stress for rods of aspect atio $\Gamma = 9$. Packing fractions ϕ are decreasing from top to bottom. he solid line has a slope of 1 corresponding to a constant shear rate. he dashed line in the key indicates the critical packing fraction ϕ_c bove which the suspension is jammed with a large yield stress, and elow which the suspension exhibits shear thickening.

Synthesis of Anisotropic Silica Colloids



Scale bar 100nm
Kuijk etal JACS 133, 2346-2349 (2011).

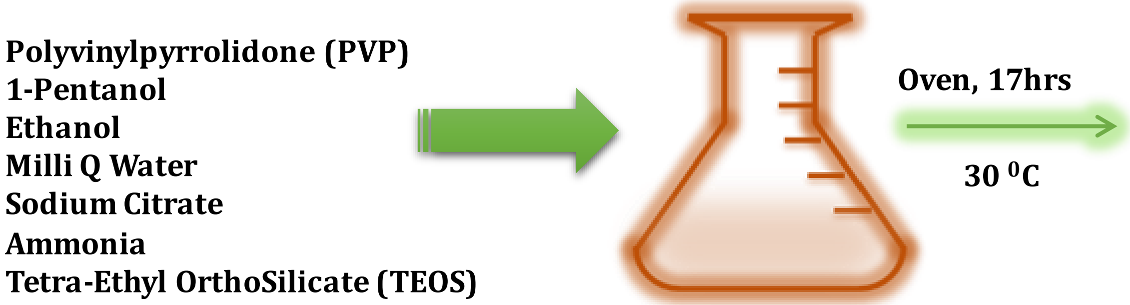
Droplet formation:

Water in pentanol

Stabilized by PVP and sodium citrate

This decides the diameter of rods

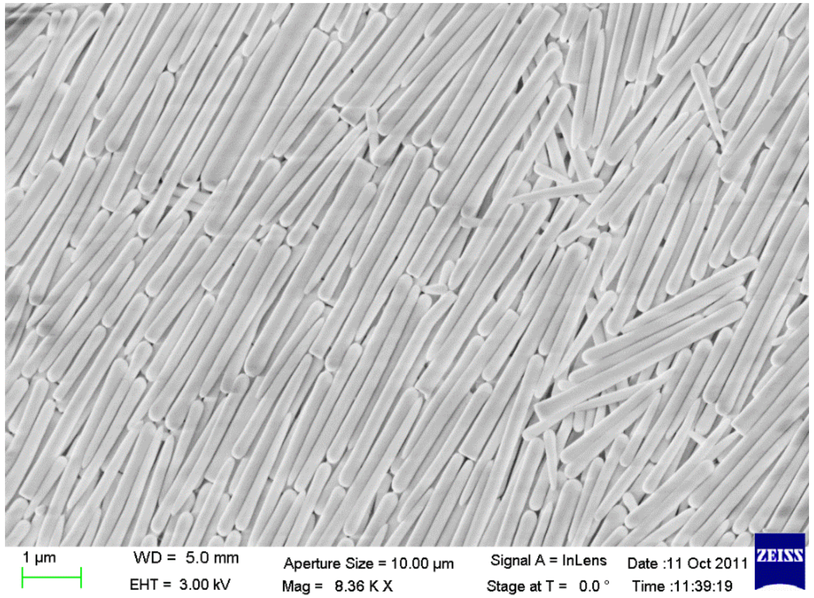
Hydrolyzed TEOS is hydrophilic
Thus goes to water emulsion droplet
silica nucleus is formed at surface
and rods grows



Polyvinylpyrrolidone (PVP)
1-Pentanol
Ethanol
Milli Q Water
Sodium Citrate
Ammonia
Tetra-Ethyl OrthoSilicate (TEOS)

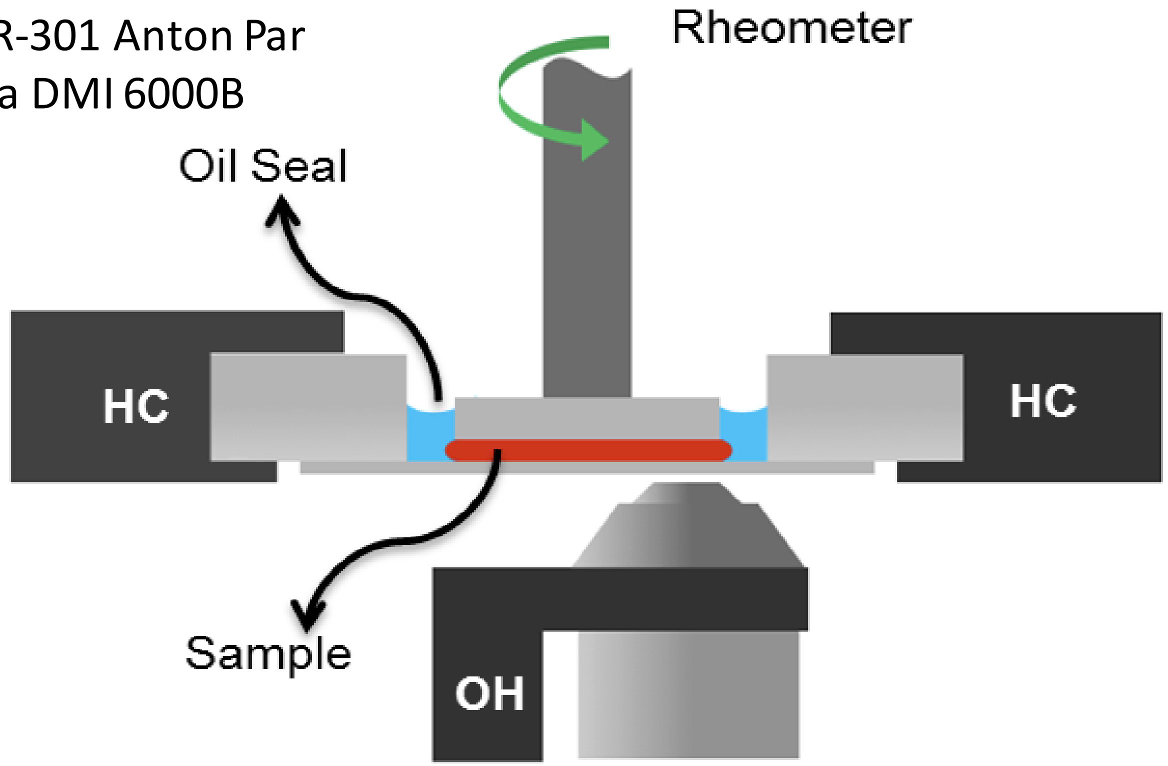
Oven, 17hrs

30 ^{0}C



Confocal Rheology at JNCASR, Bangalore in Prof Rajesh Ganapathy's group

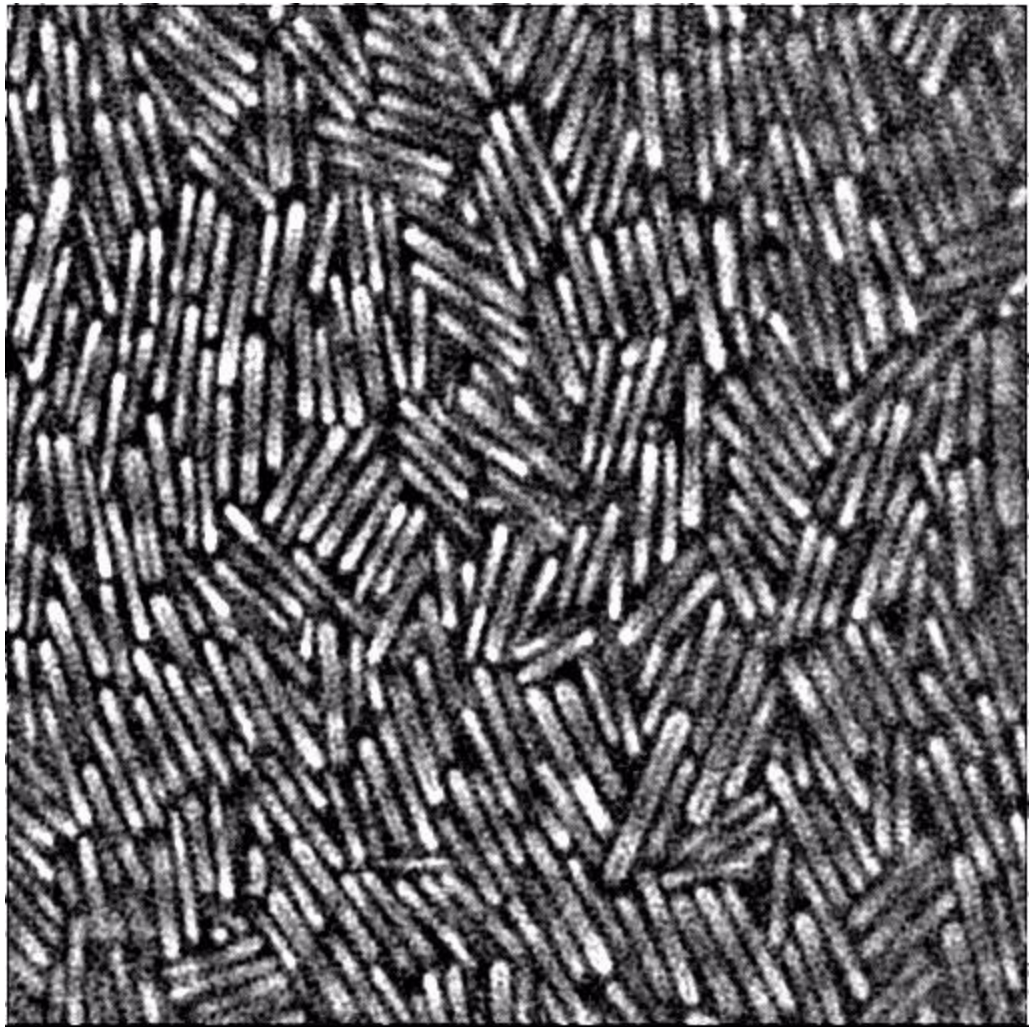
MCR-301 Anton Par
Leica DMI 6000B



HC: Heating/Cooling Coils
OH: Objective Heater

Length ~ 4 microns
Diameter ~ 500 nm
Polydispersity < 10 %

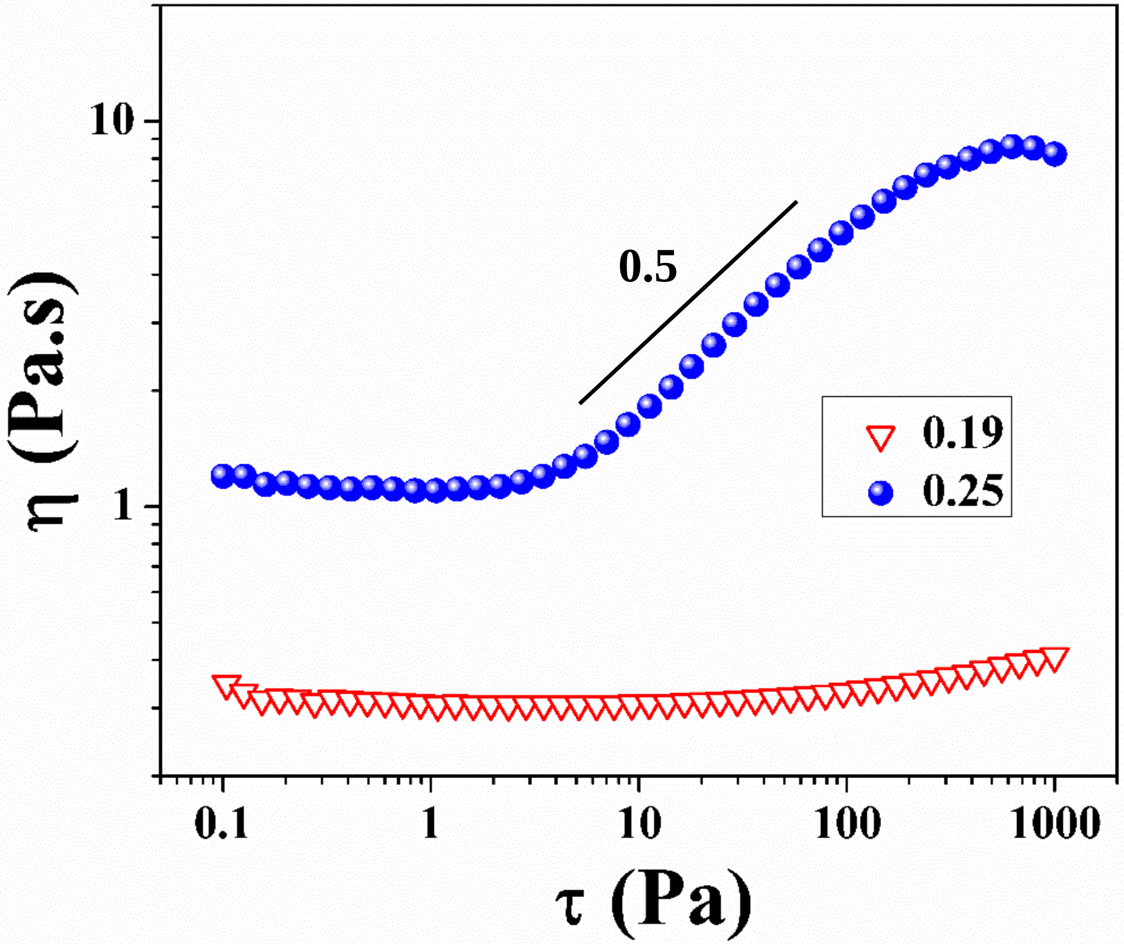
Confocal Laser Scanning Microscopy (CLSM) Images

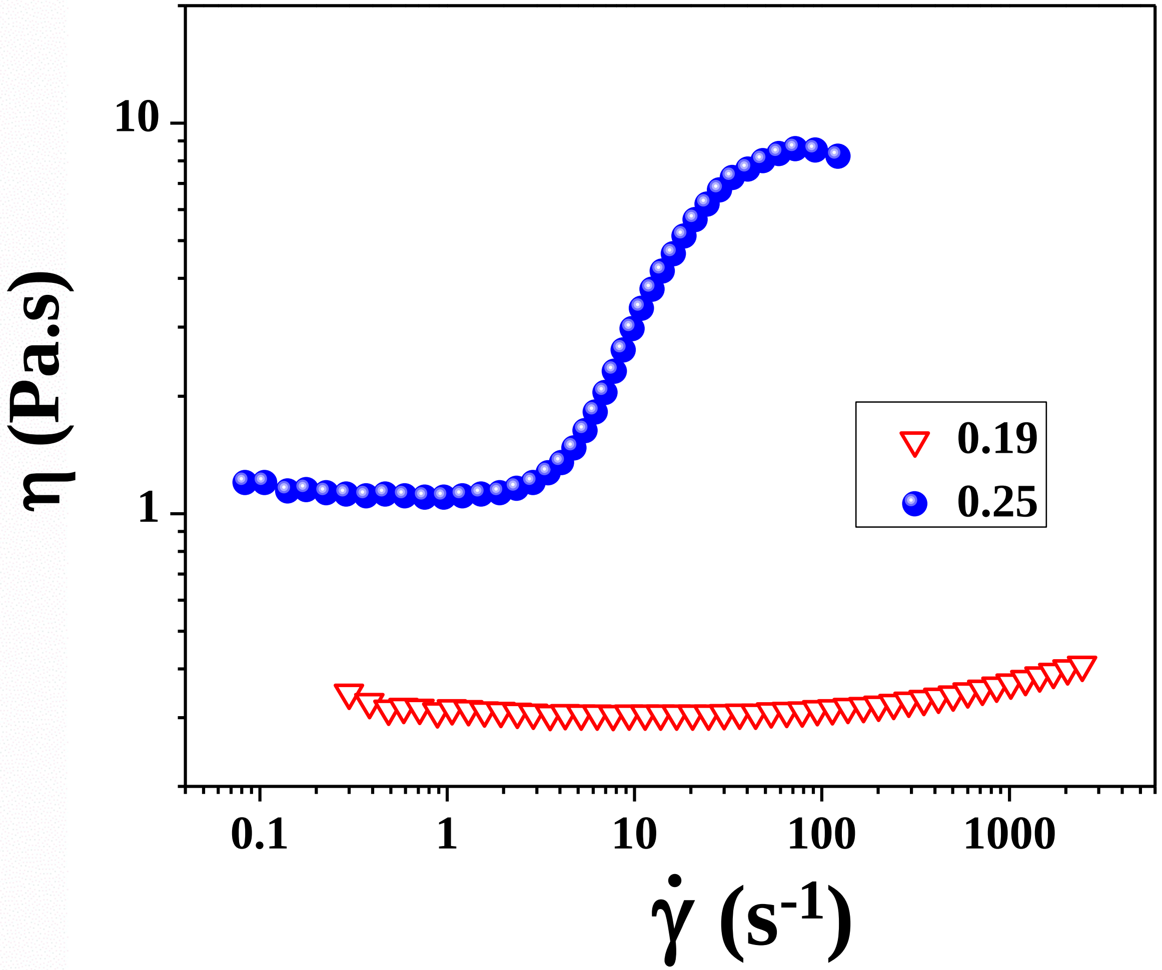


Plain silica rods

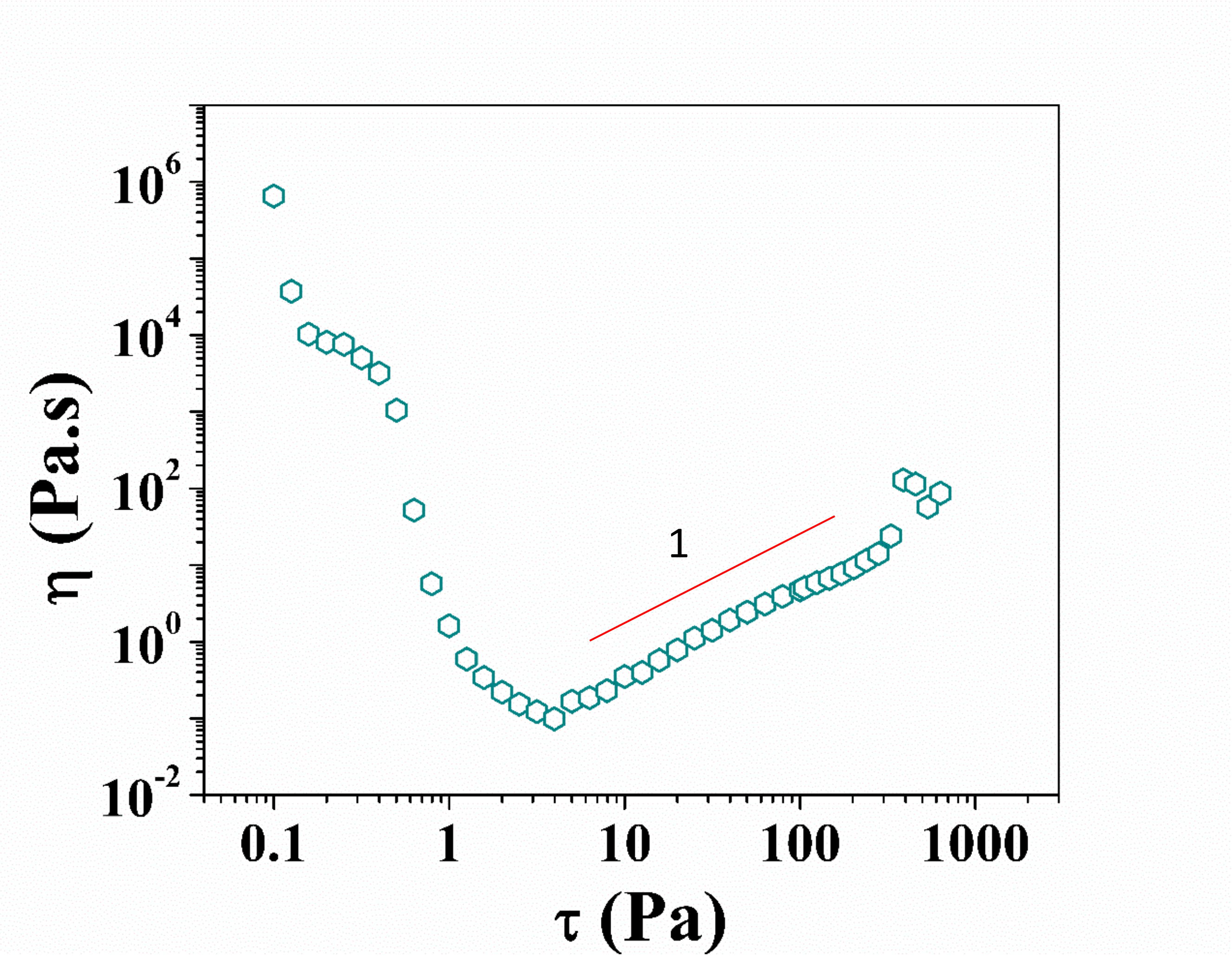
Continuous shear thickening, $\phi = 0.25$ CP

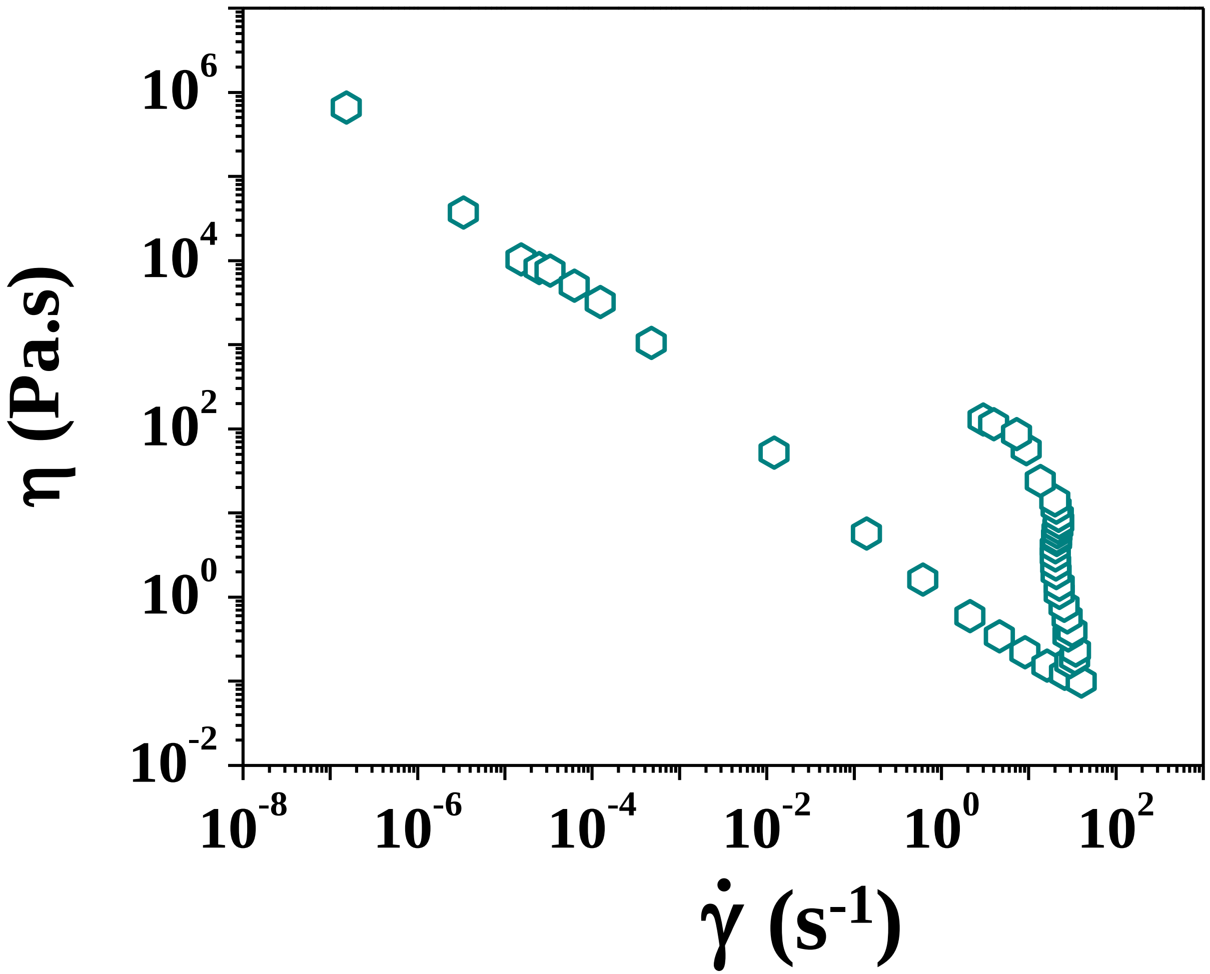
$\eta \sim \tau^{\beta}$



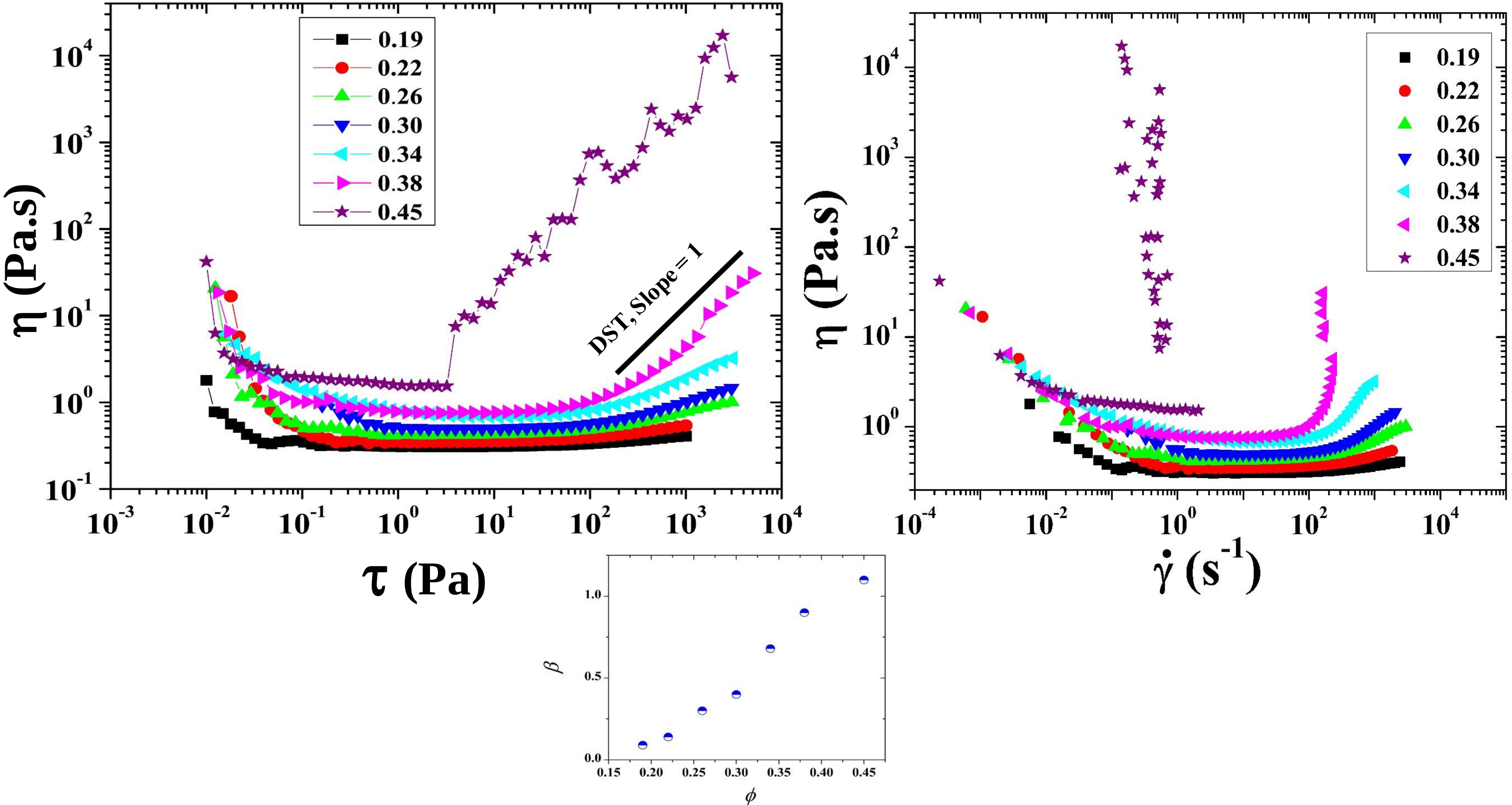


Discontinuous shear thickening: ϕ=0.4 in CP





Viscosity vs Shear stress and shear rate : T= 25 ^{0}C in CP

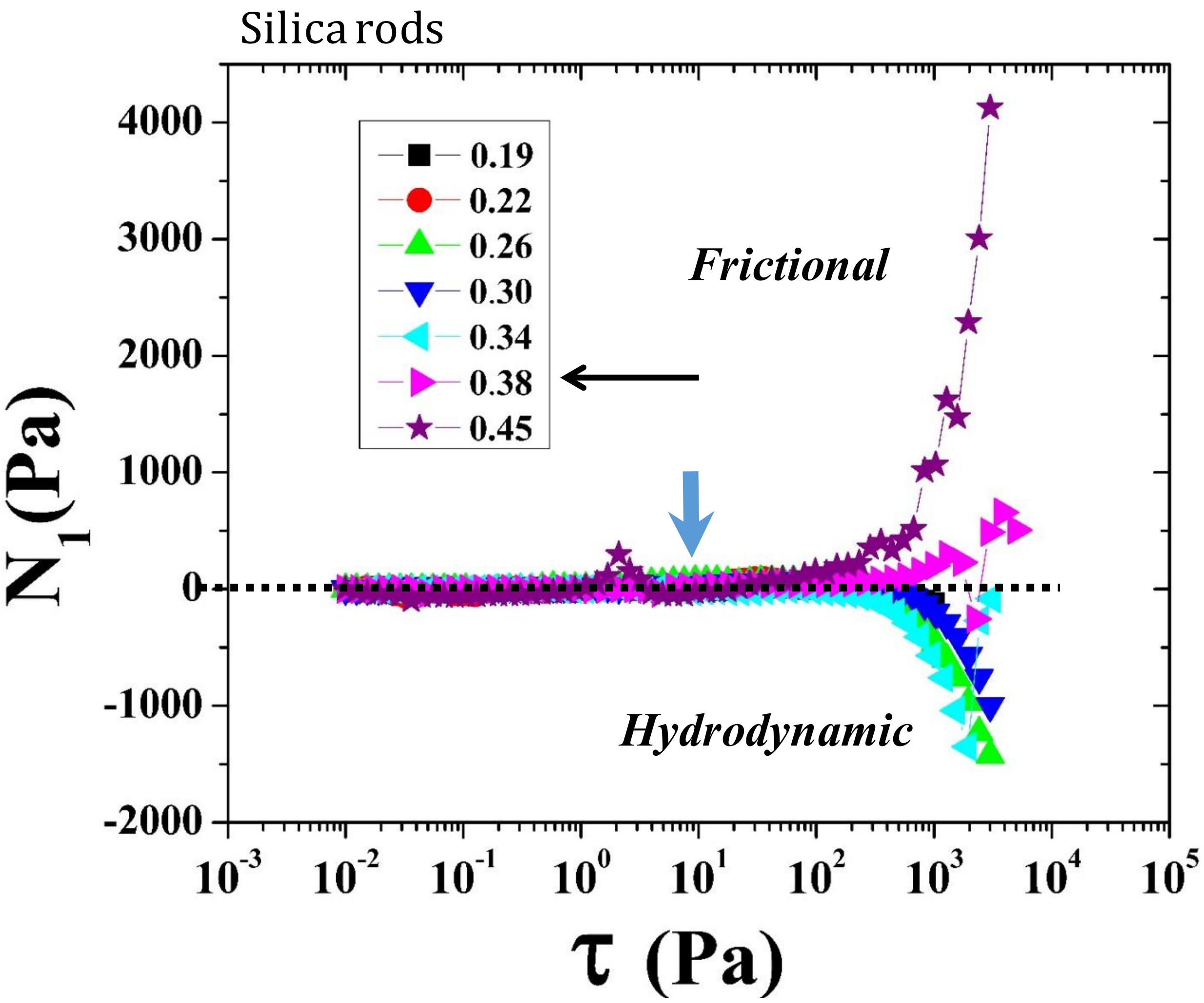


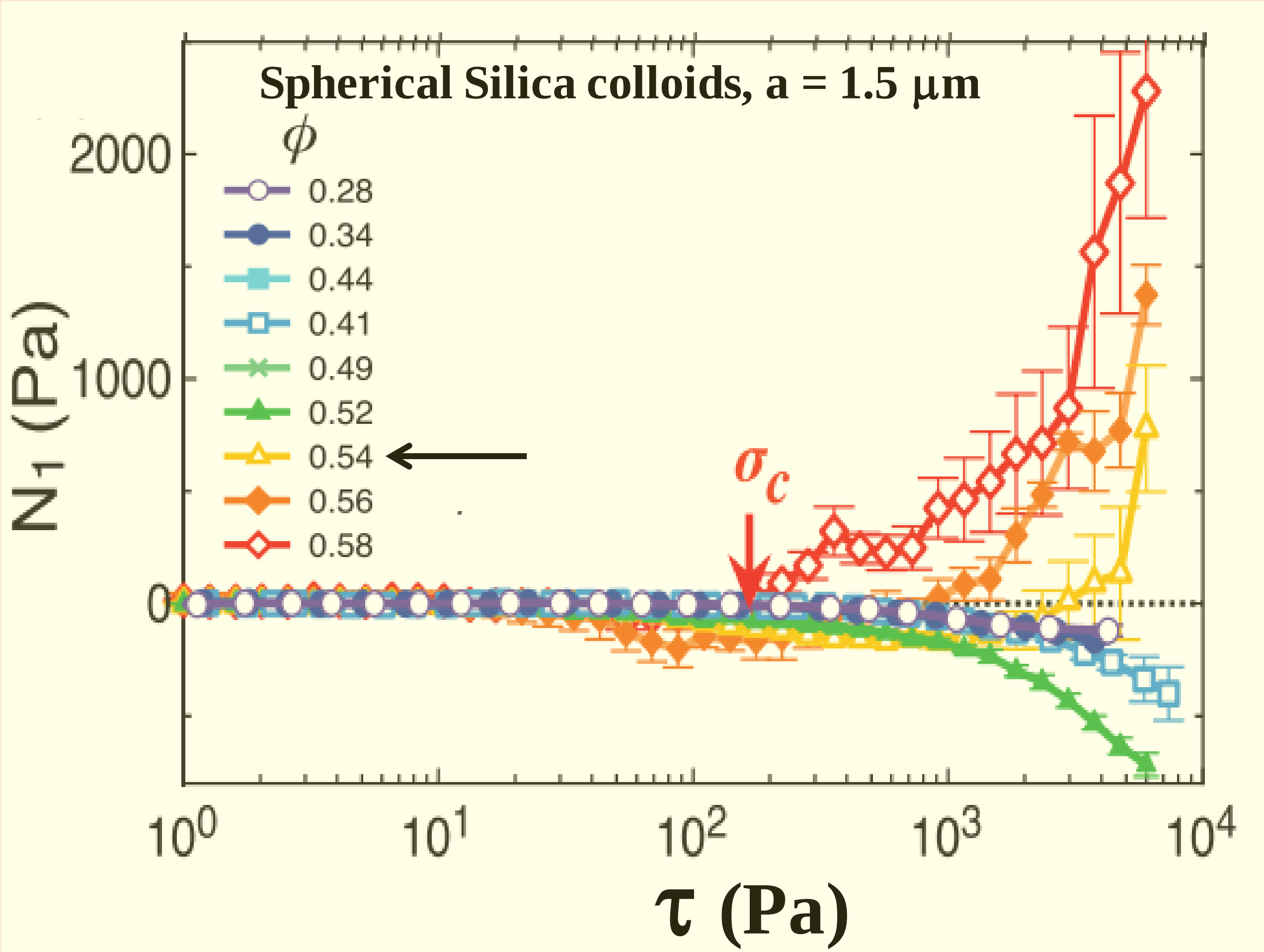
Normal Stress :Contact friction or hydrodynamic

First normal stress difference $N_1 = \Sigma_{11} - \Sigma_{22}$

$N_1 < 0$, Hydrodynamic Forces

$N_1 > 0$, Frictional contacts





J. Royer et al. Phys. Rev. Lett. 116, 188301 (2016)
N. Lin et al. Phys. Rev. Lett. 115, 228304 (2015)

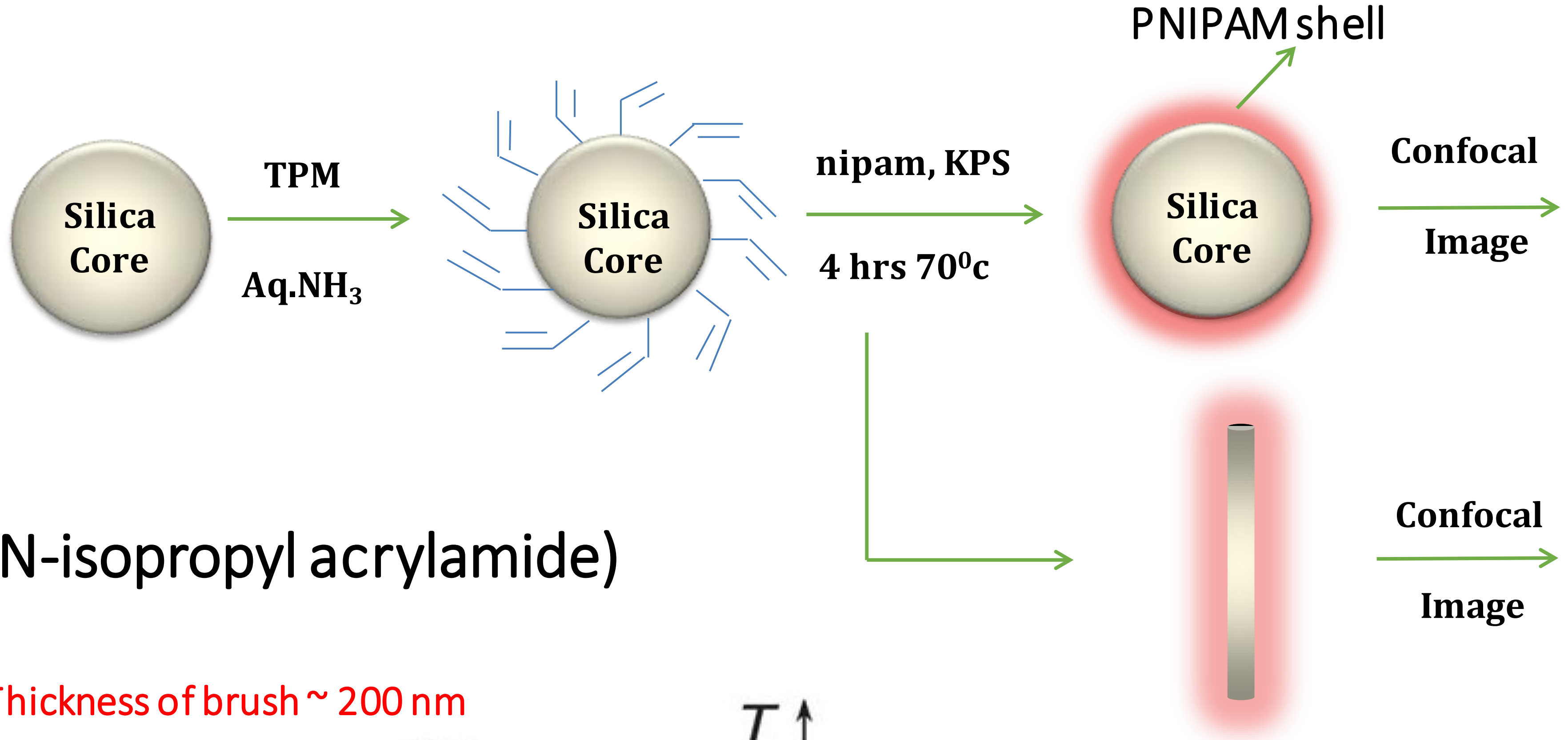
Colloidal rods shear thickened at lower concentrations in comparison to spheres.

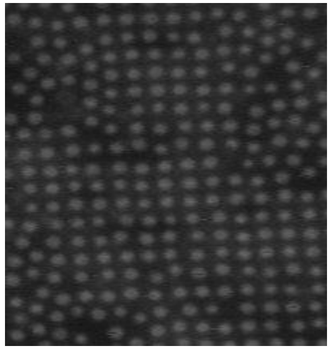
N_1 behaves similar in spheres and rods showing that friction plays a dominating role in ST

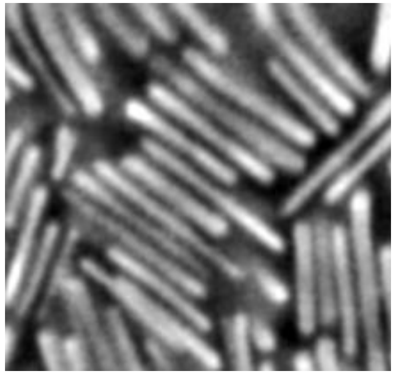
Is it possible to control friction between the colloids?

Answer: Yes.

Tailoring surface : Core-Shell colloids

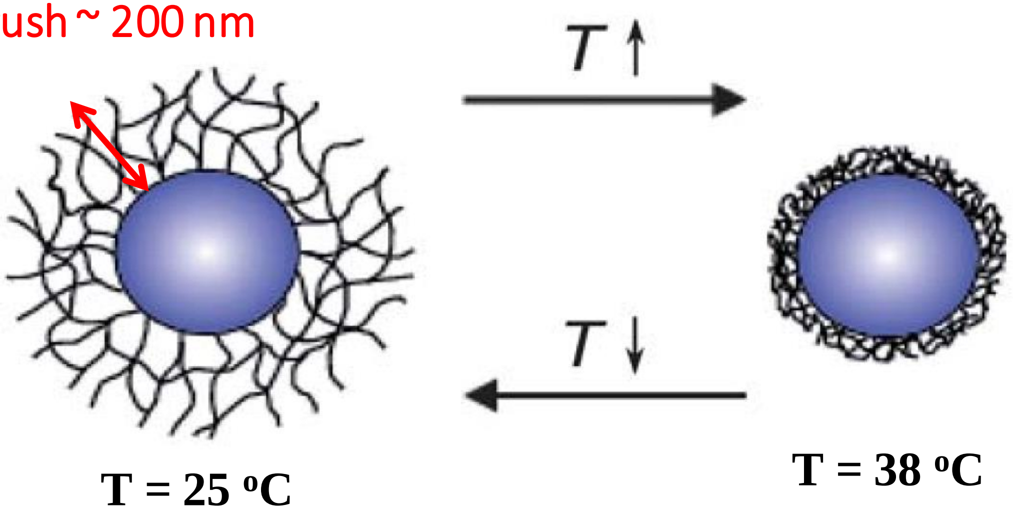




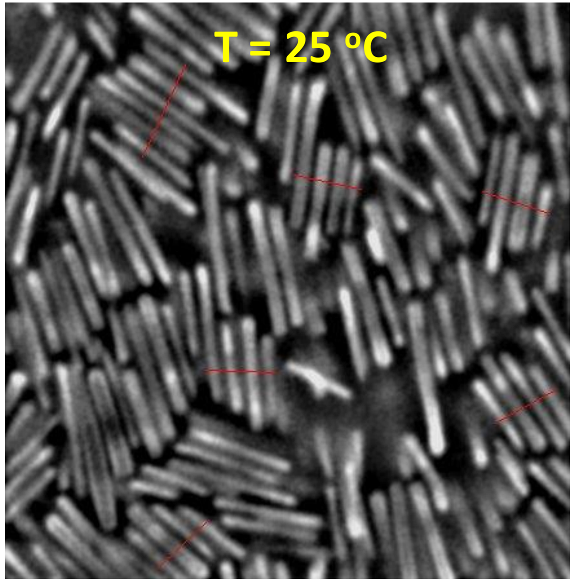


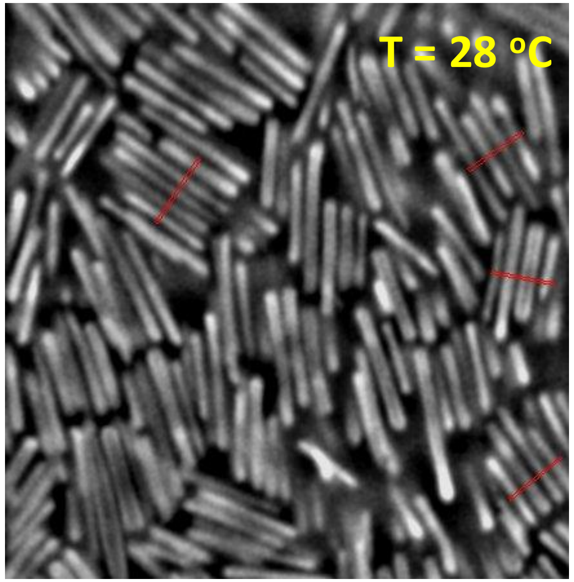
Poly(N-isopropyl acrylamide)

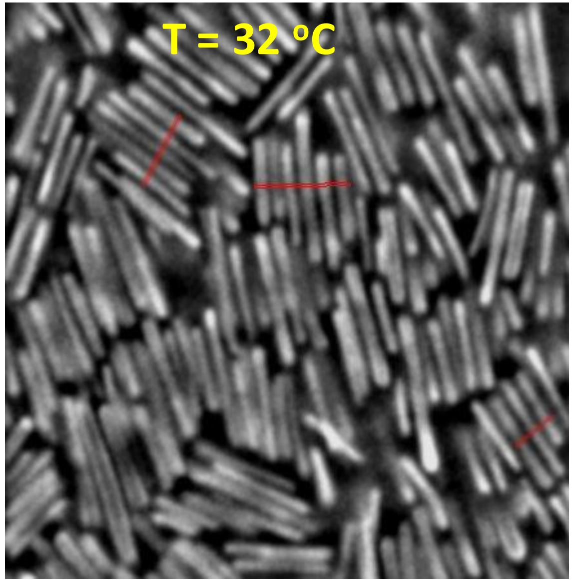
Thickness of brush ~ 200 nm

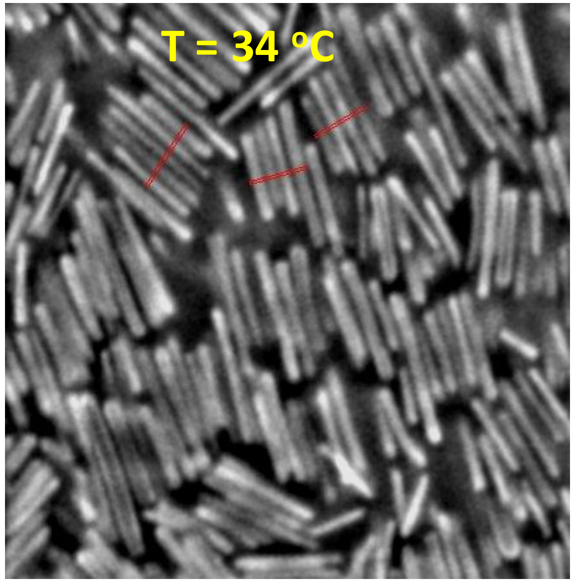


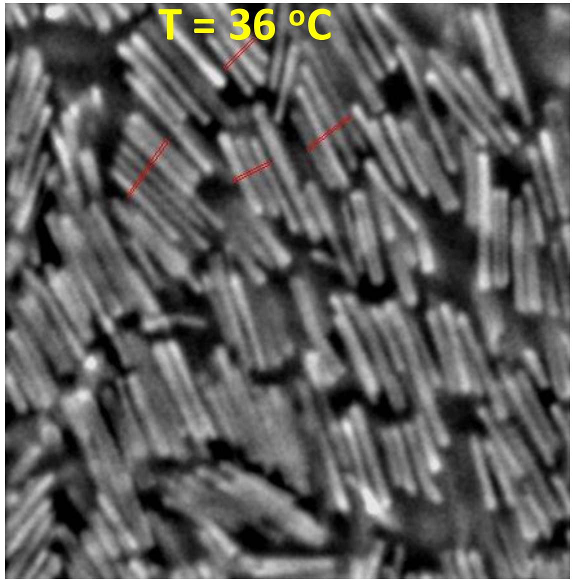
Pnipam brush thickness decreases with increasing temperature

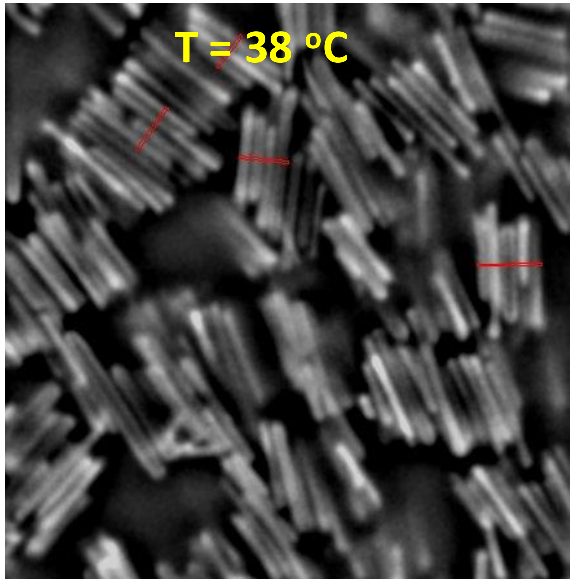




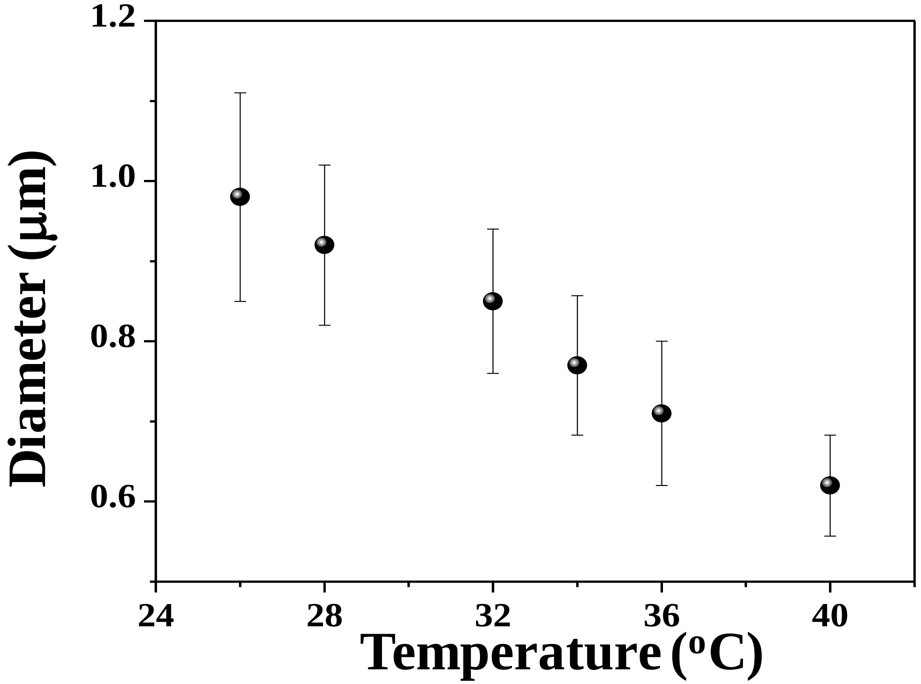








Silica rods coated with pnipam polymer brush - swells at 25 °C and shrinks at 38 °C

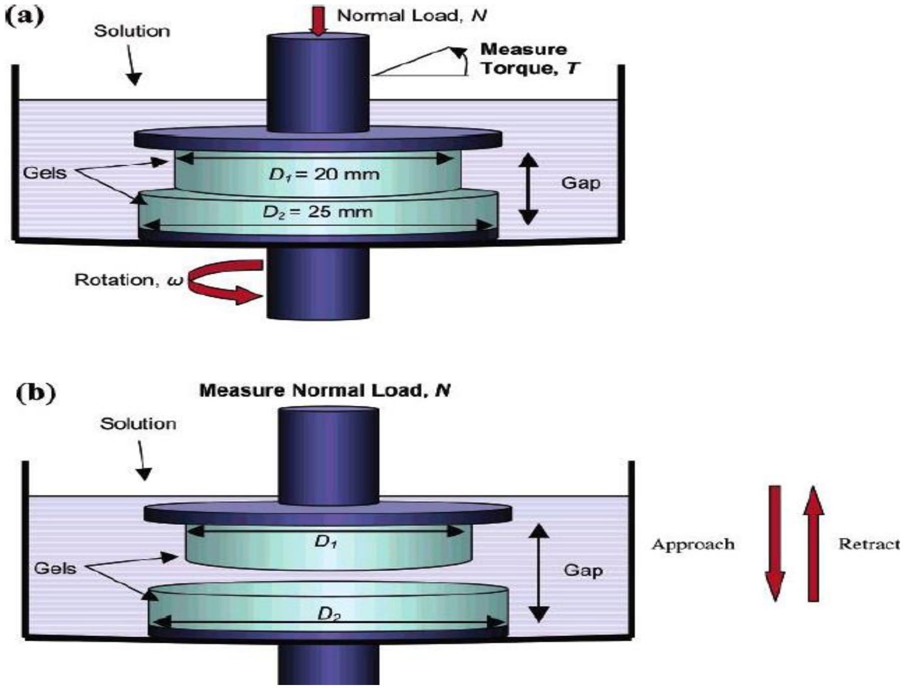


Langmuir **2007,** *23,* 250−257

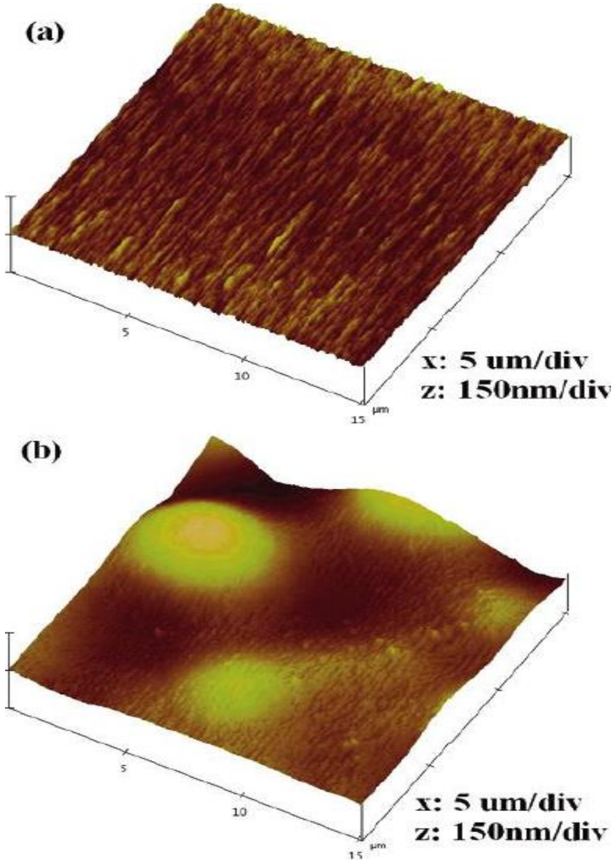
Switchable Friction of Stimulus-Responsive Hydrogels†

Debby P. Chang,‡,§ John E. Dolbow,*,§,∥ and Stefan Zauscher*,‡,§

Department of Mechanical Engineering & Materials Science, Center for Biologically Inspired Materials and Material Systems, and Department of Civil & Environmental Engineering, Duke University, Durham, North Carolina

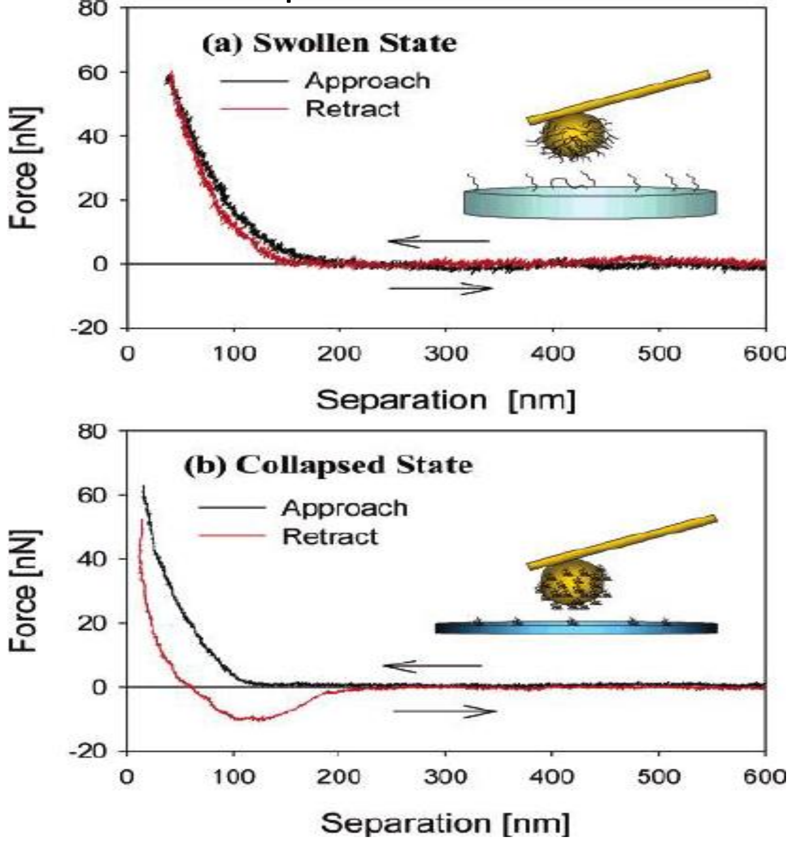


Rheometer apparatus for measuring gel-gel friction and gel-gel adhesion experiments

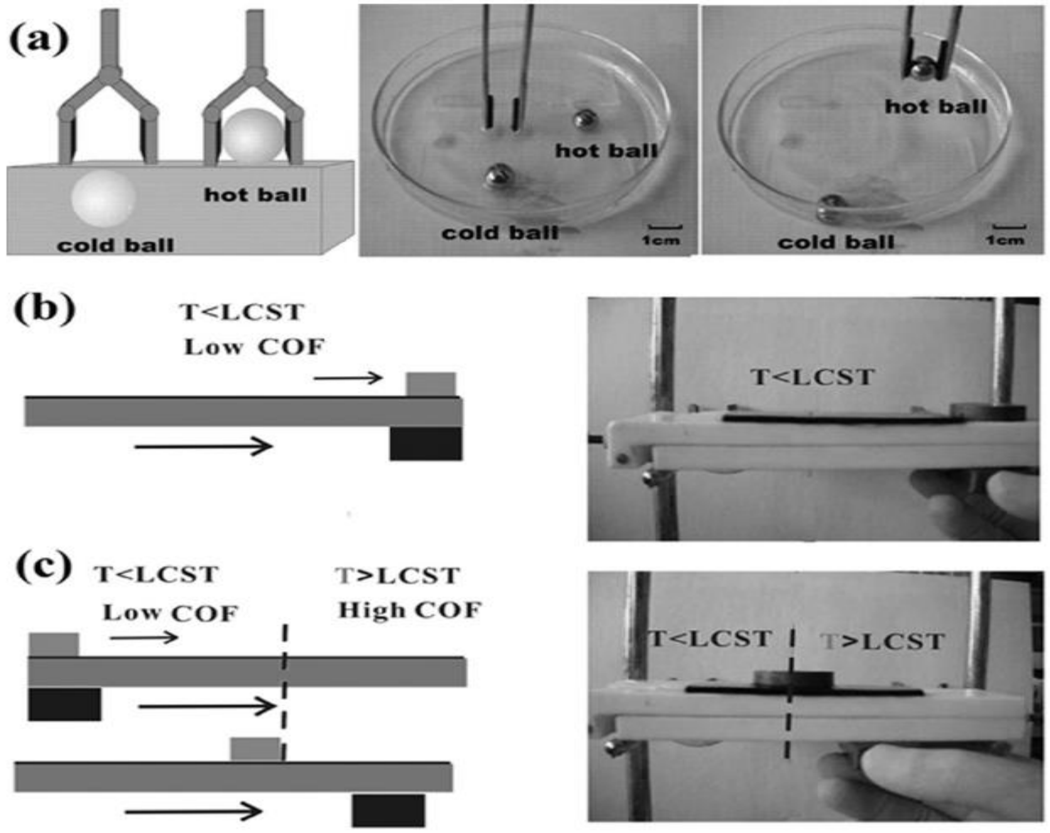


AFM measurements indicate surface roughness is larger in collapsed state

Adhesive forces weak in collapsed state

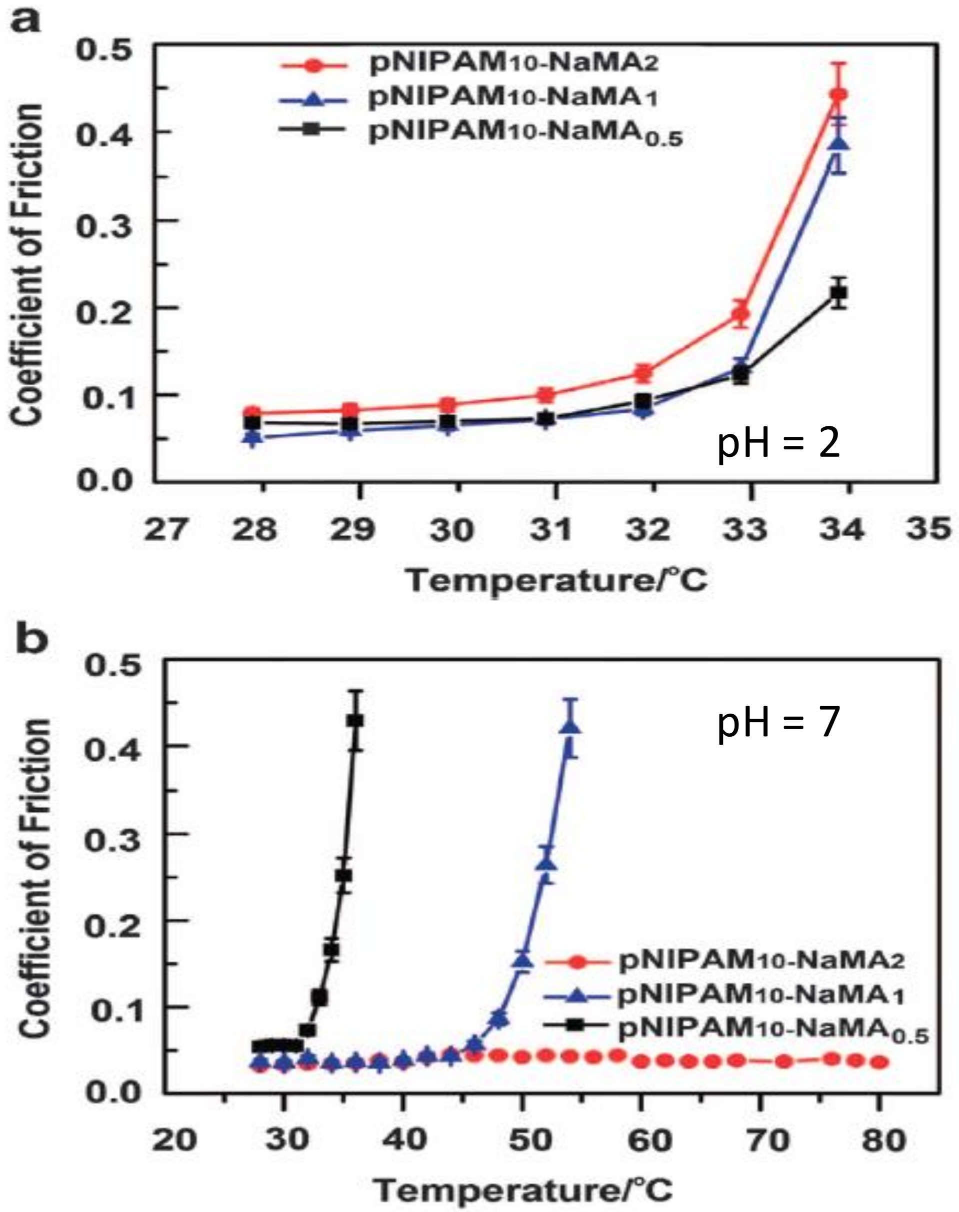


Tuning Friction Using PNIPAM Coatings



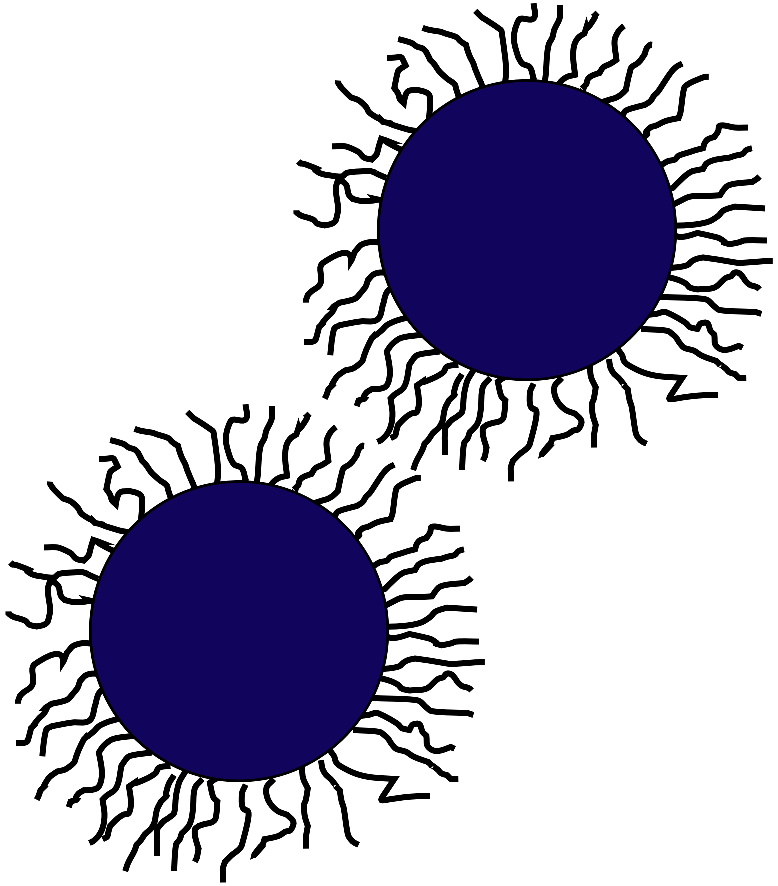
Tweezers Coated with GO-PNIPAM brushes

Wu et al., Macromol. Rapid Comm. (2013)

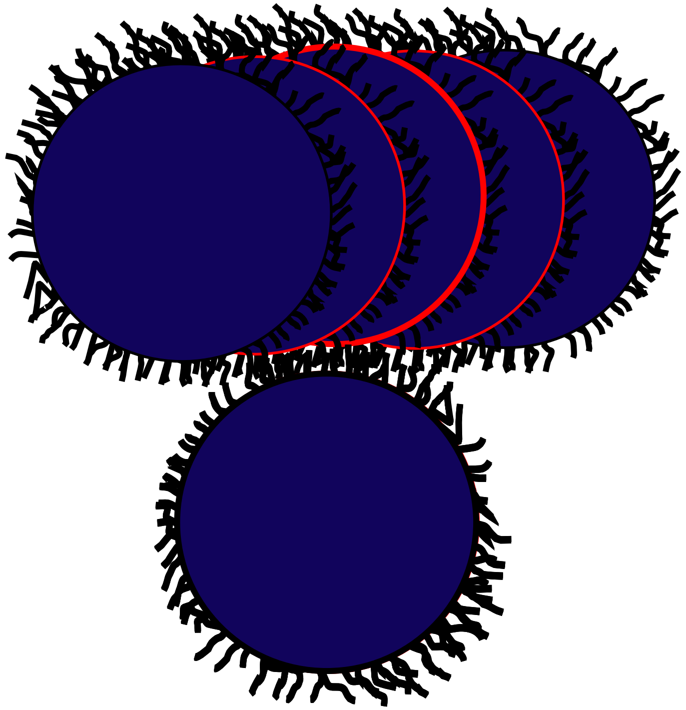


Wu et al., NPG Asia Materials (2014)

Soft particles at 25 °C

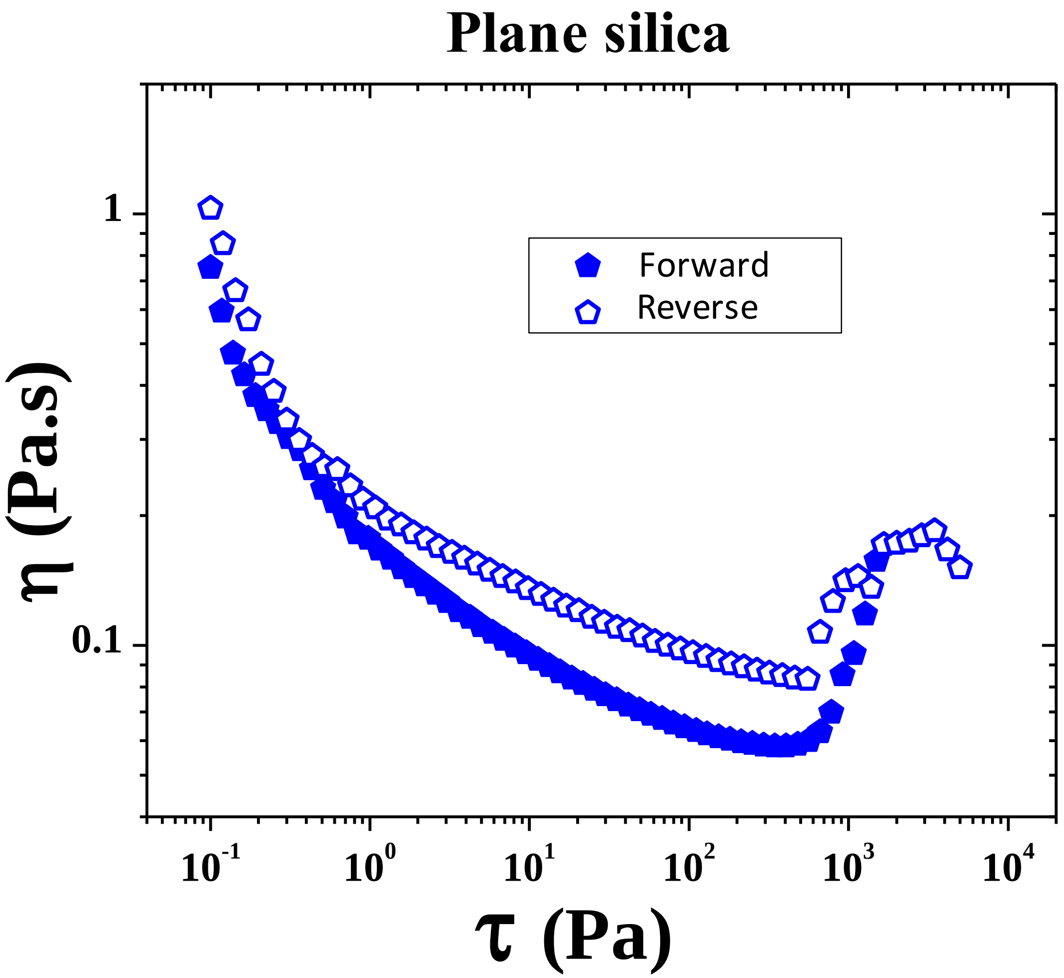


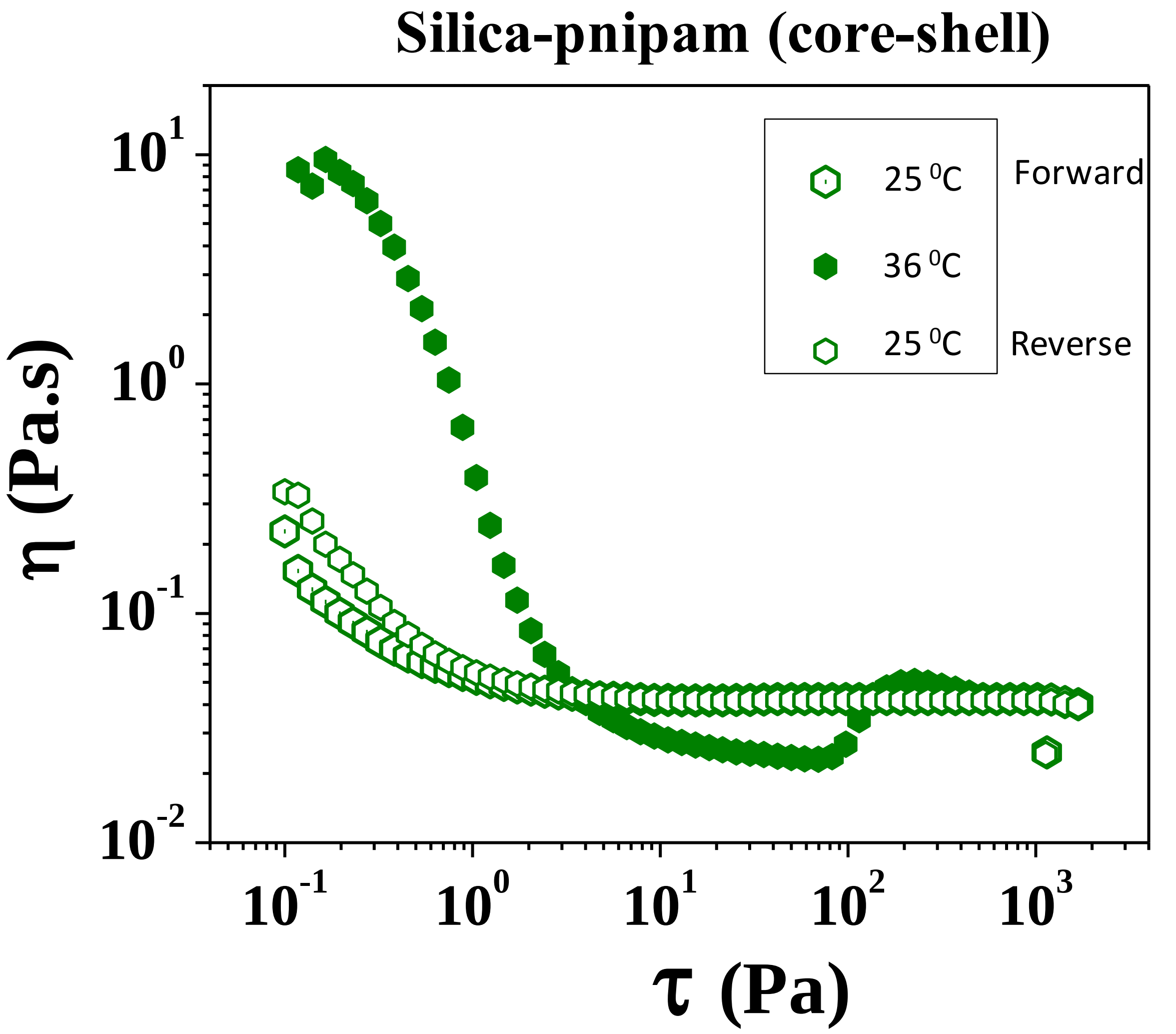
Collapsed pnipam brush particles at 38 ^{o}C



Spherical colloids, a = 1 mm, $\phi = 0.5$

PP, Gap=75 microns


Plane silica

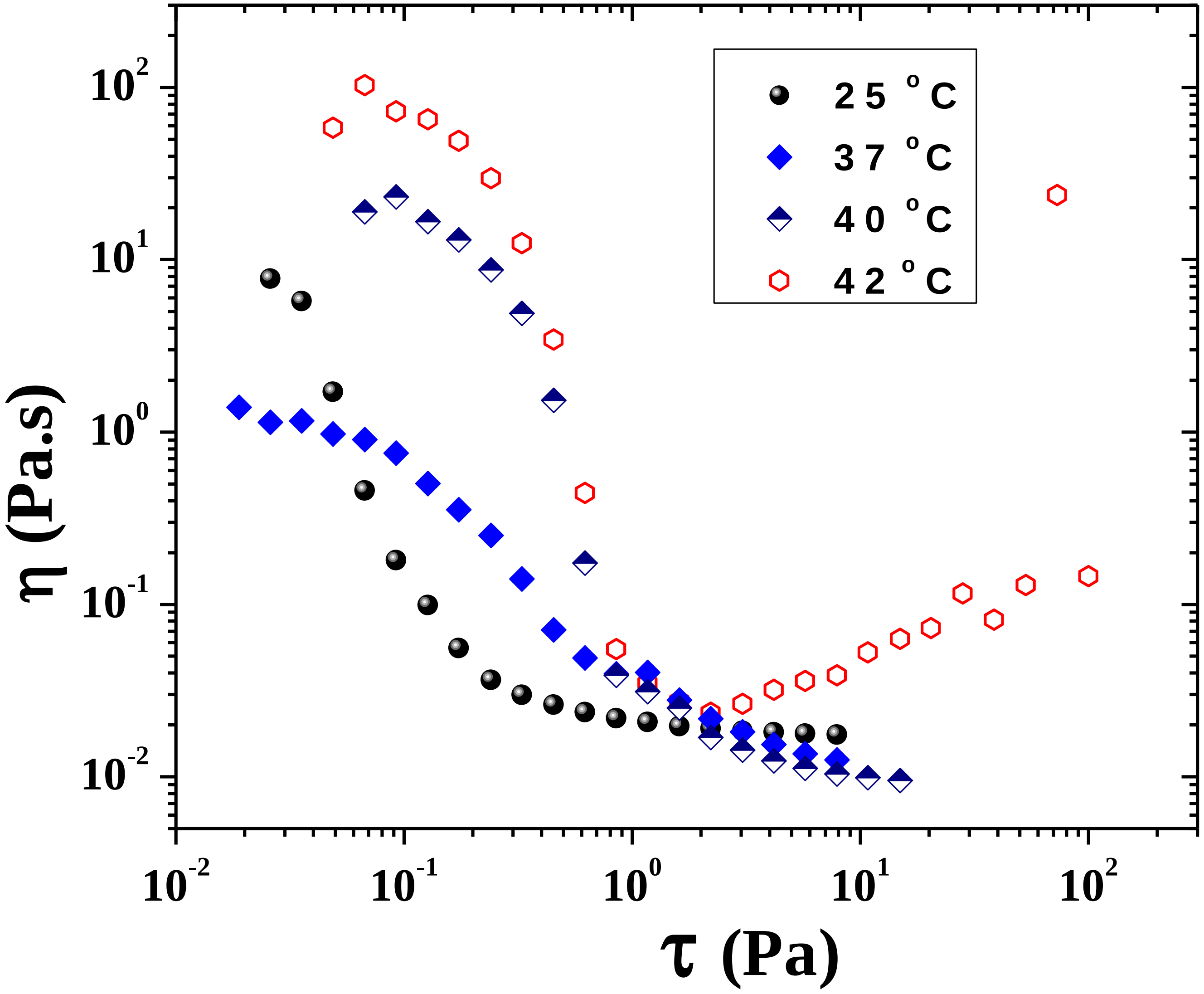

Silica-pnipam (core-shell)

Spheres behave similarly except decrease in τ_c

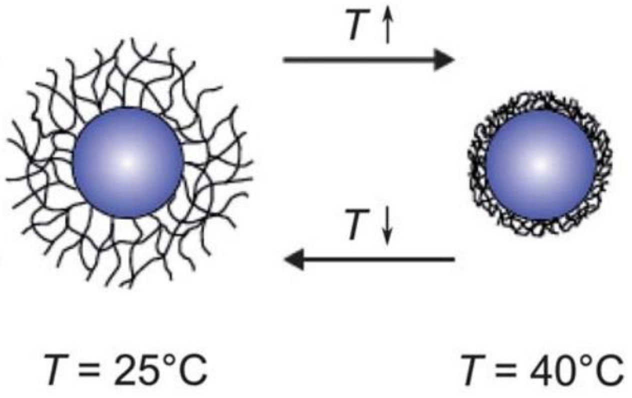
Polystyrene-pnipam , a = 1 mm

ϕ= 0.52

PP,Gap=75 microns



Pnipam brush collapses above 40 ºC for polystyrene particles

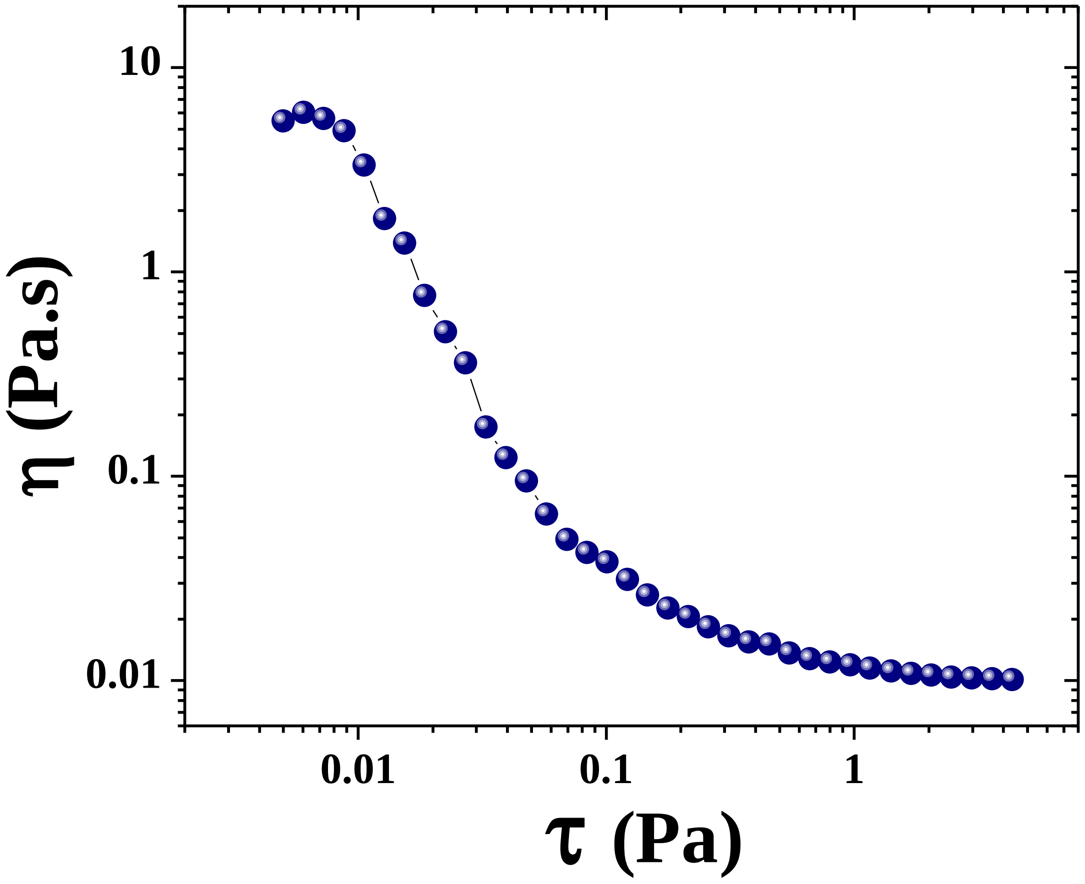


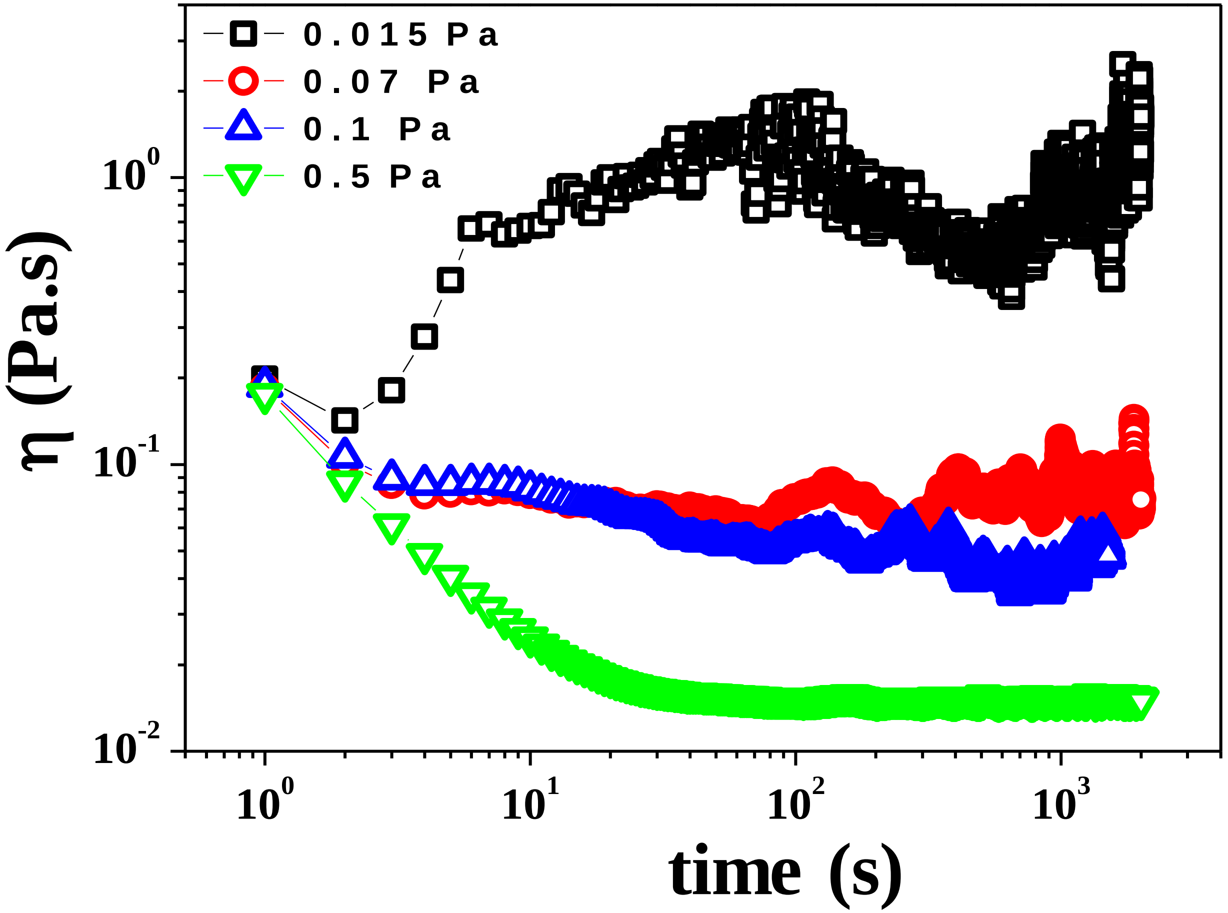
Koniger et al. Soft Matter, 9, 1418 (2013)

Core-shell Rods(silica-pnipam)

PP (gap=40 microns)

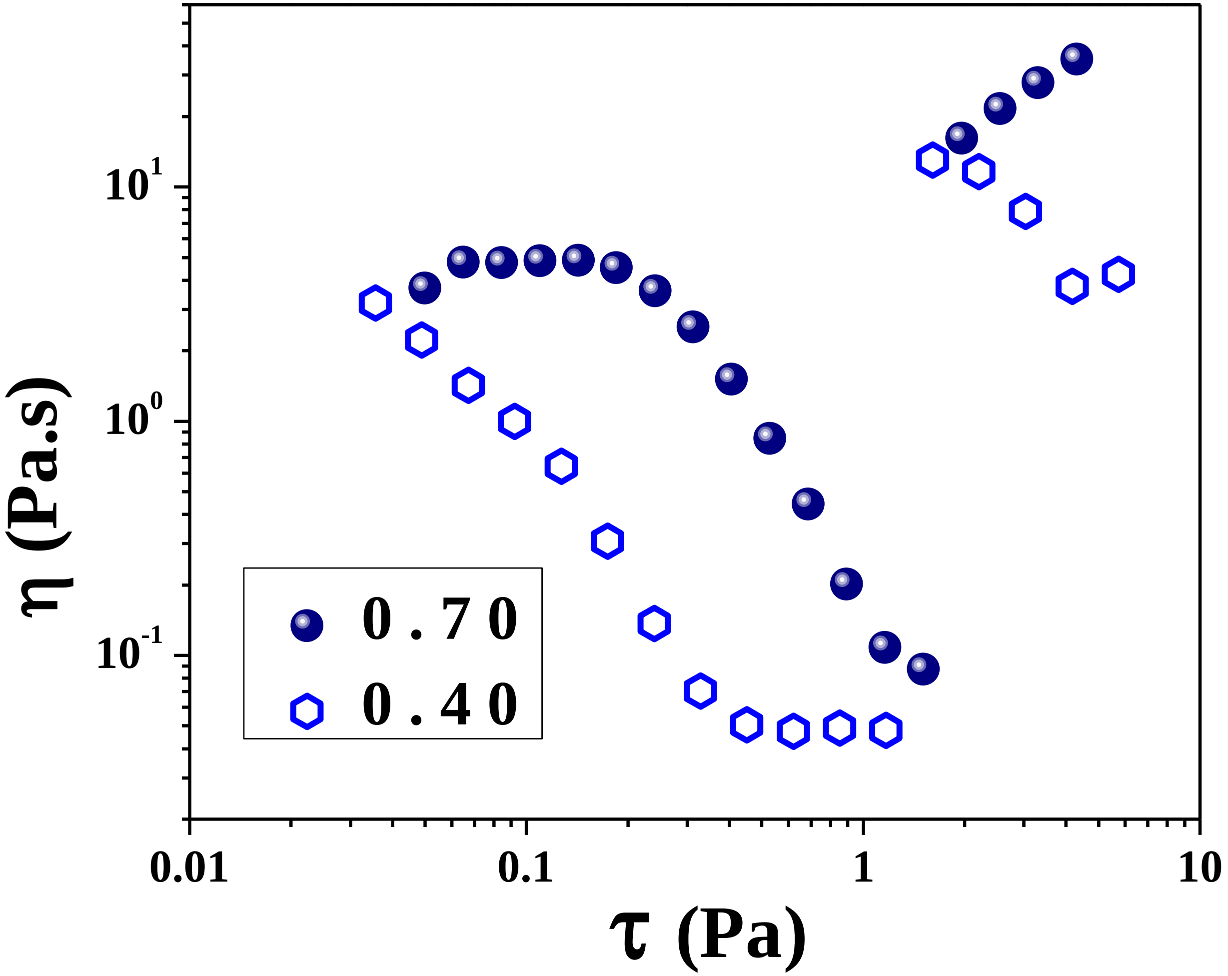
$T = 25\ ^{o}C,\ \phi = 0.4$, PP

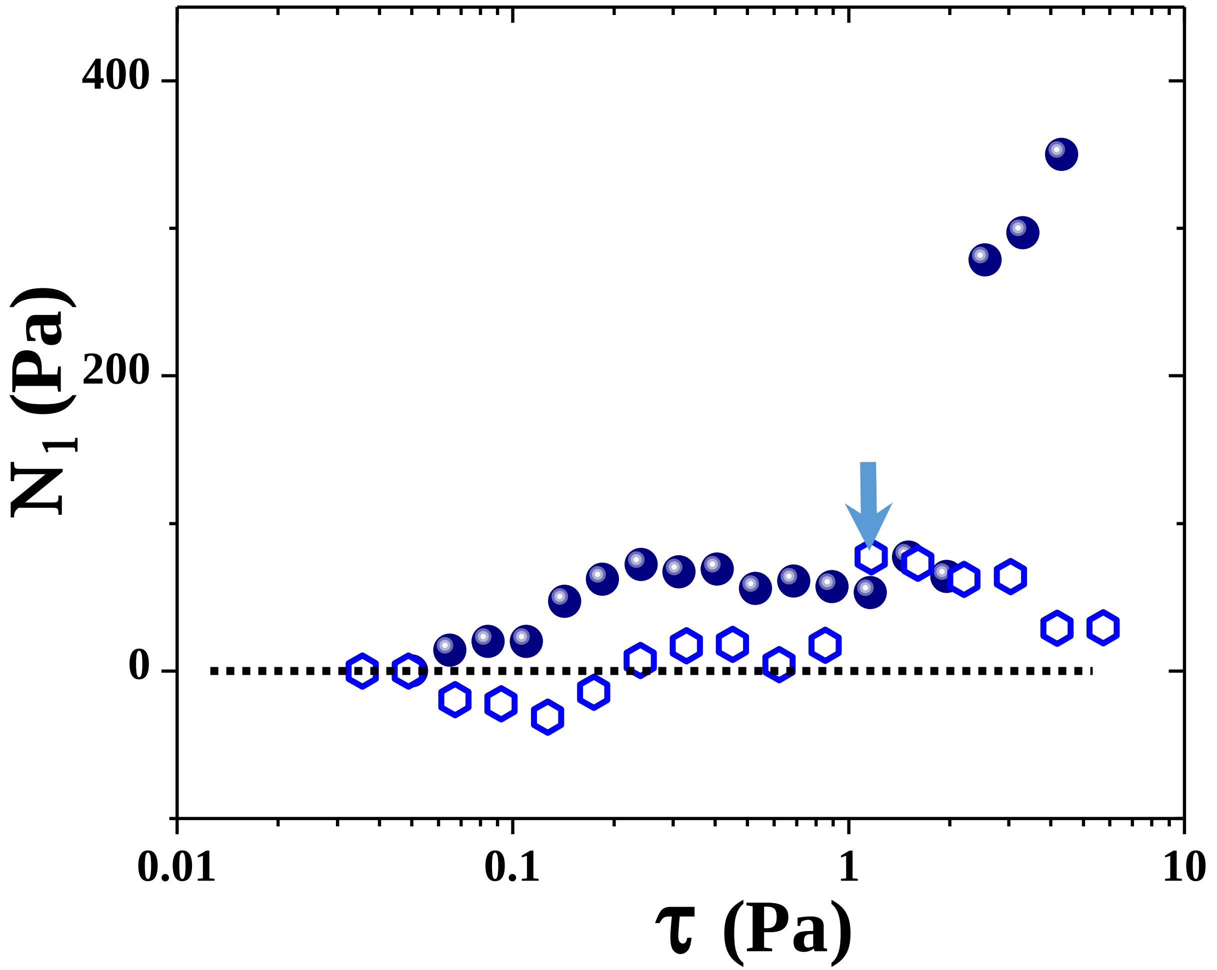




Shear thickening at 38 ºC

PP (40 microns)

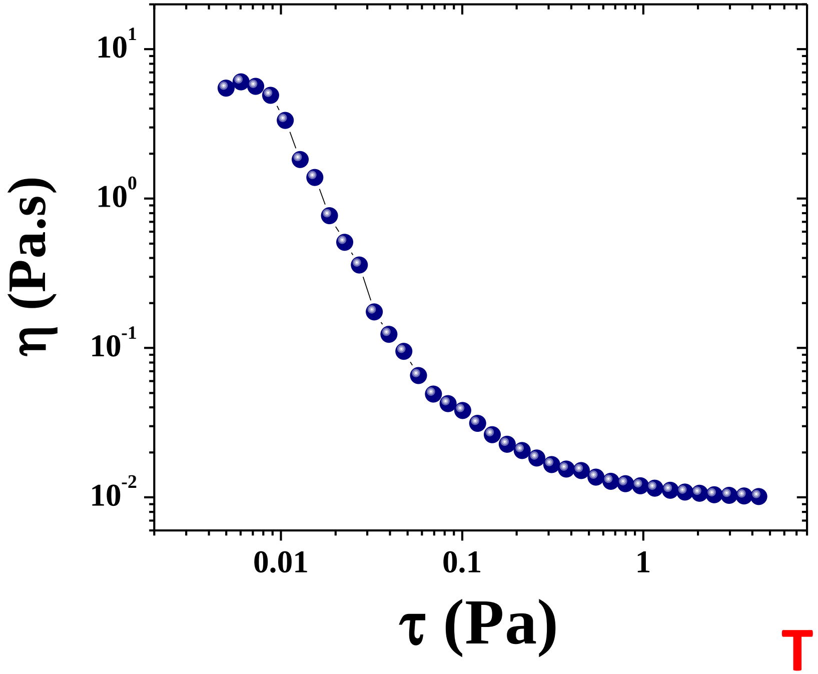


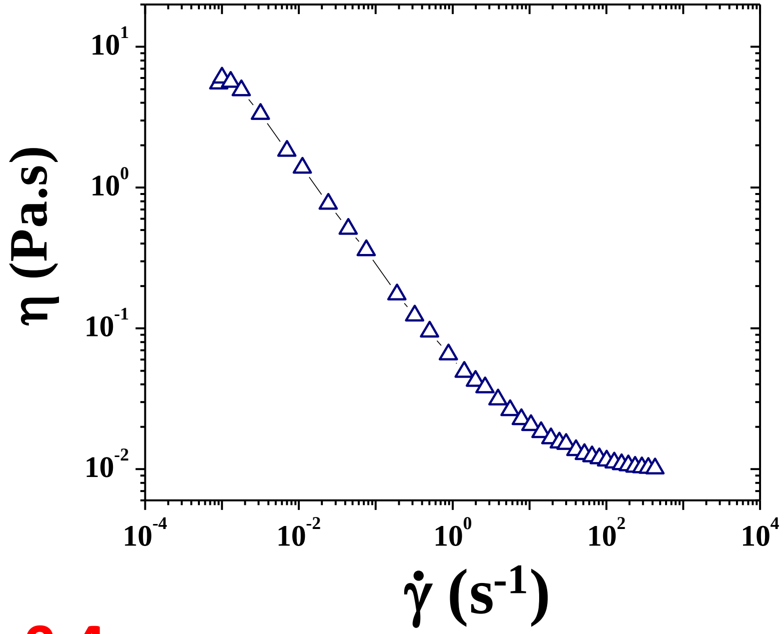


ϕ = 0.7 at 25 C
= 0.43 at 38 C

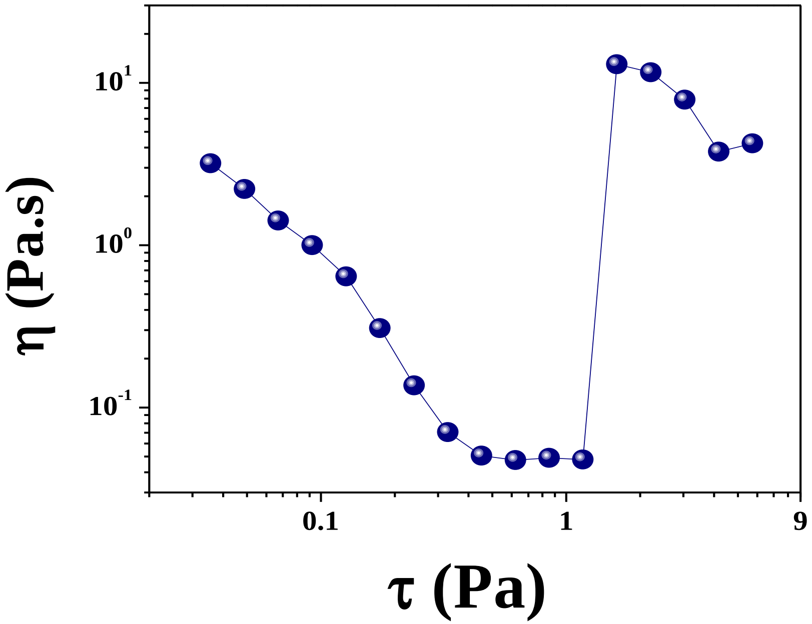
ϕ = 0.40 at 25 C
= 0.24 at 38 C

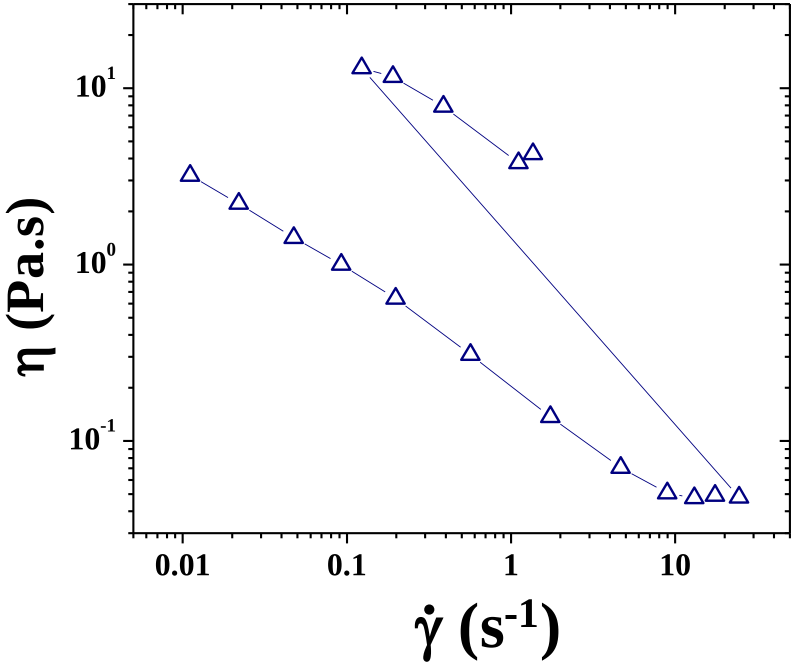
T = 25 C, ϕ = 0.4



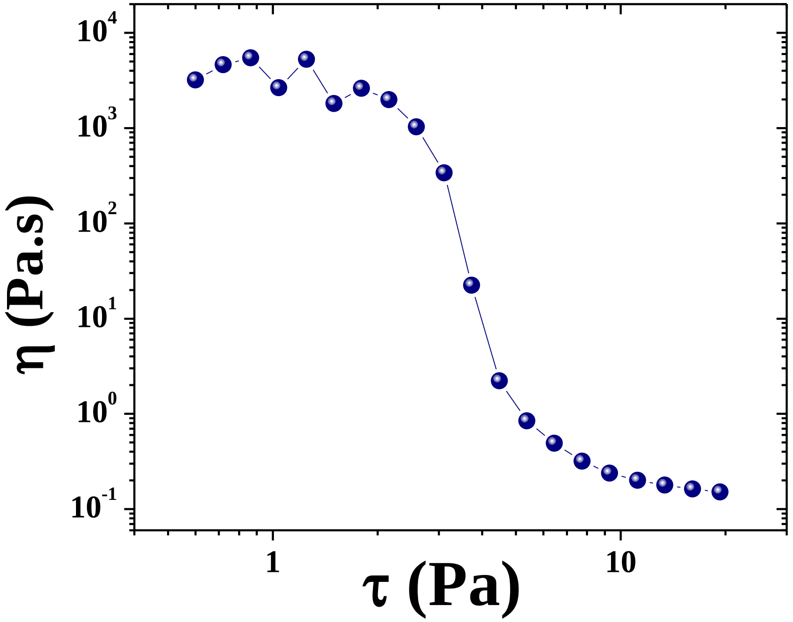


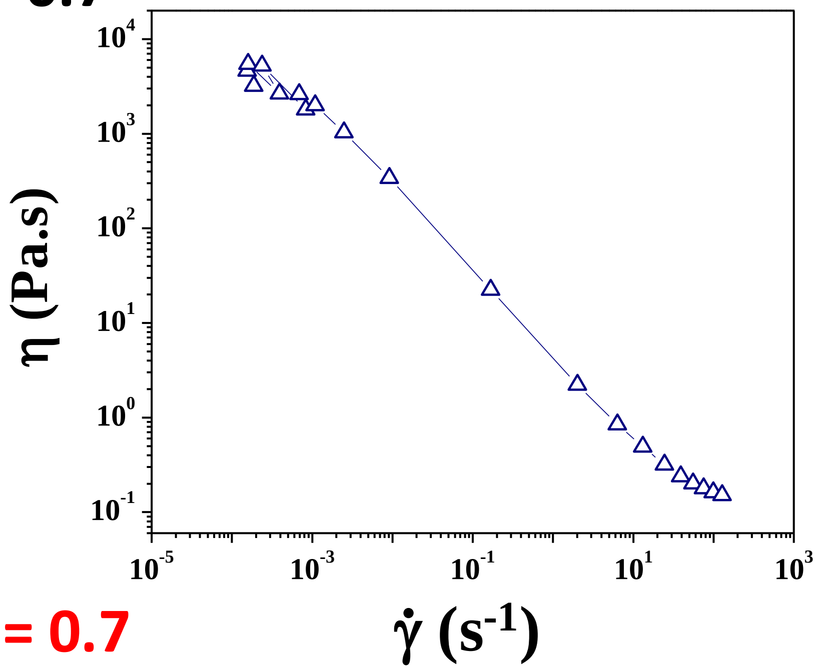
T = 38 C, ϕ = 0.4



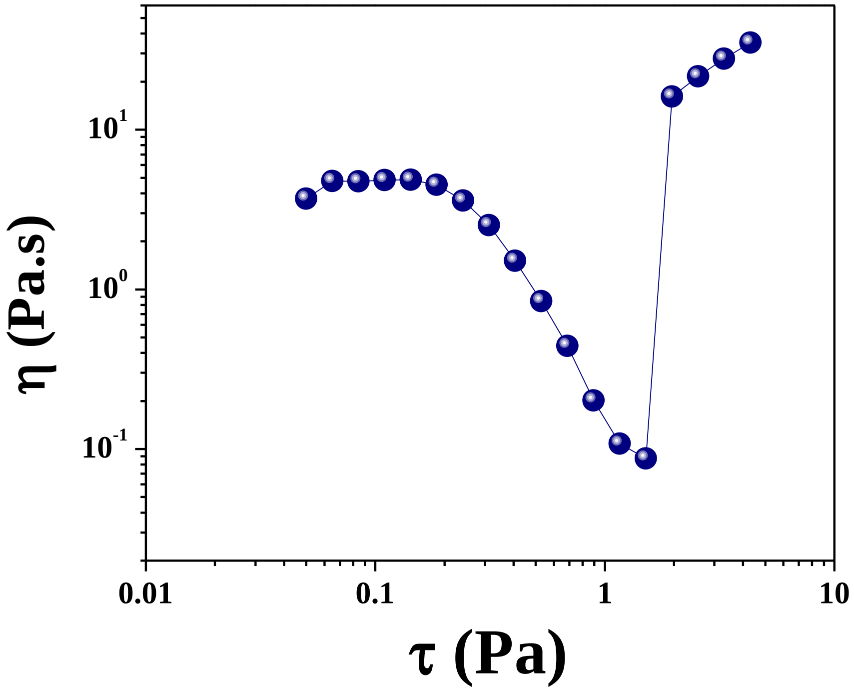


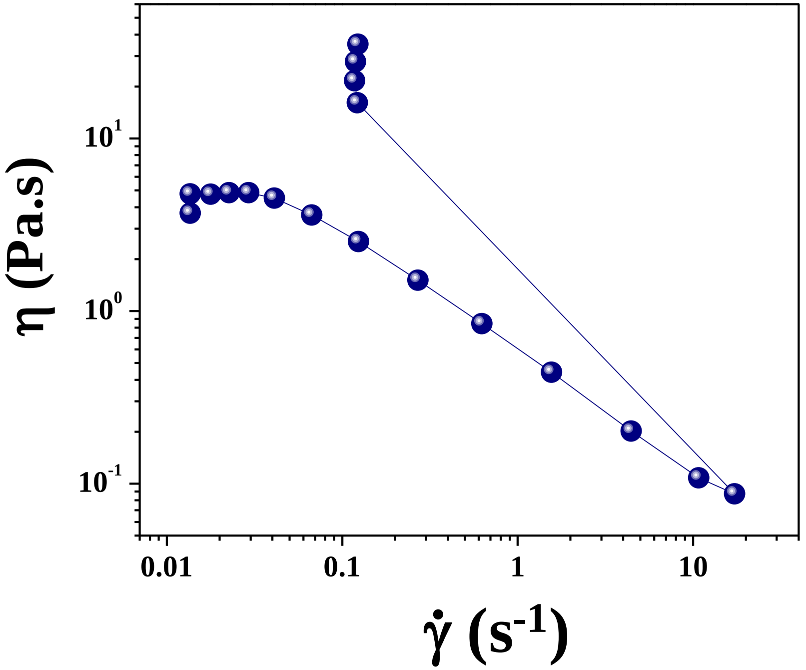
T = 25 C, ϕ = 0.7





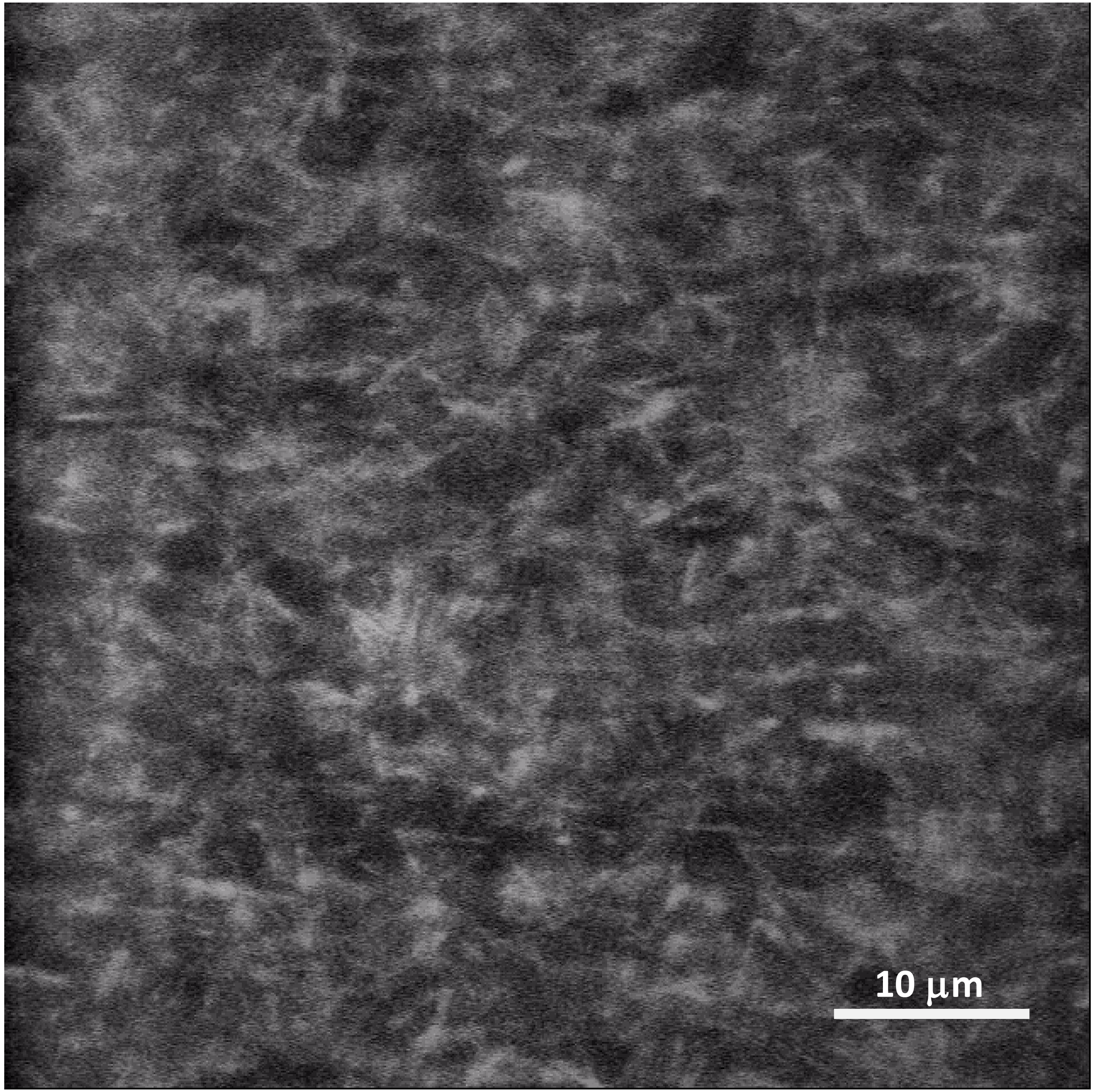
T = 38 C, ϕ = 0.7





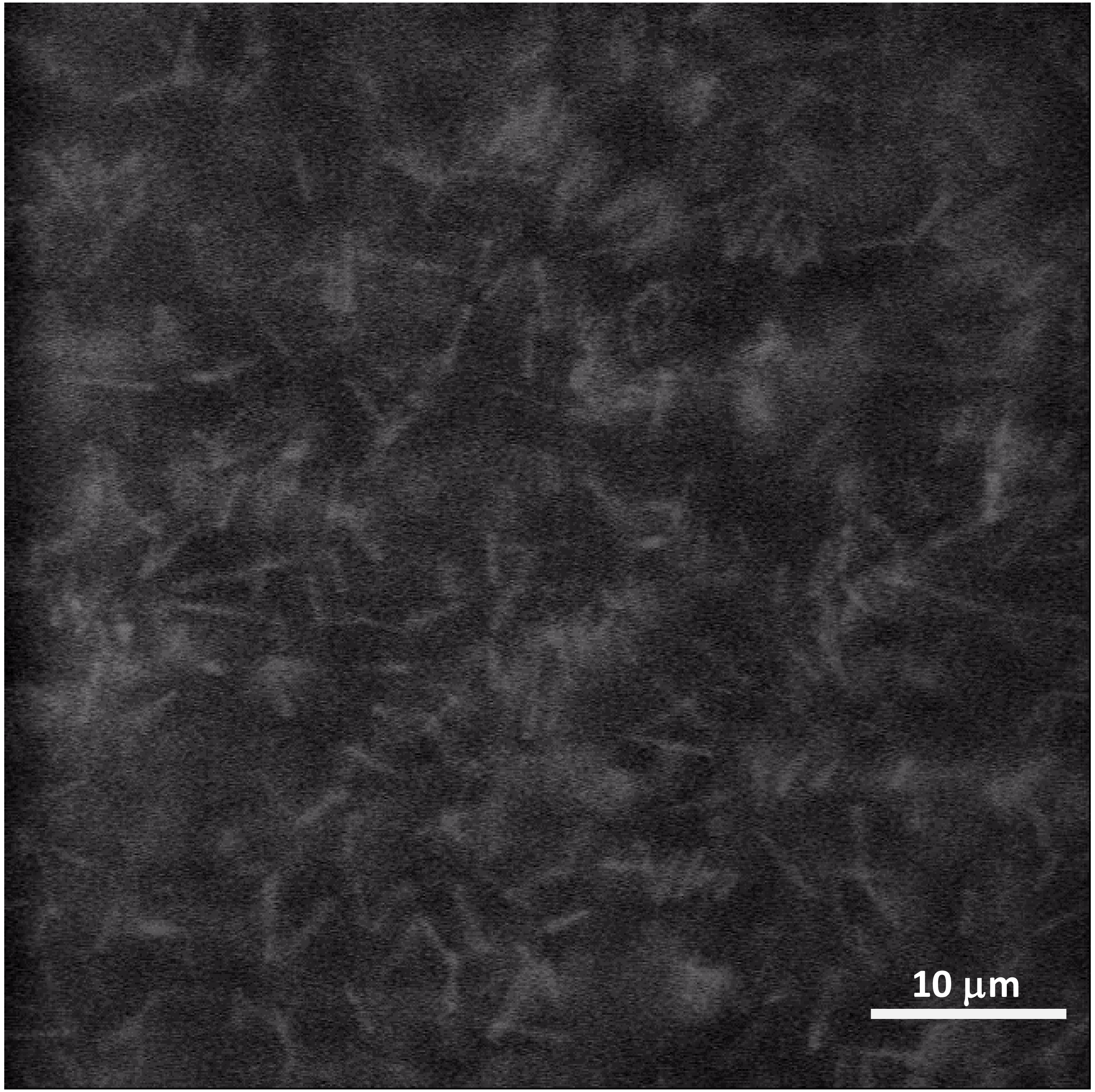
Silica-PNIPAM Rods

T = 25 ^{o}C, ϕ = 0.4



T = 38 ºC, ϕ = 0.4

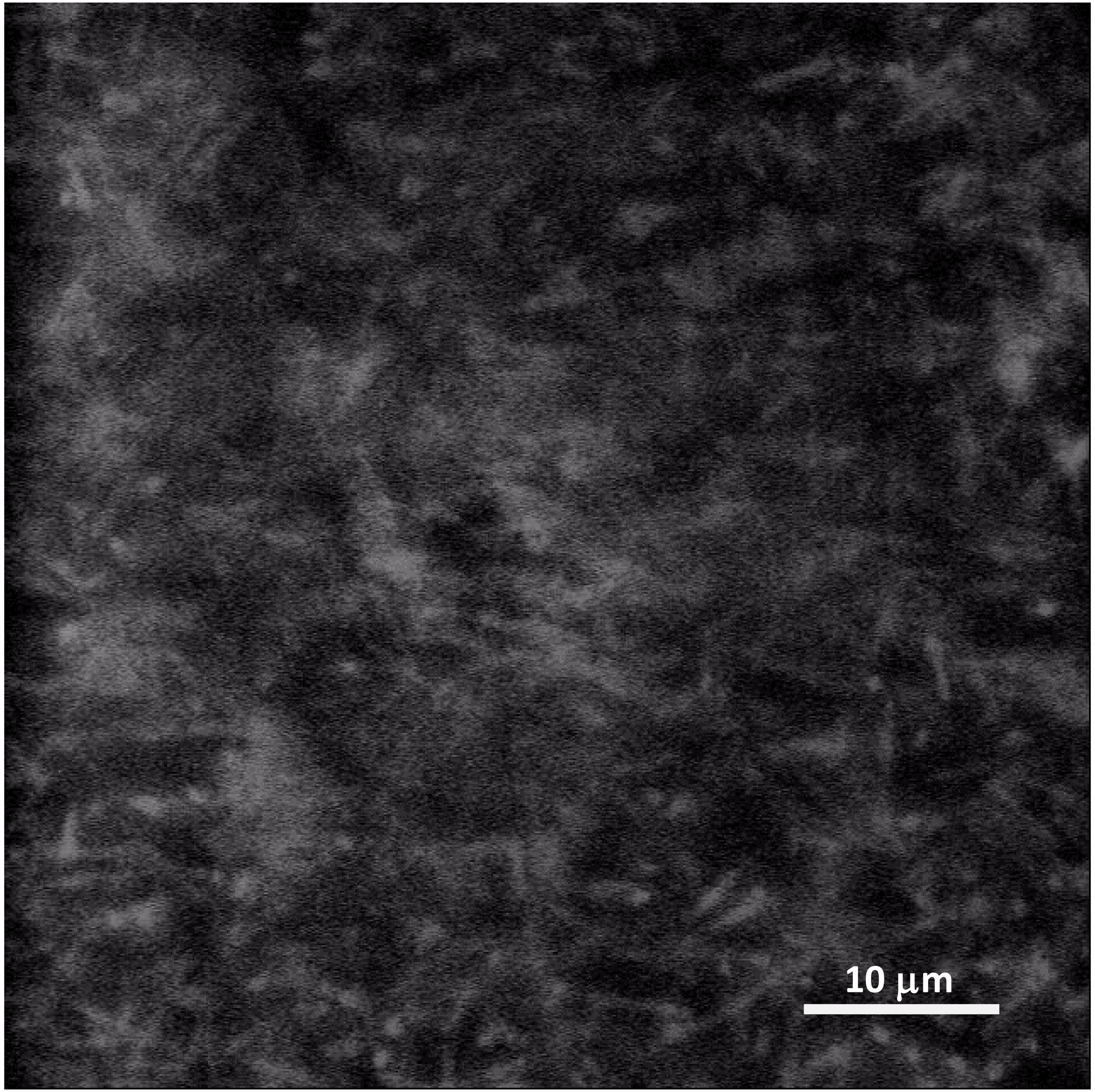
Silica-PNIPAM Rods



Gap spanning particle network

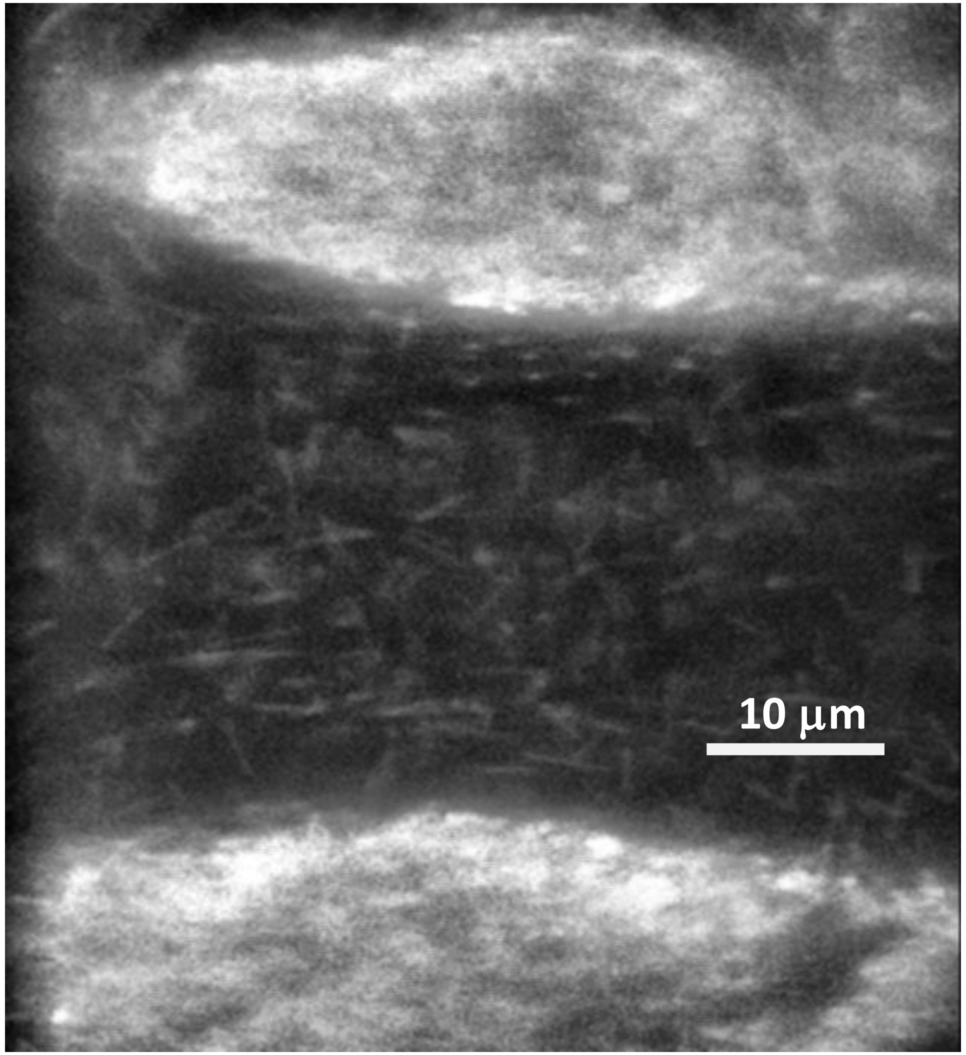
Silica-PNIPAM Rods

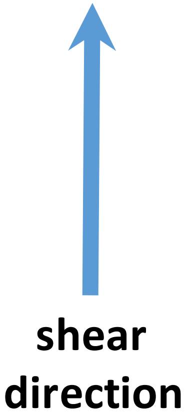
$T = 38\ ^{o}C, \phi = 0.4$



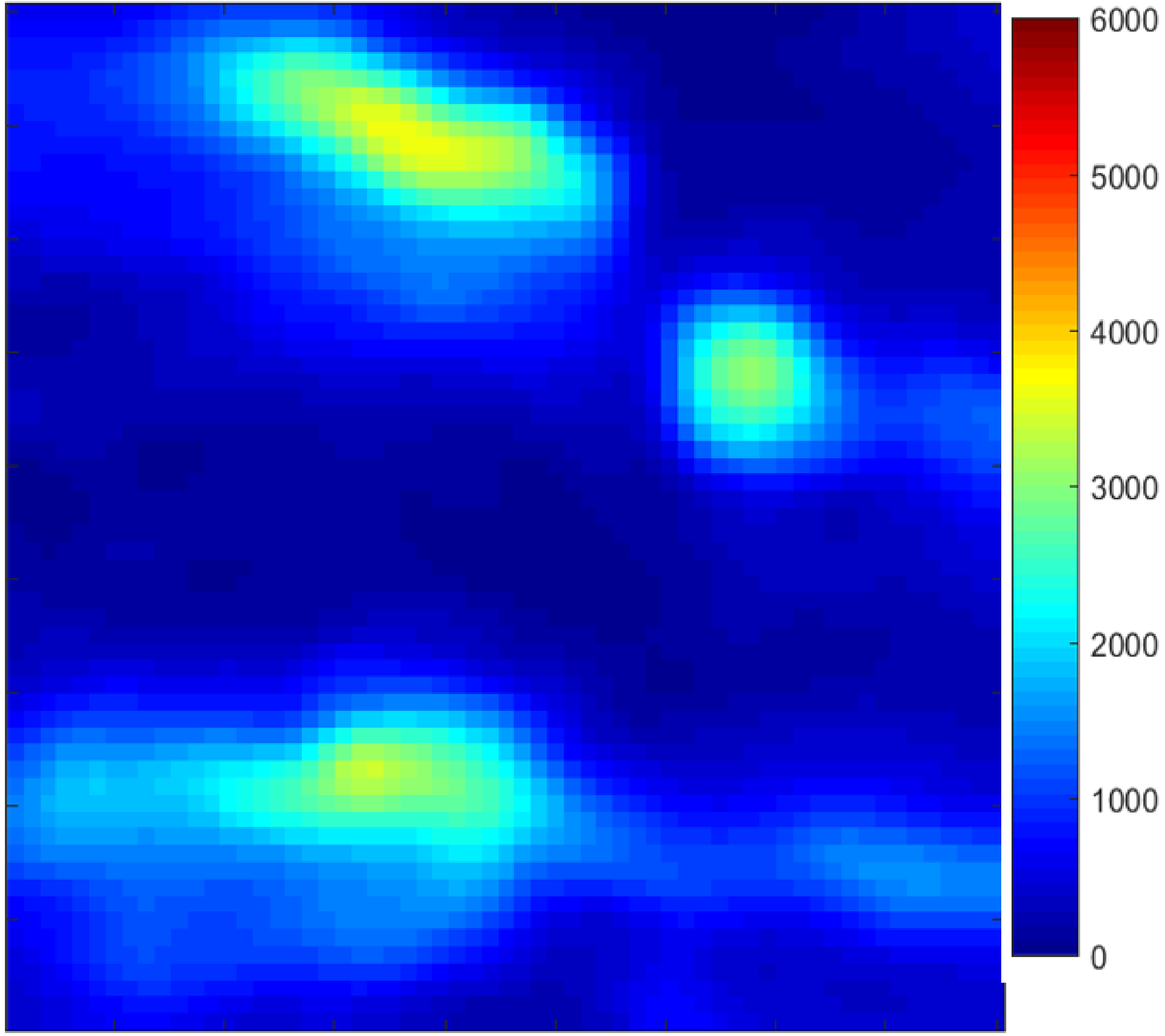
Bright clusters: similar to heterogeneities seen at boundaries during ST

Bright clusters during ST in pnipam coated colloids





Stress heterogeneities in ST of Silica colloids using BSM



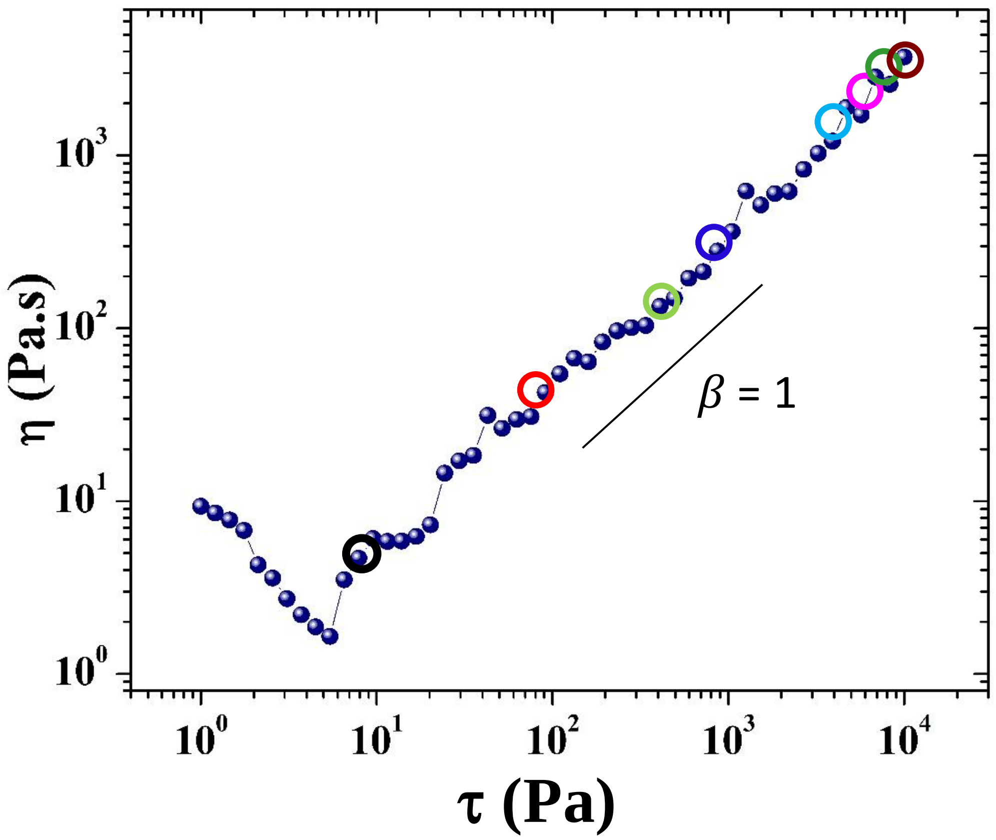
The length scale in shear direction is determined by the gap between the rheometer plates

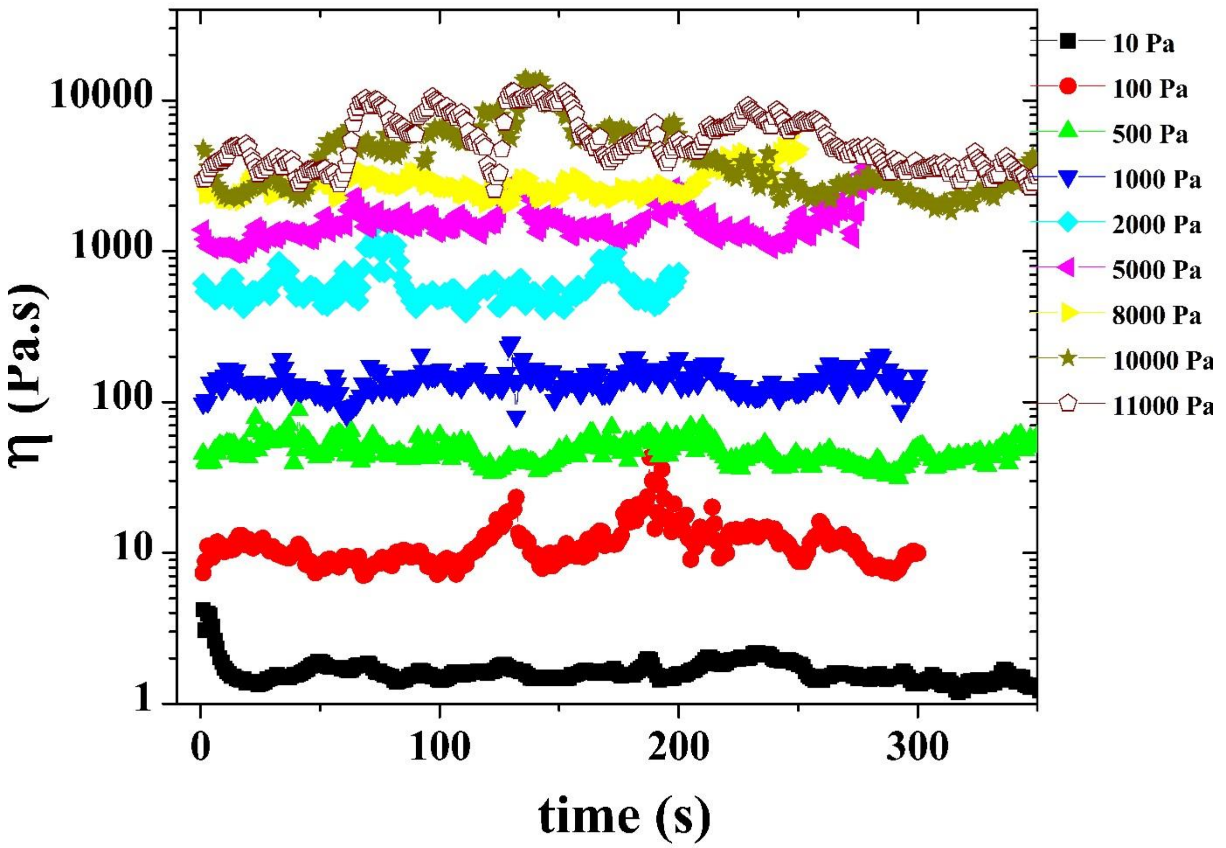
Rathee et al. PNAS, 114, 8740 (2017)

Role of gap thickness in PP
and
waiting time at each stress value?

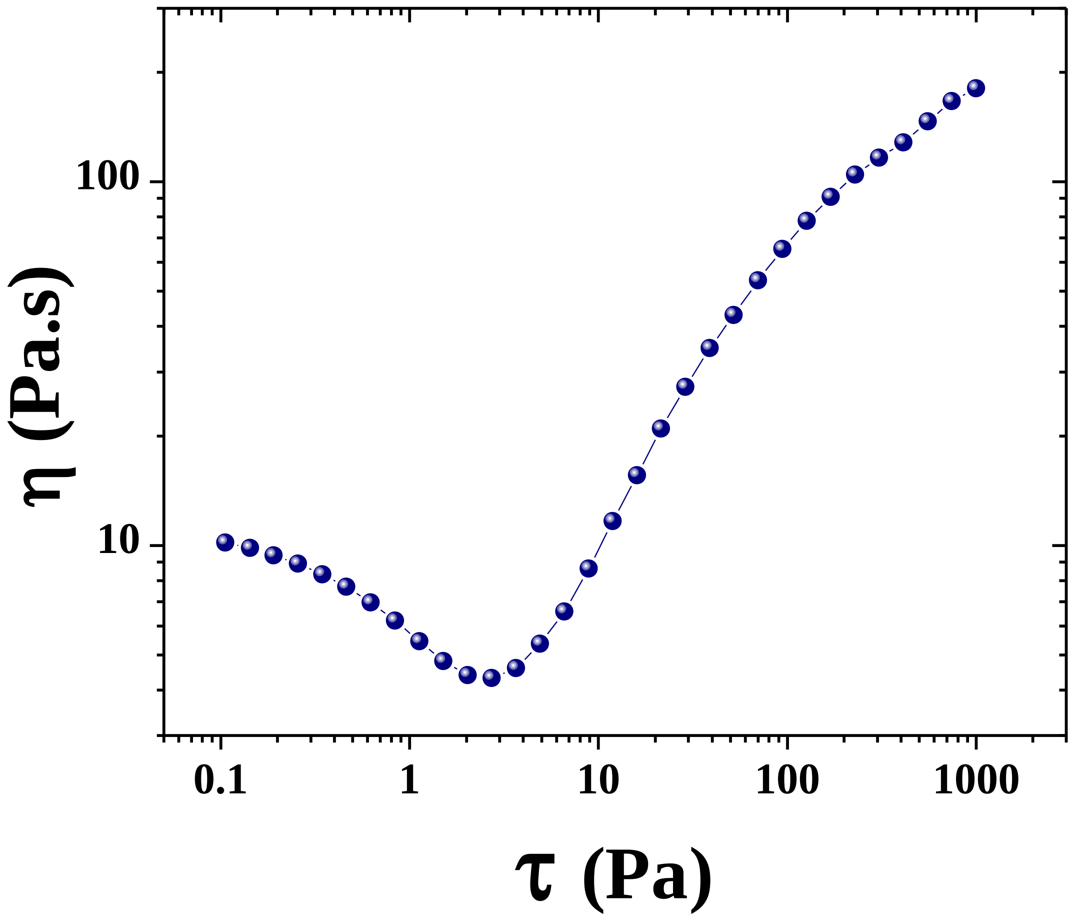
Silica Rods in CP

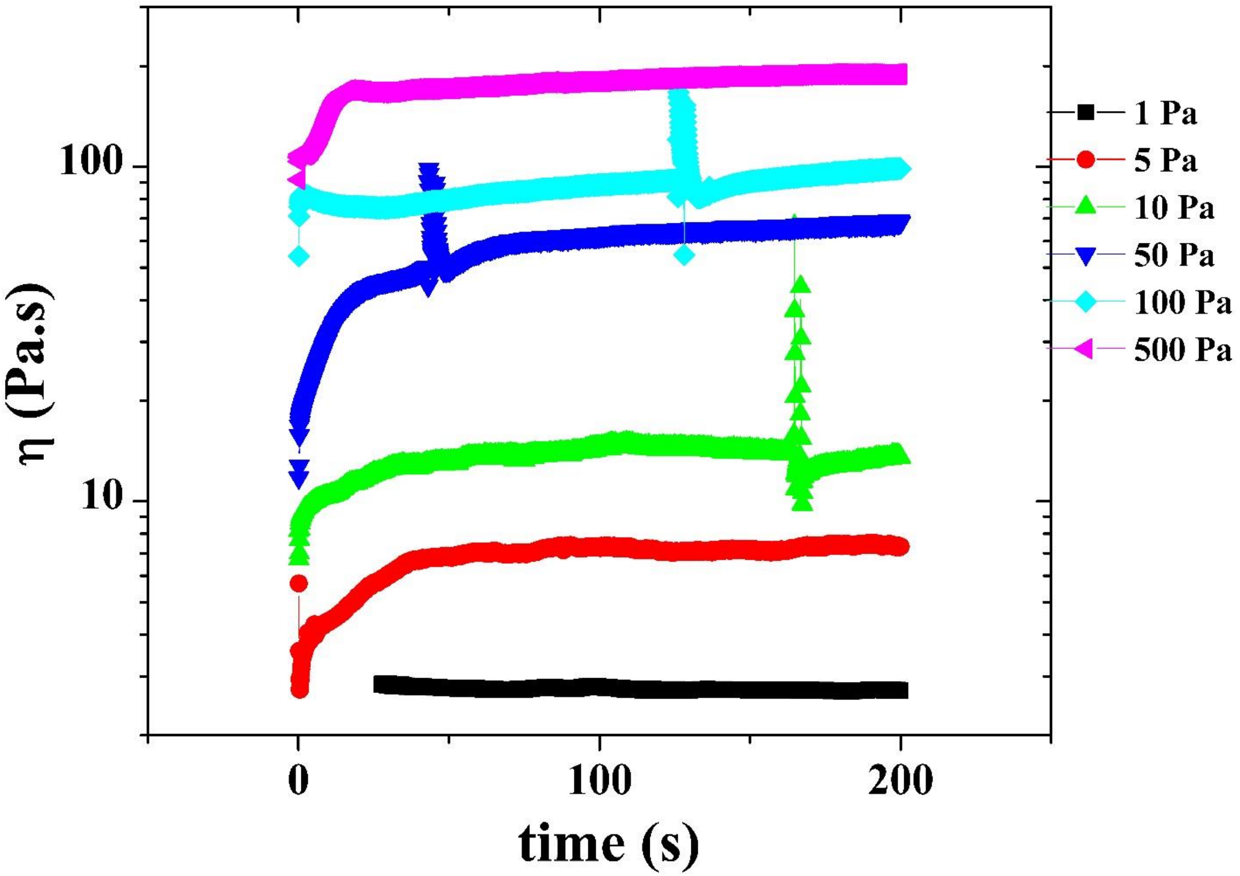
$\phi = 0.45$



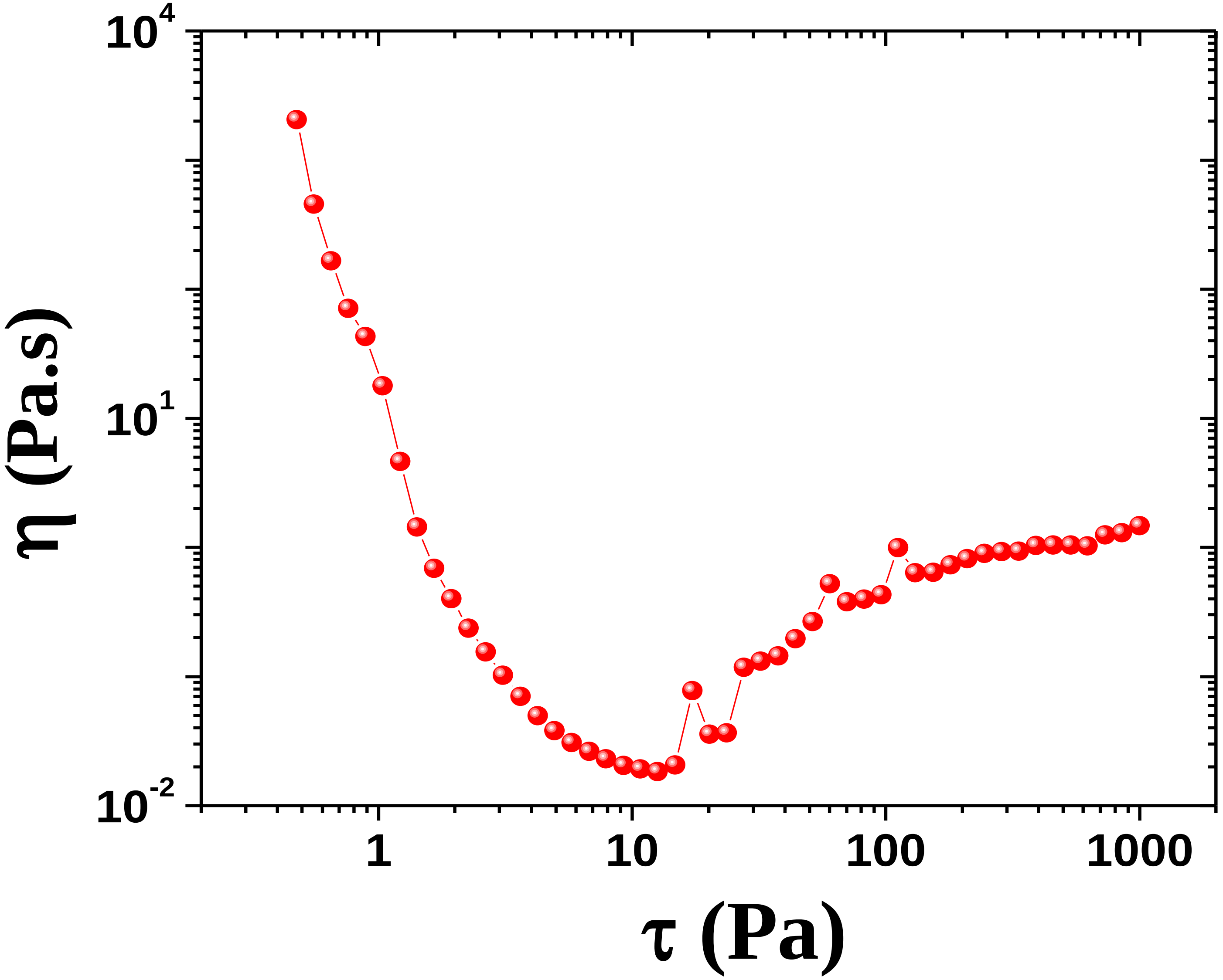


Silica Rods in PP Gap = 200 μm $\phi = 0.45$



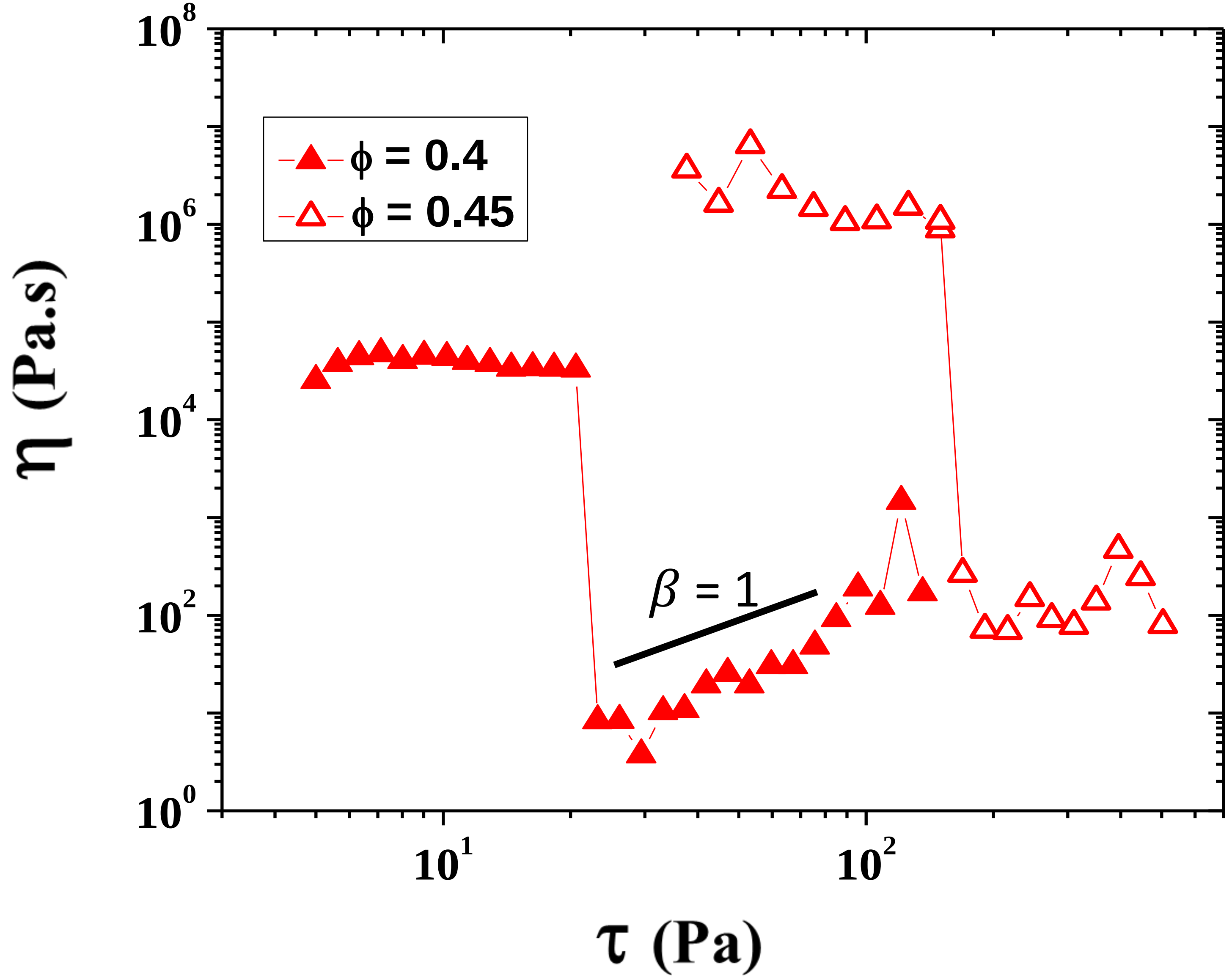


Silica Rods in PP Gap = 70 μm $\phi = 0.45$



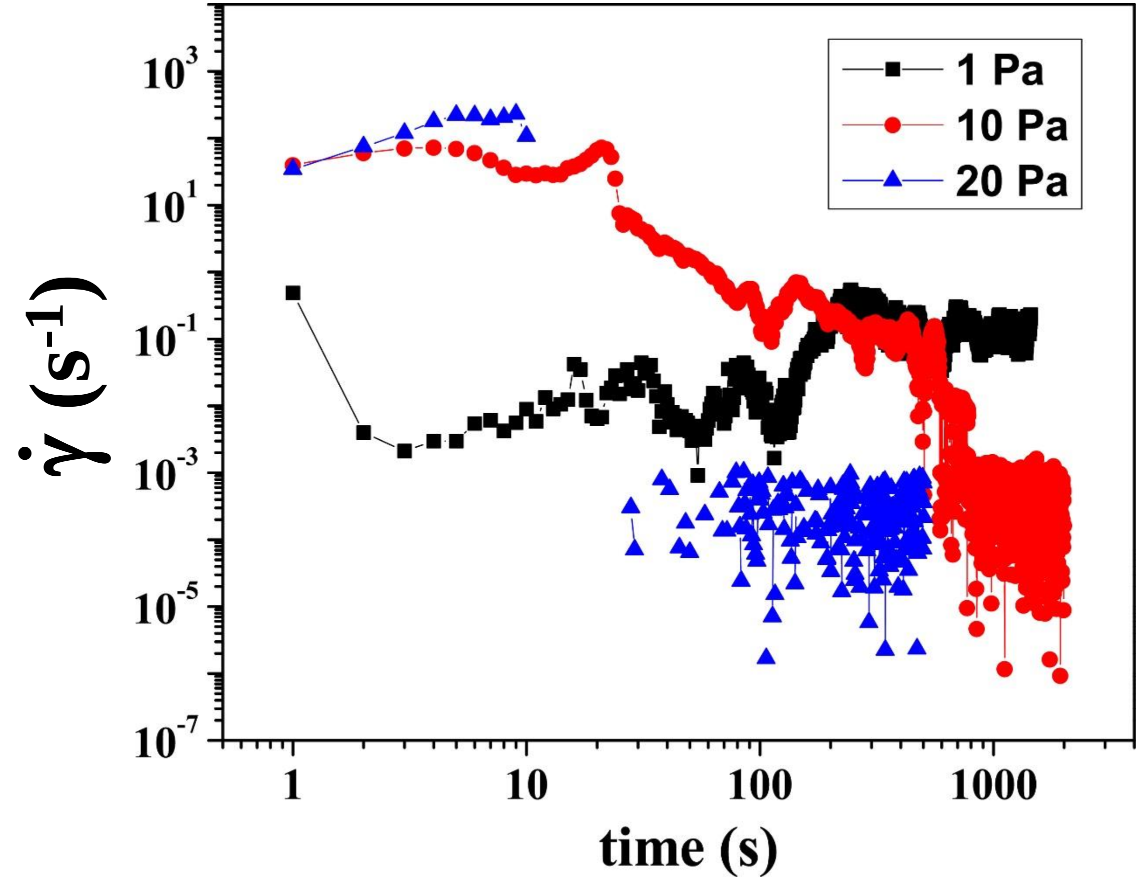
Silica Rods in PP Gap = 20 μm $\phi = 0.45$

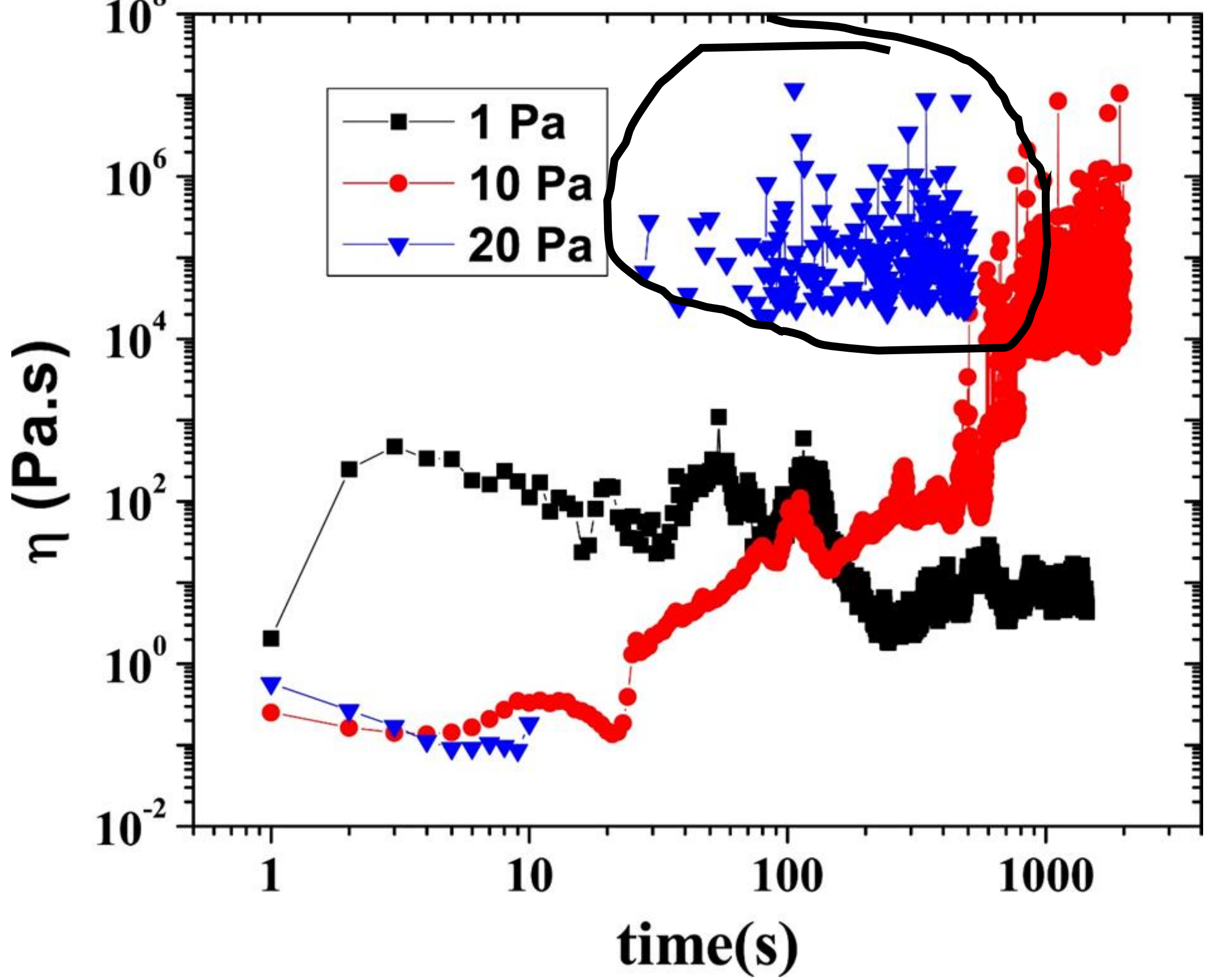
Waiting time :30 sec



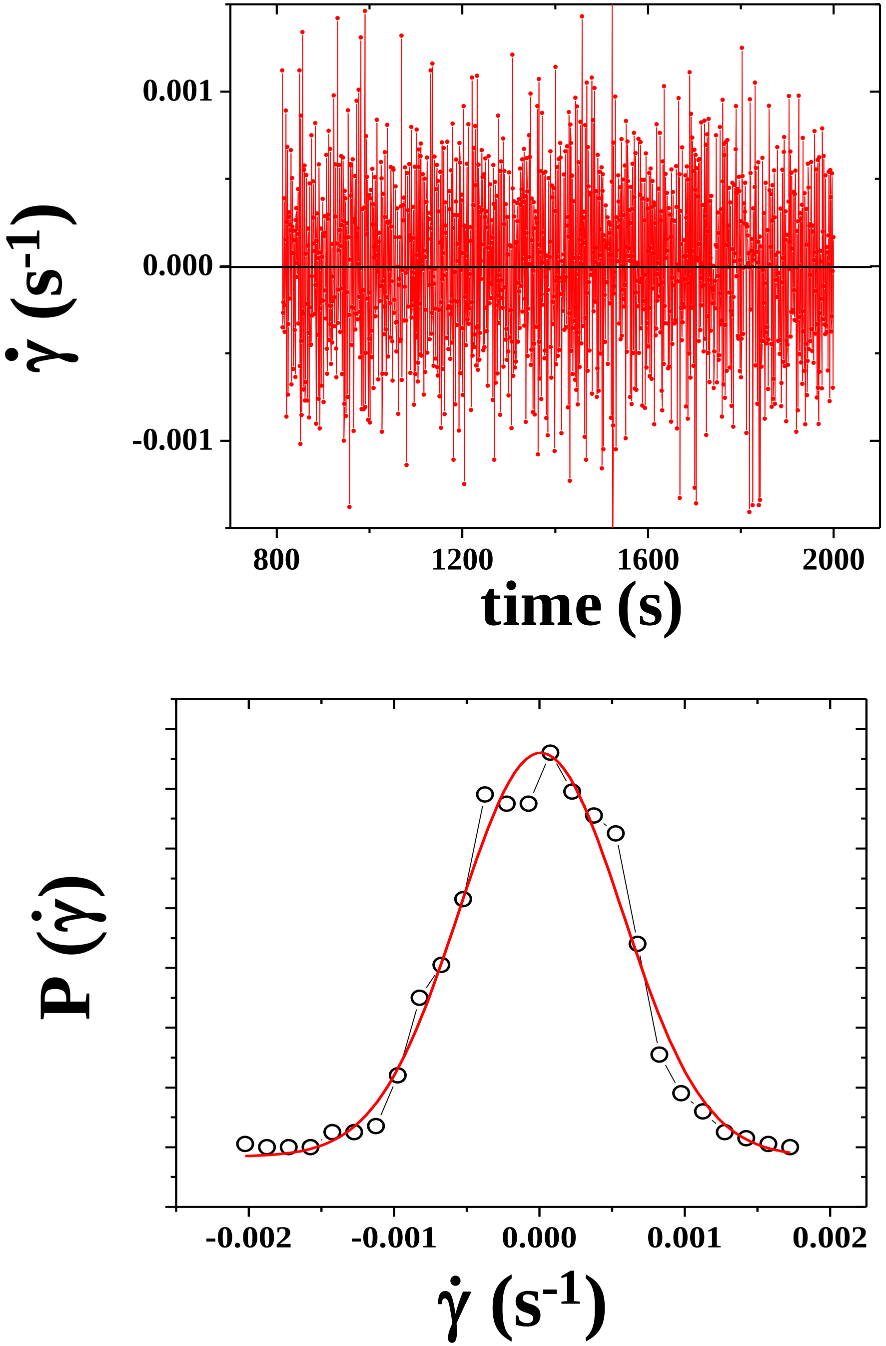
At fixed Shear Stress, as a func. of time

ϕ = 0.4, silica rods
gap = 20 μm

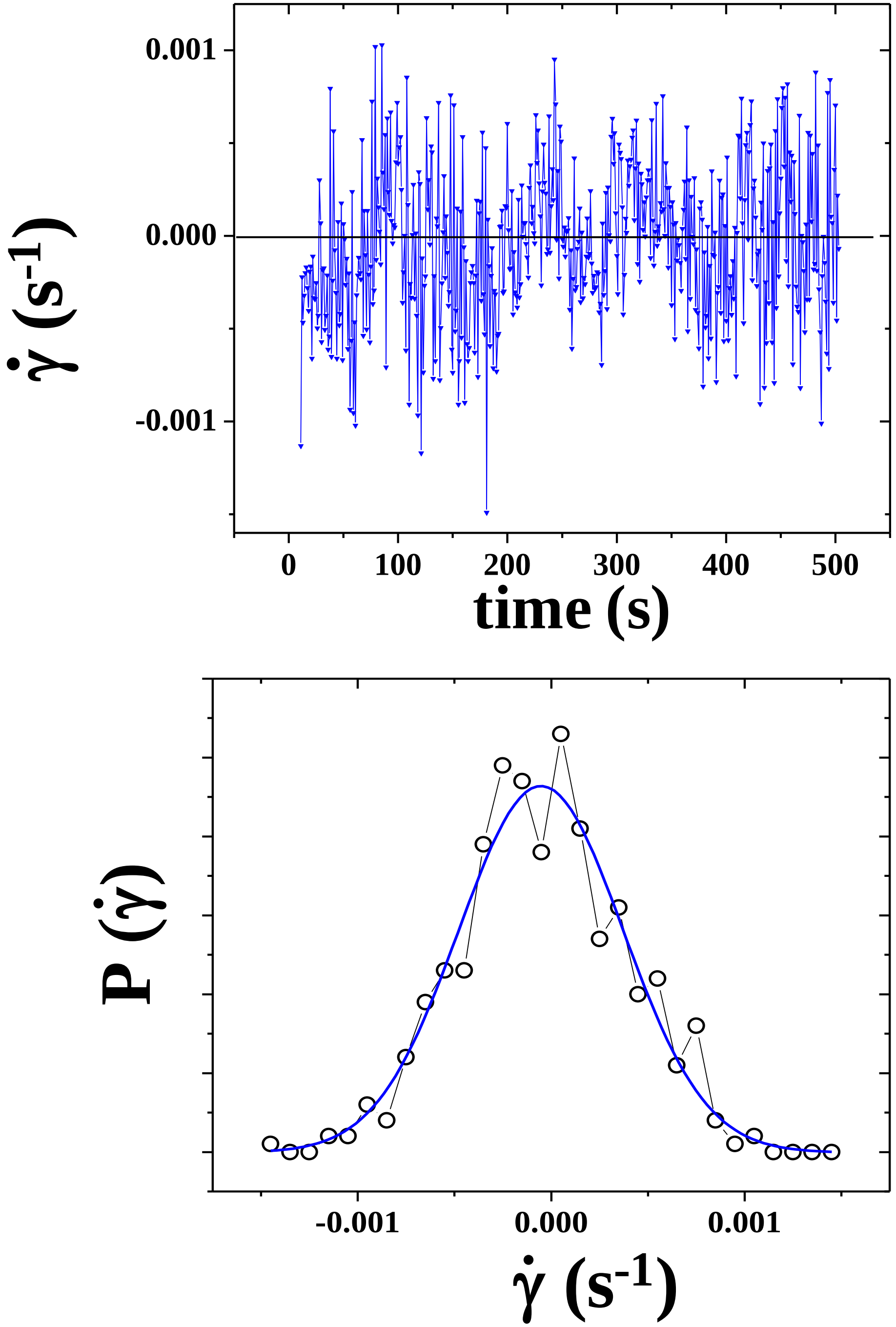




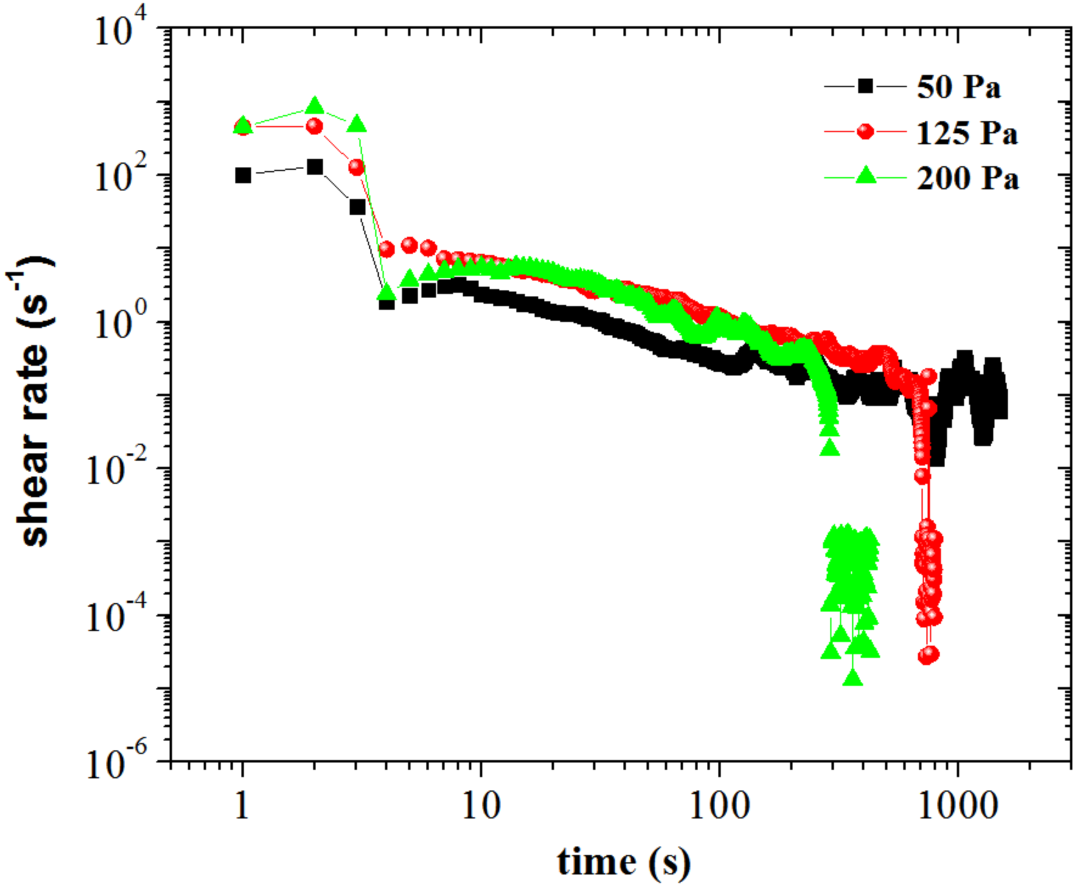
τ = 10 Pa

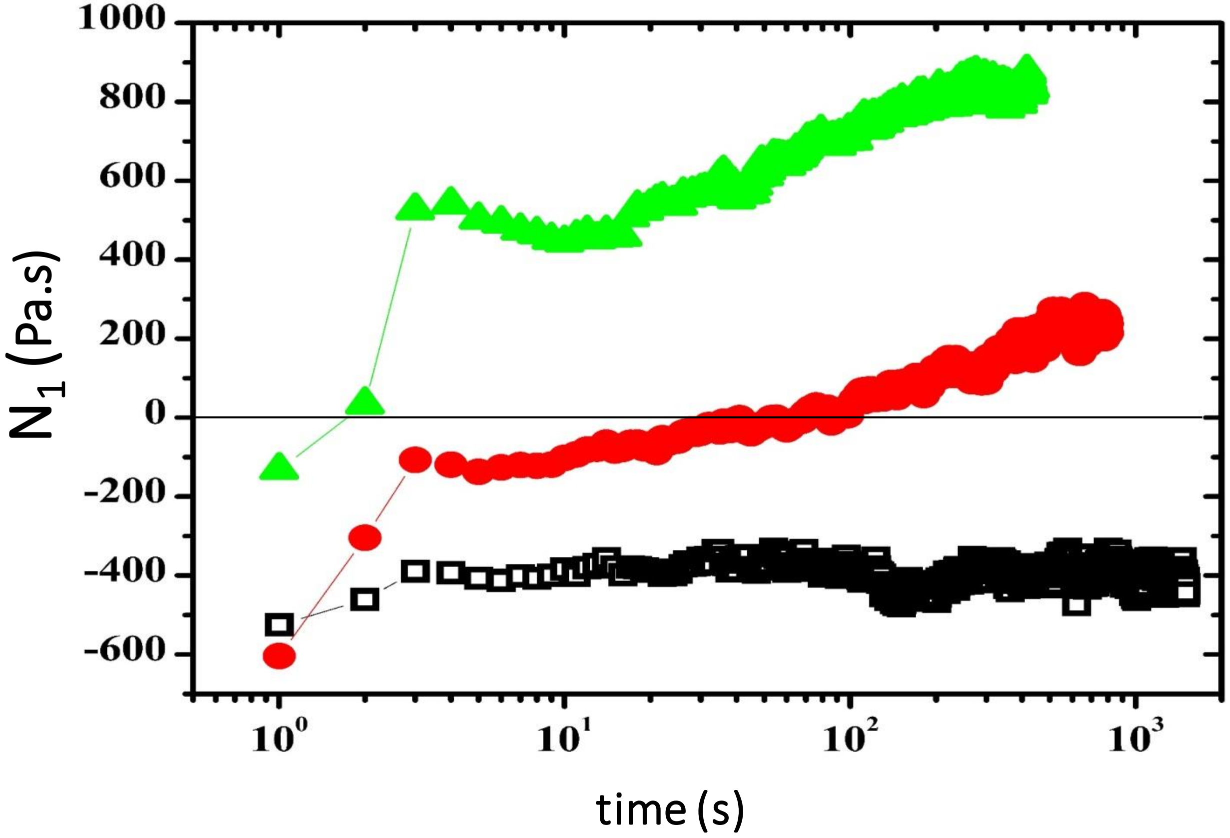


τ = 20 Pa

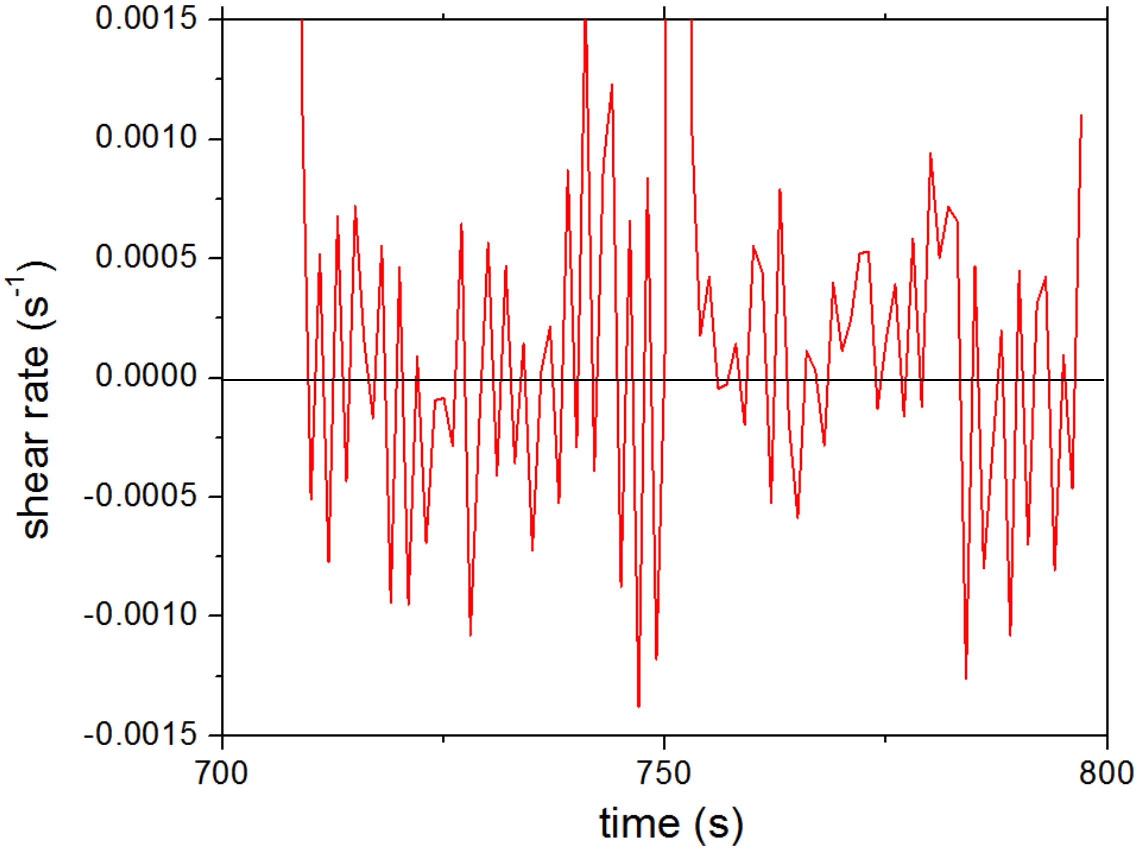


Silica Rods $\phi=0.45$ PP , Gap=20 microns

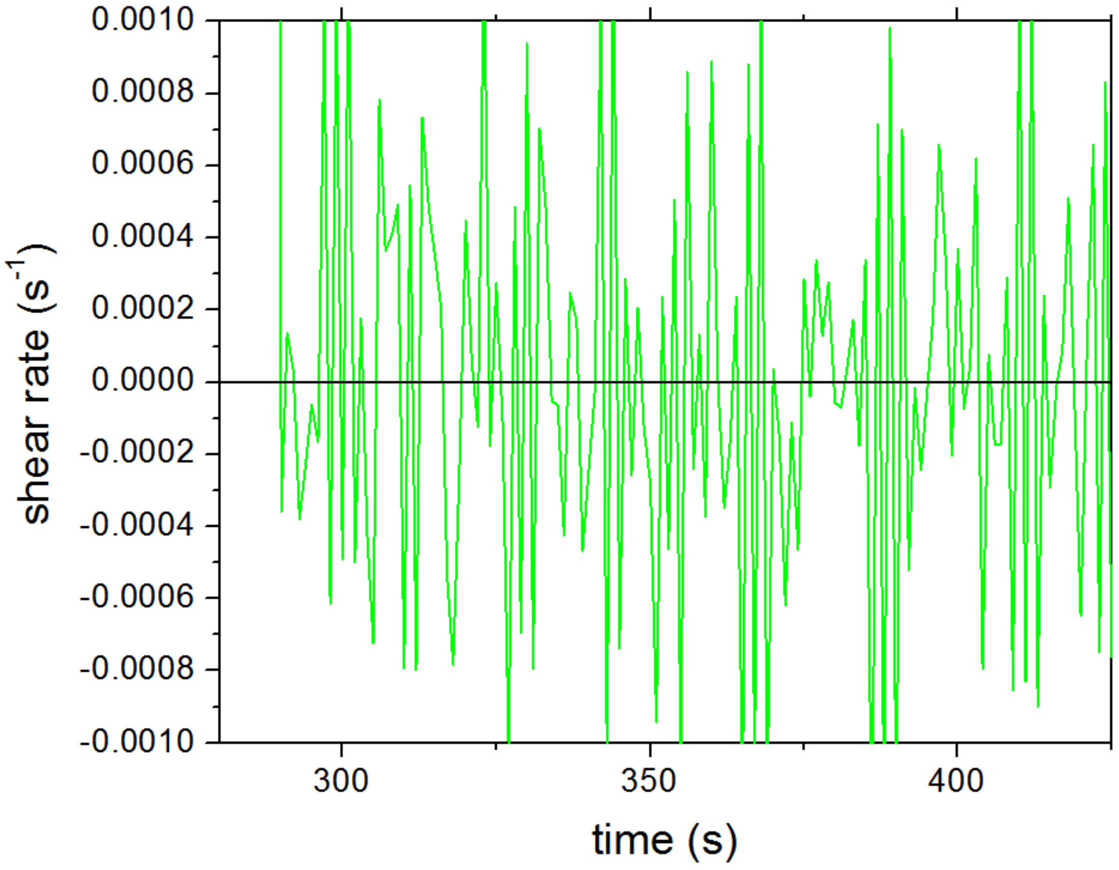




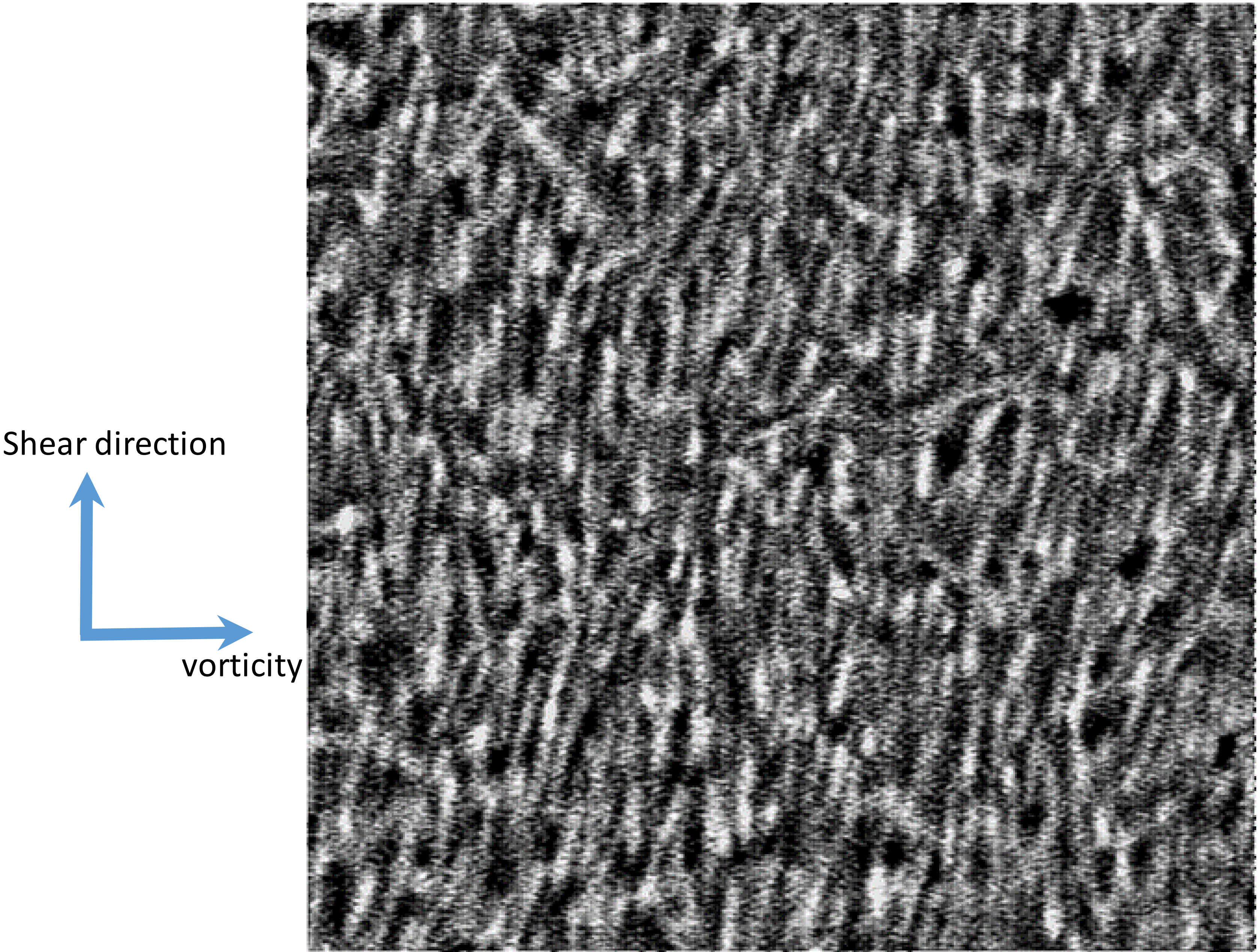
τ = 125 Pa



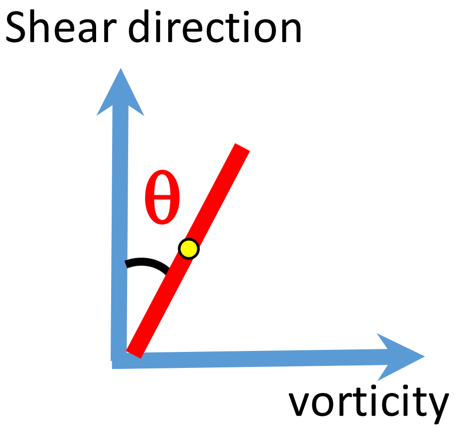
τ = 200 Pa

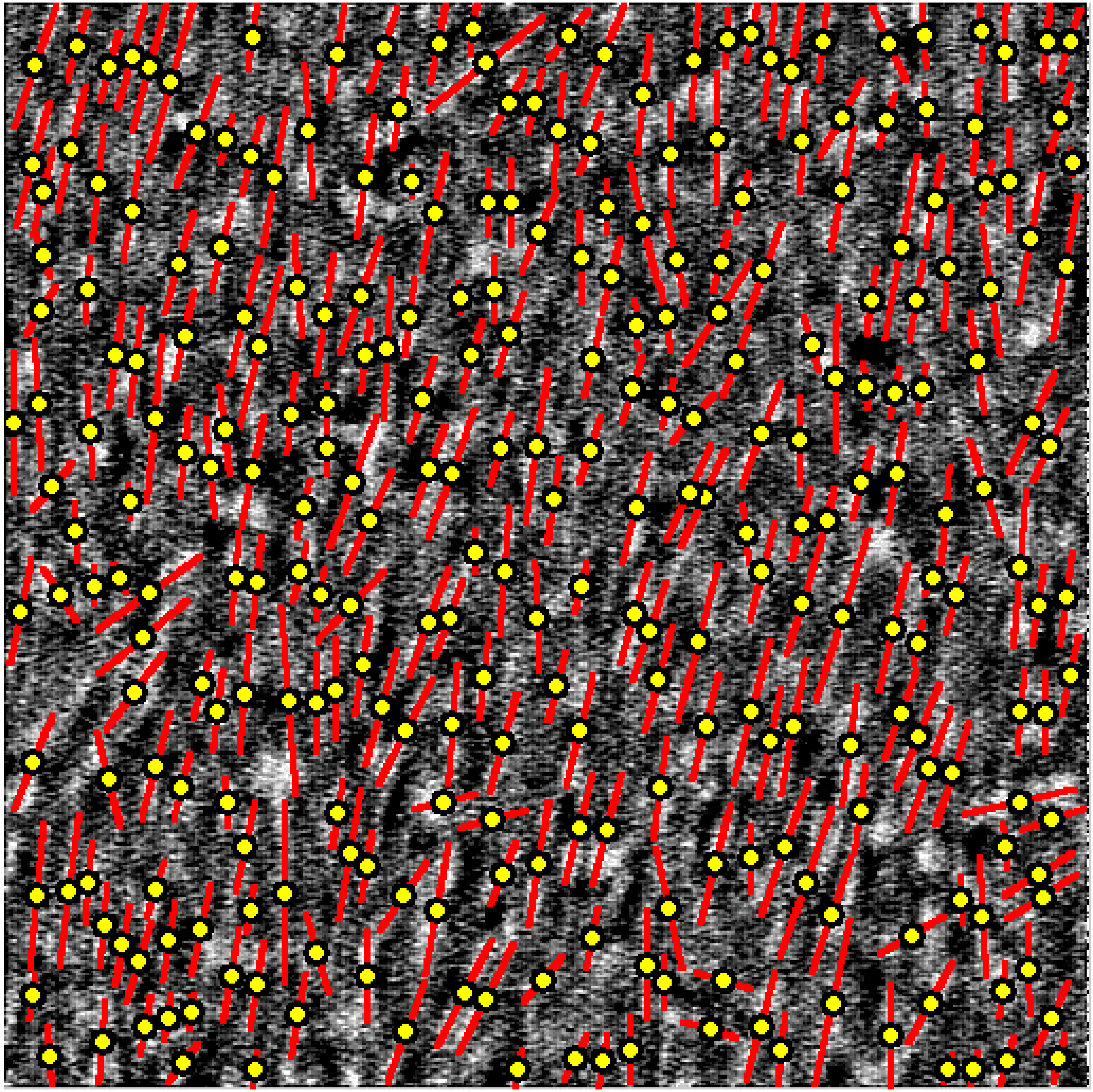


τ = 125 Pa – shear thinning to shear thickened jammed state

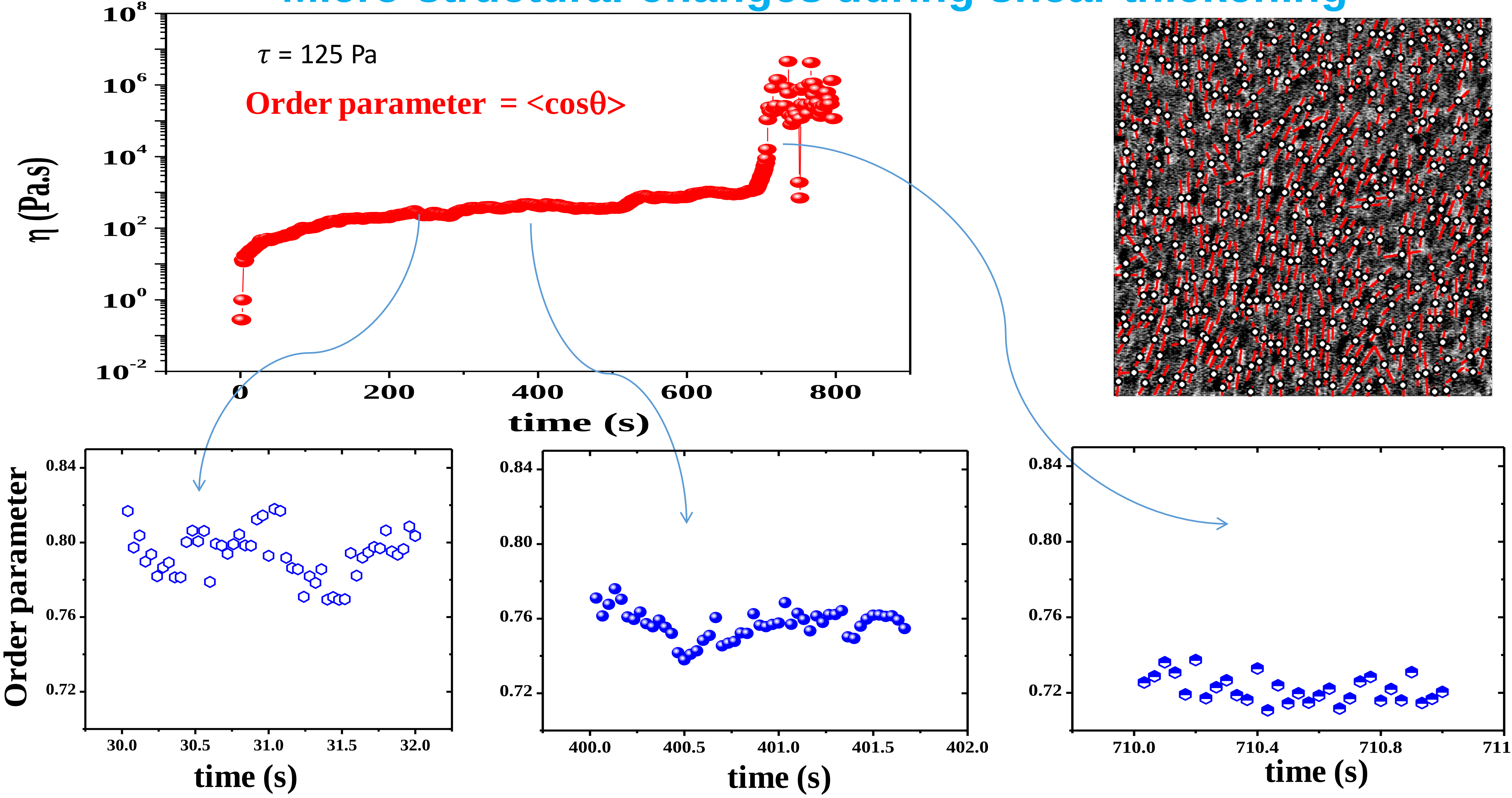


Tracked rods



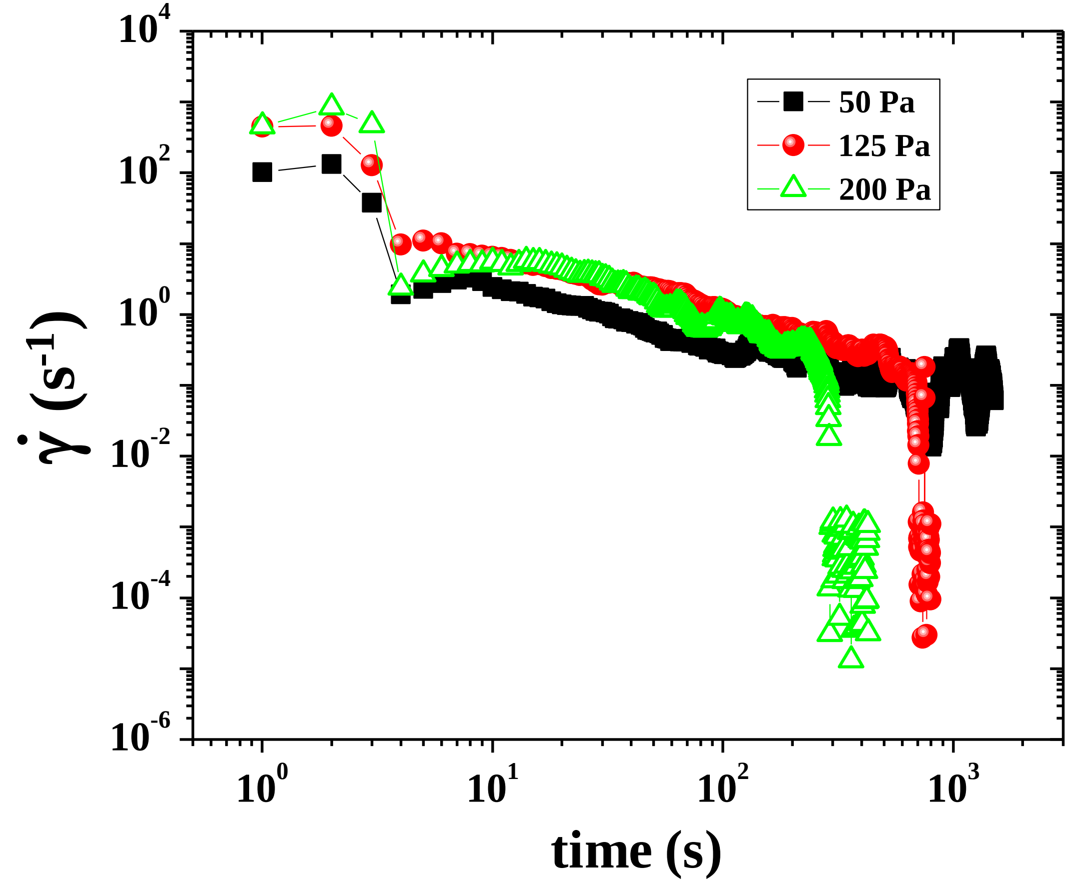


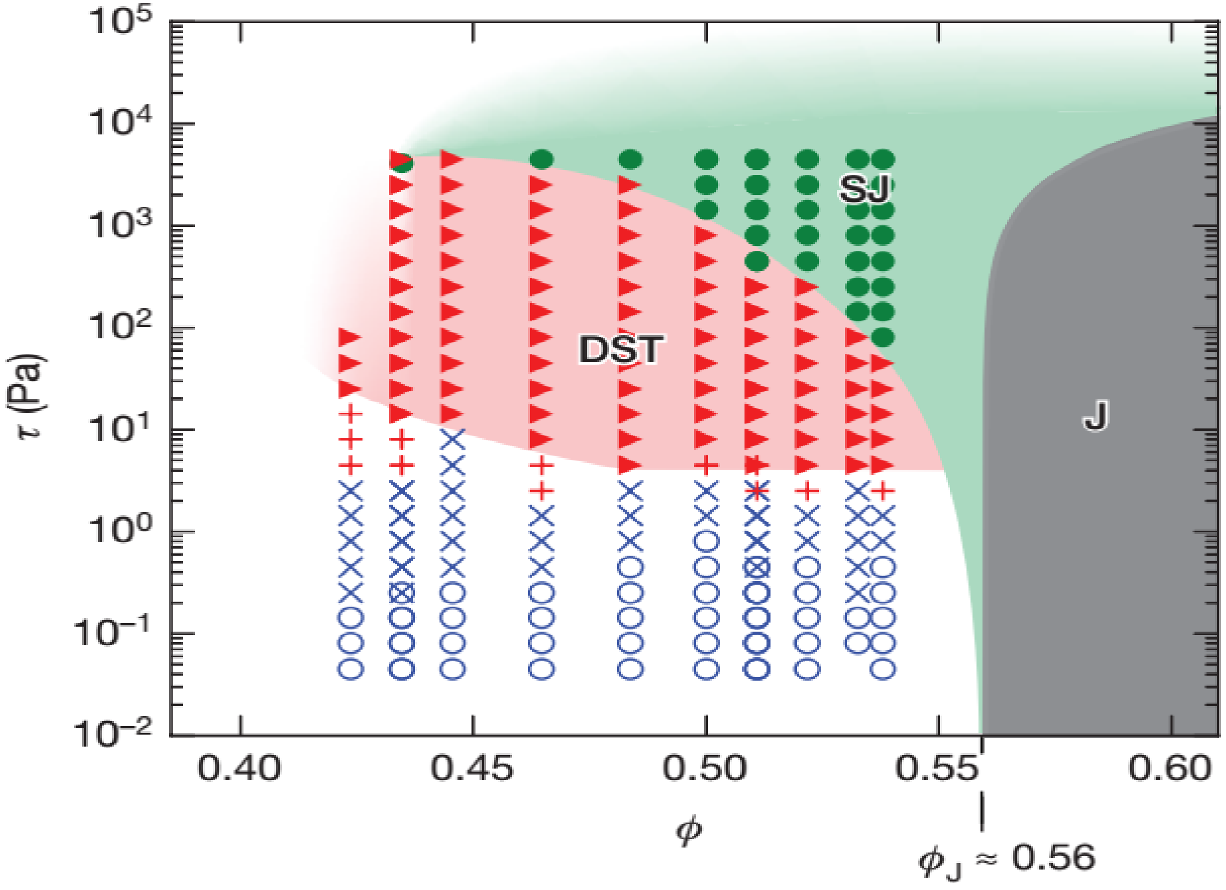
Micro-structural changes during shear thickening



No order-disorder transition

Shear Jamming at long times ??





Ivo et al. Nature 532, 214 (2016)

Frictional contact force chains spanning the entire system are formed as a function of time. This is possible when gap is small and particles are anisotropic.

Concluding this part …

Spheres have point contacts but rods can have line or point contacts and can cause shear thickening at smaller volume fractions.

Evidence of friction is provided by coating the rods with a thermo-responsive polymer coating on the silica particles.

Friction co-efficient increases by an order of magnitude when the polymer brush shrinks above LCST, resulting in DST.

Confinement and longer waiting time results in shear jammed state.

What happens when particles are very rough?

Now revisiting our earlier results on carbon nanotube (CNT) suspensions

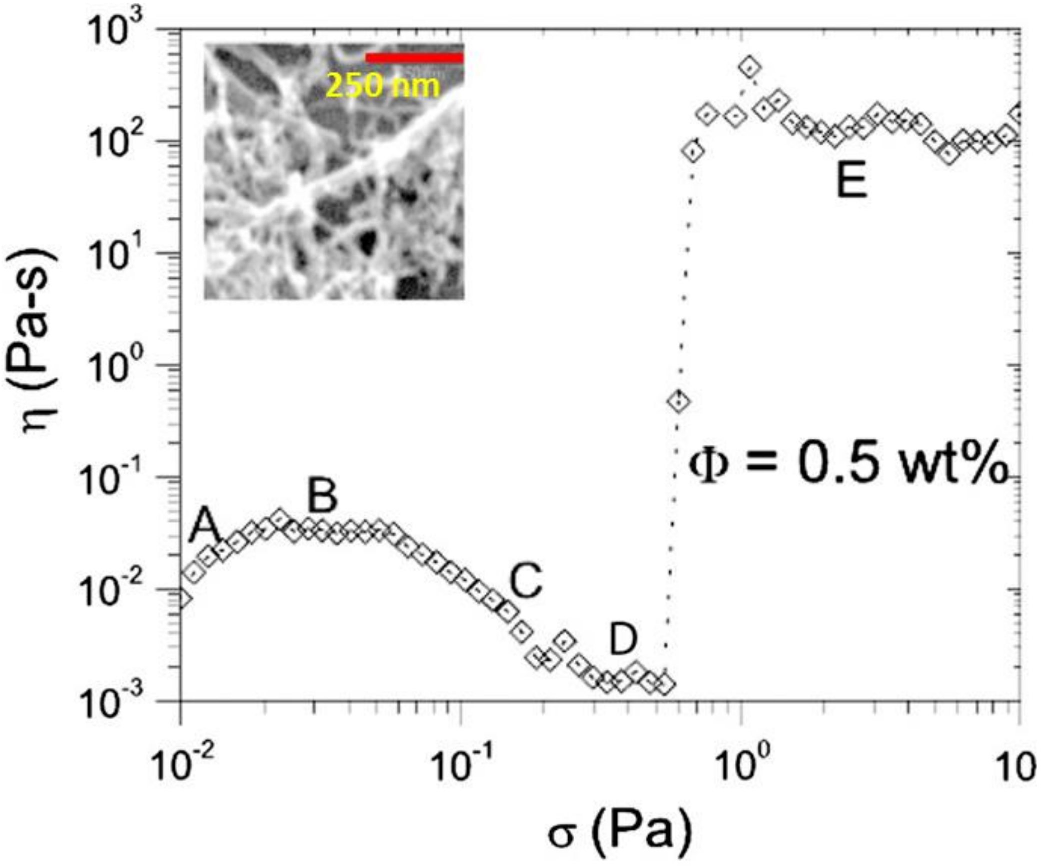
MWNT (15-30 nm dia, ~1 μm length) dispersed in NMP (0.5-10 wt %)
forming large macroscopic (20-100 μm) *fractal* objects

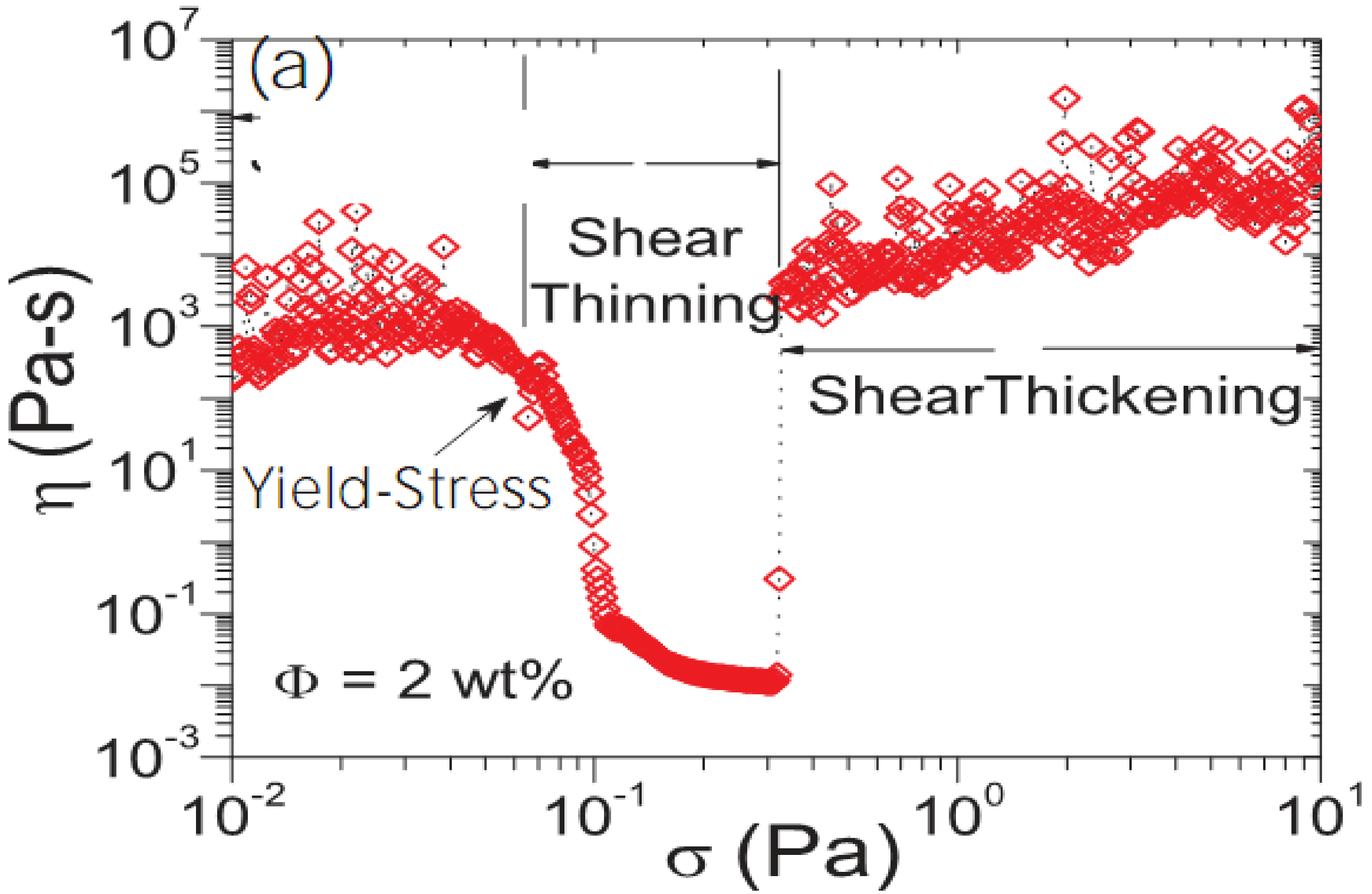
NOT dense suspension in the conventional sense!

Discontinuous shear thickening in confined dilute carbon nanotube suspensions

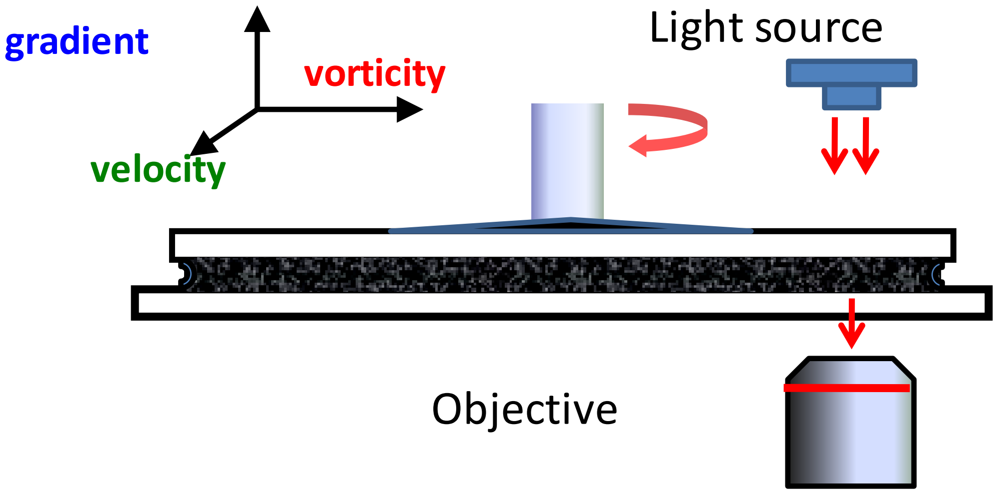
Sayantan Majumdar[a], Rema Krishnaswamy[b], and A. K. Sood[a,b,1]

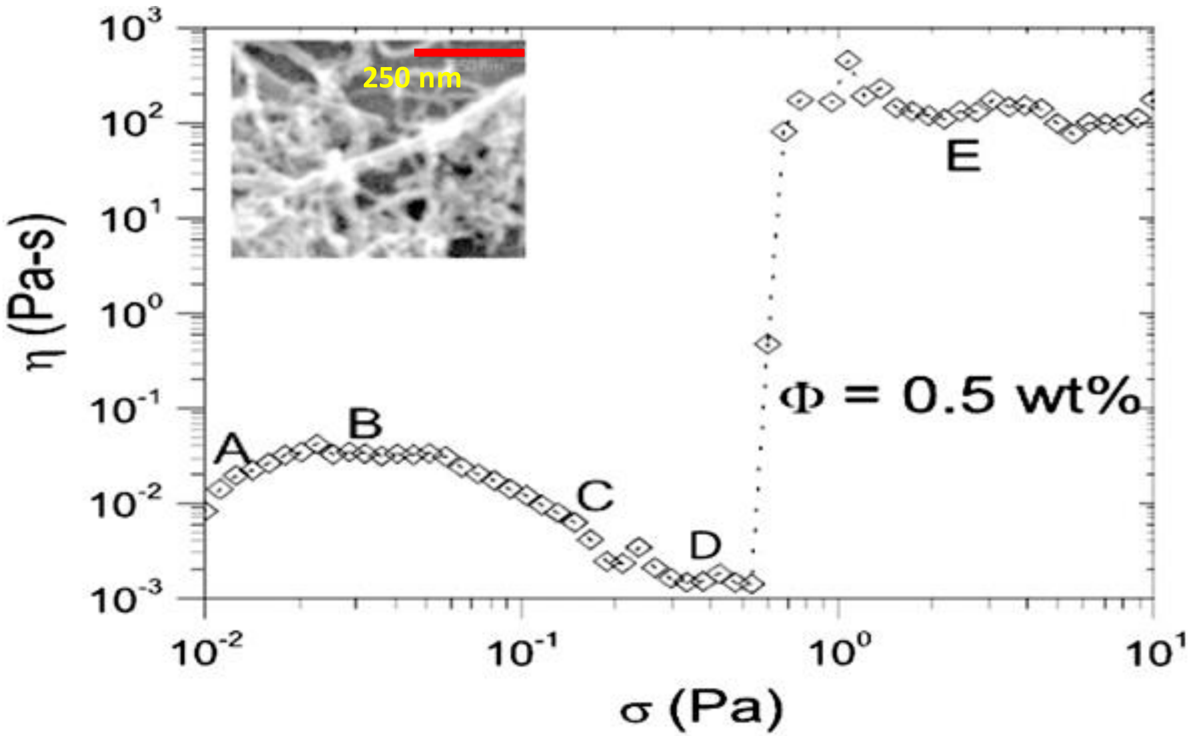
PNAS (2011)

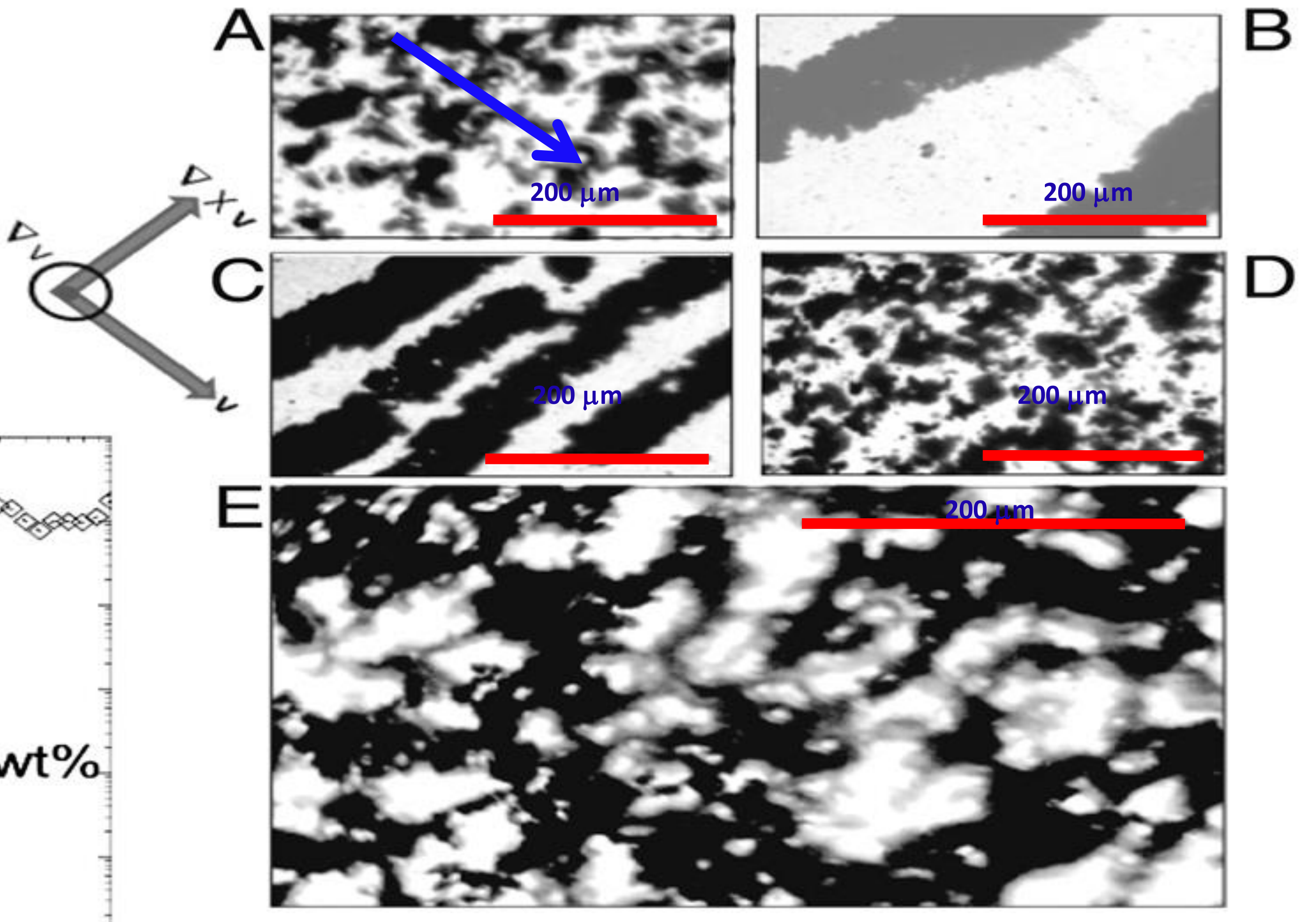


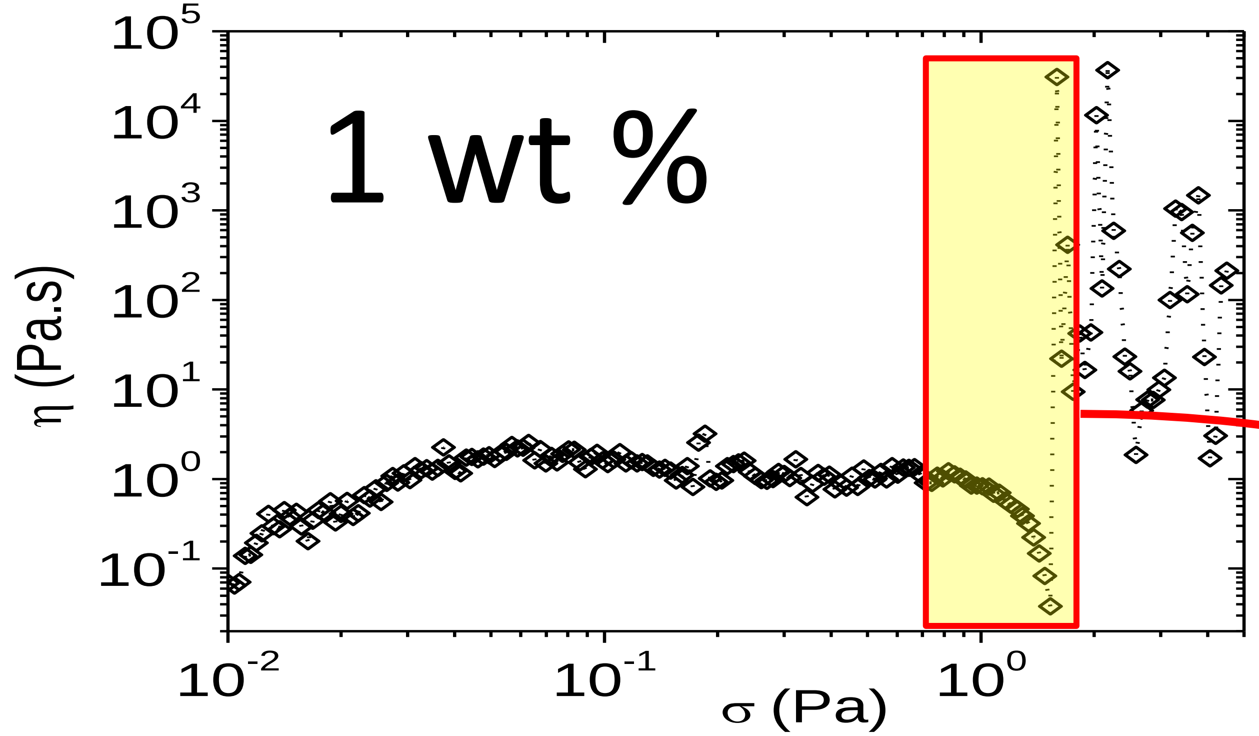


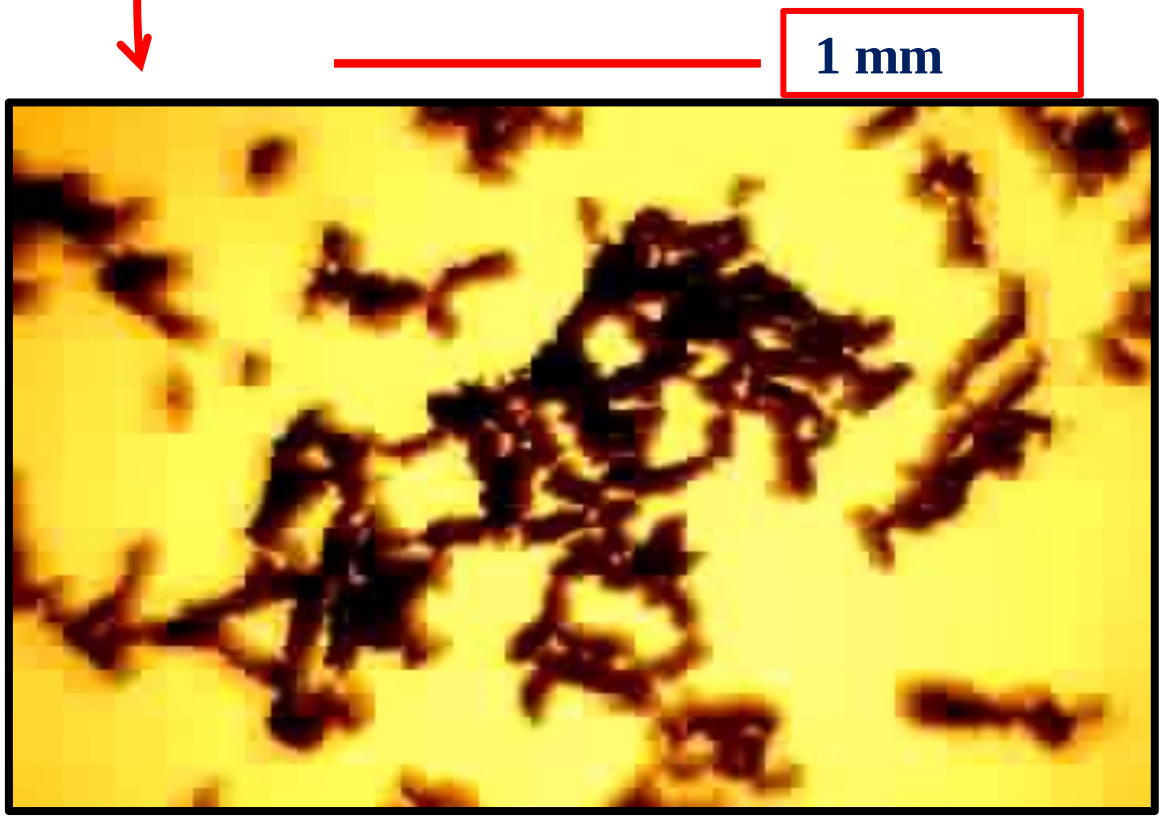
RHEOLOGY AND IN-SITU IMAGING STUDIES



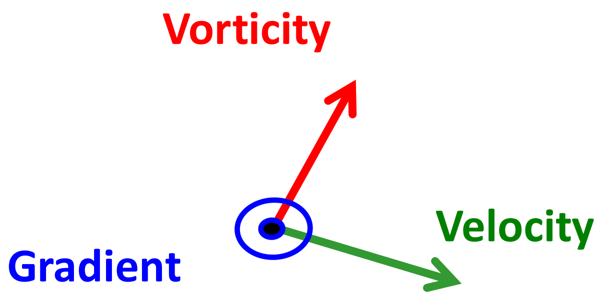





1 wt %
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
η (Pa.s)
10^{-2}
10^{-1}
10^{0}
σ (Pa)

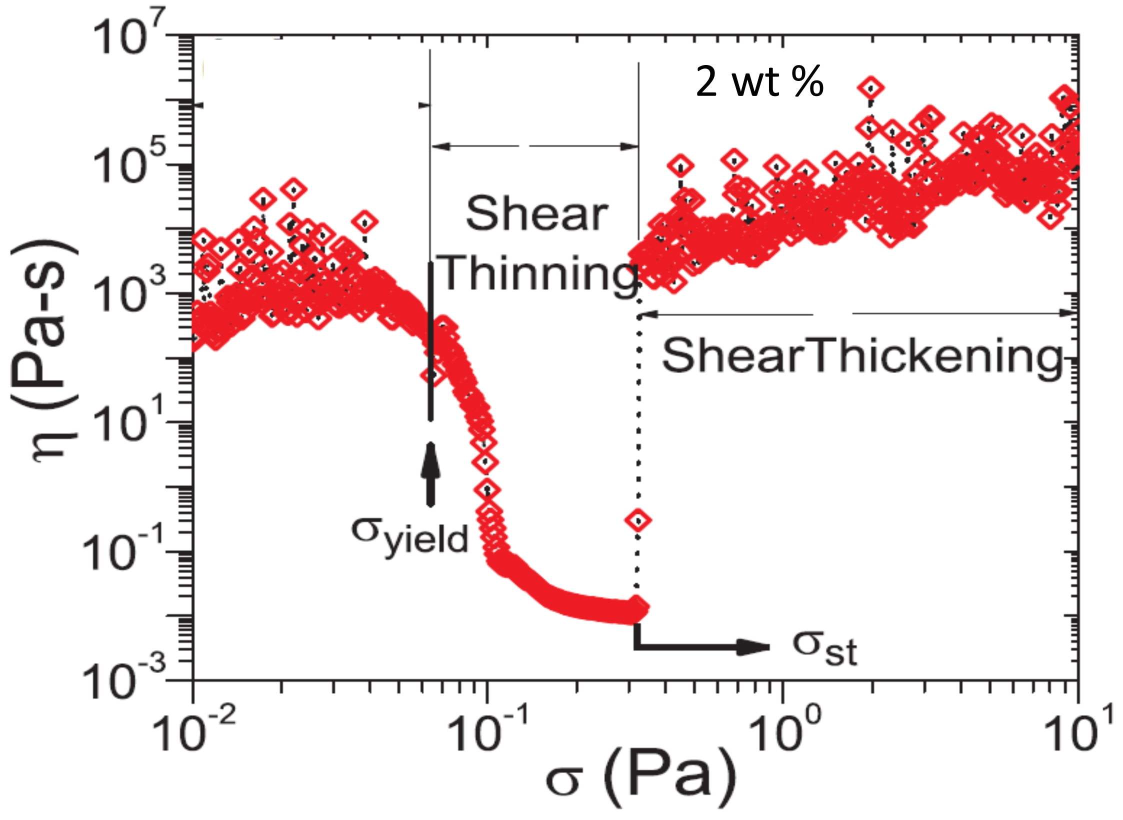

1 mm

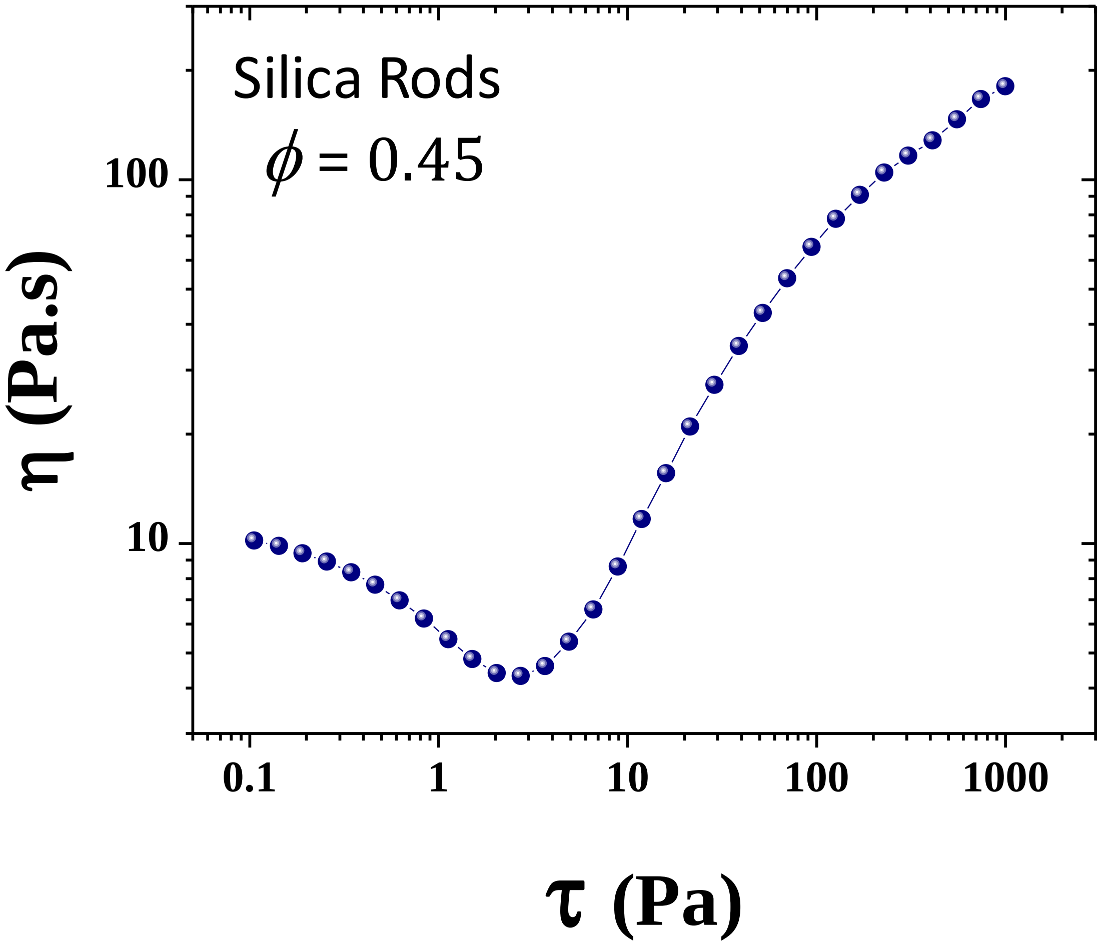
Movie


Vorticity
Velocity
Gradient

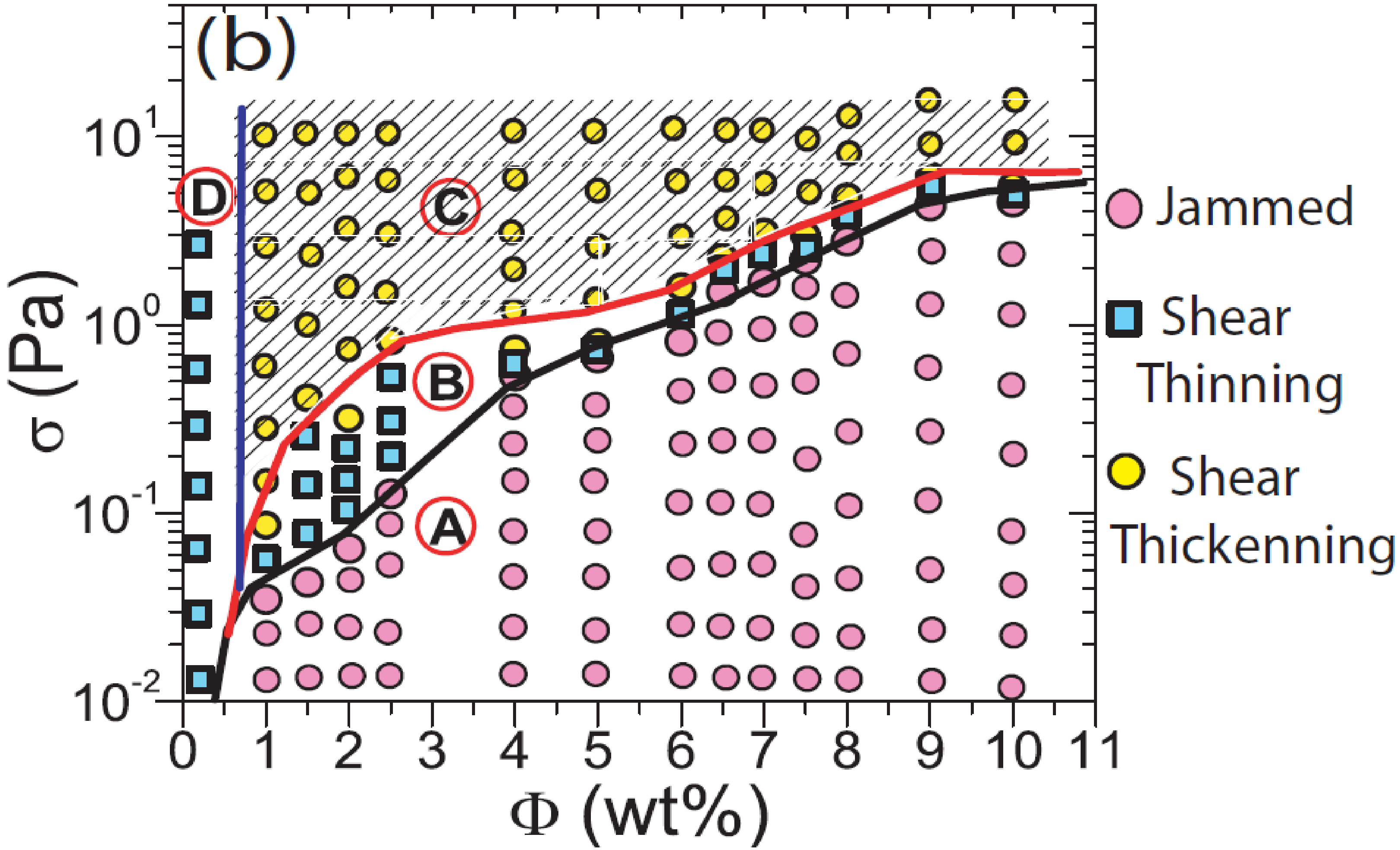
UNUSUAL VISCOSITY-STRESS DEPENDENCE!

Note the sharp increase! Contrast with smoother dependence (for e.g. in silica rods)

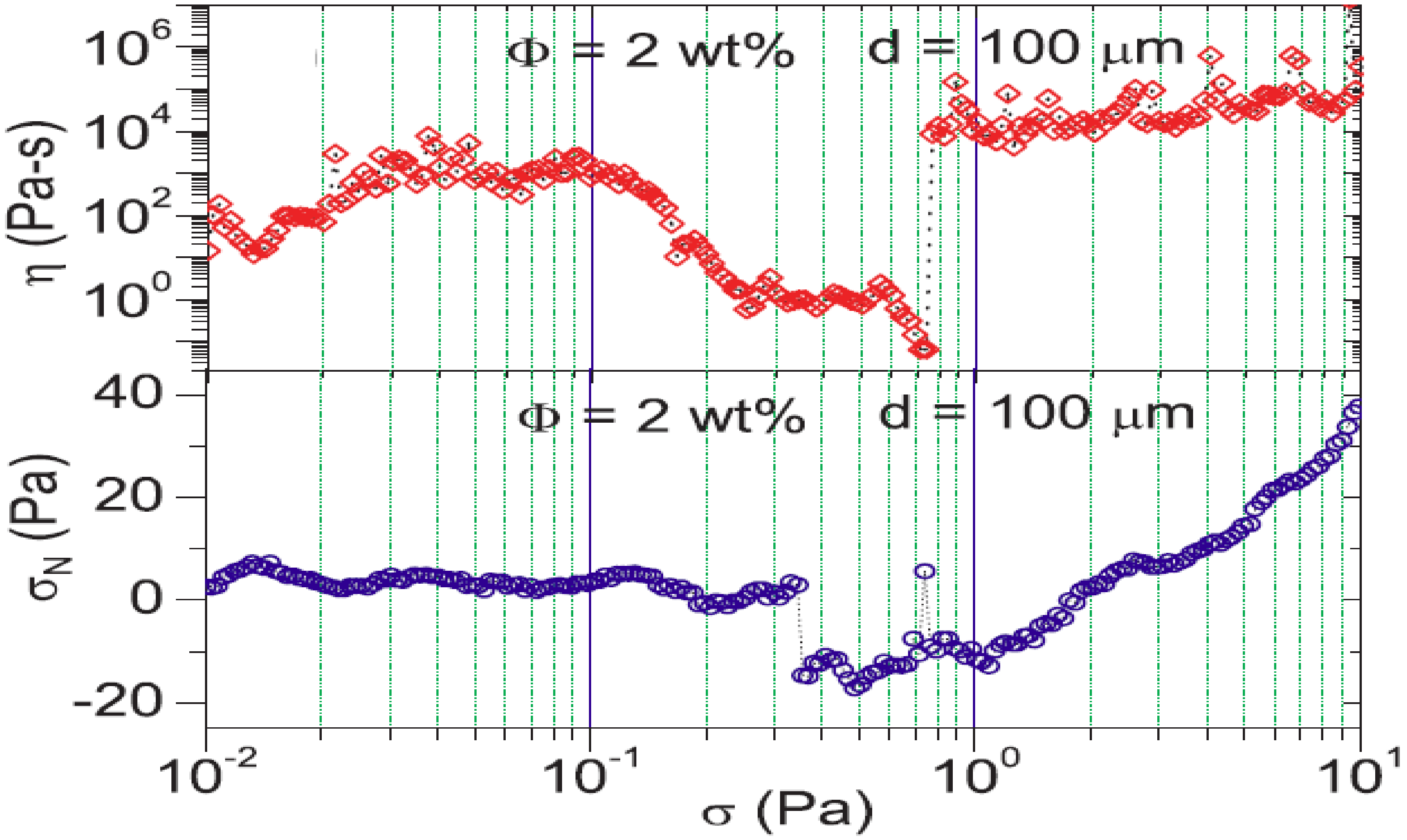


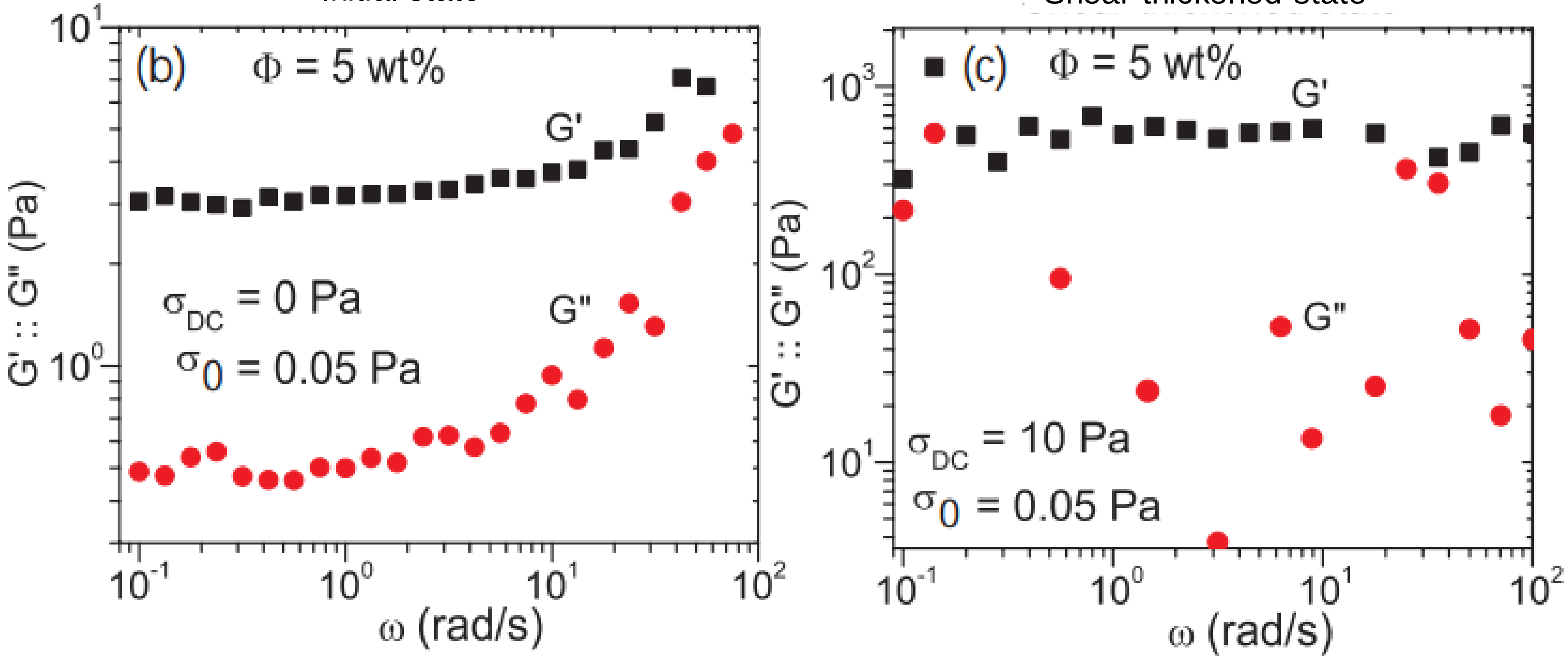


FLOW-CURVE AND PHASE DIGM. FOR DILUTE MWNT SUSPENSIONS



Normal Stress Difference measured in PP Geometry



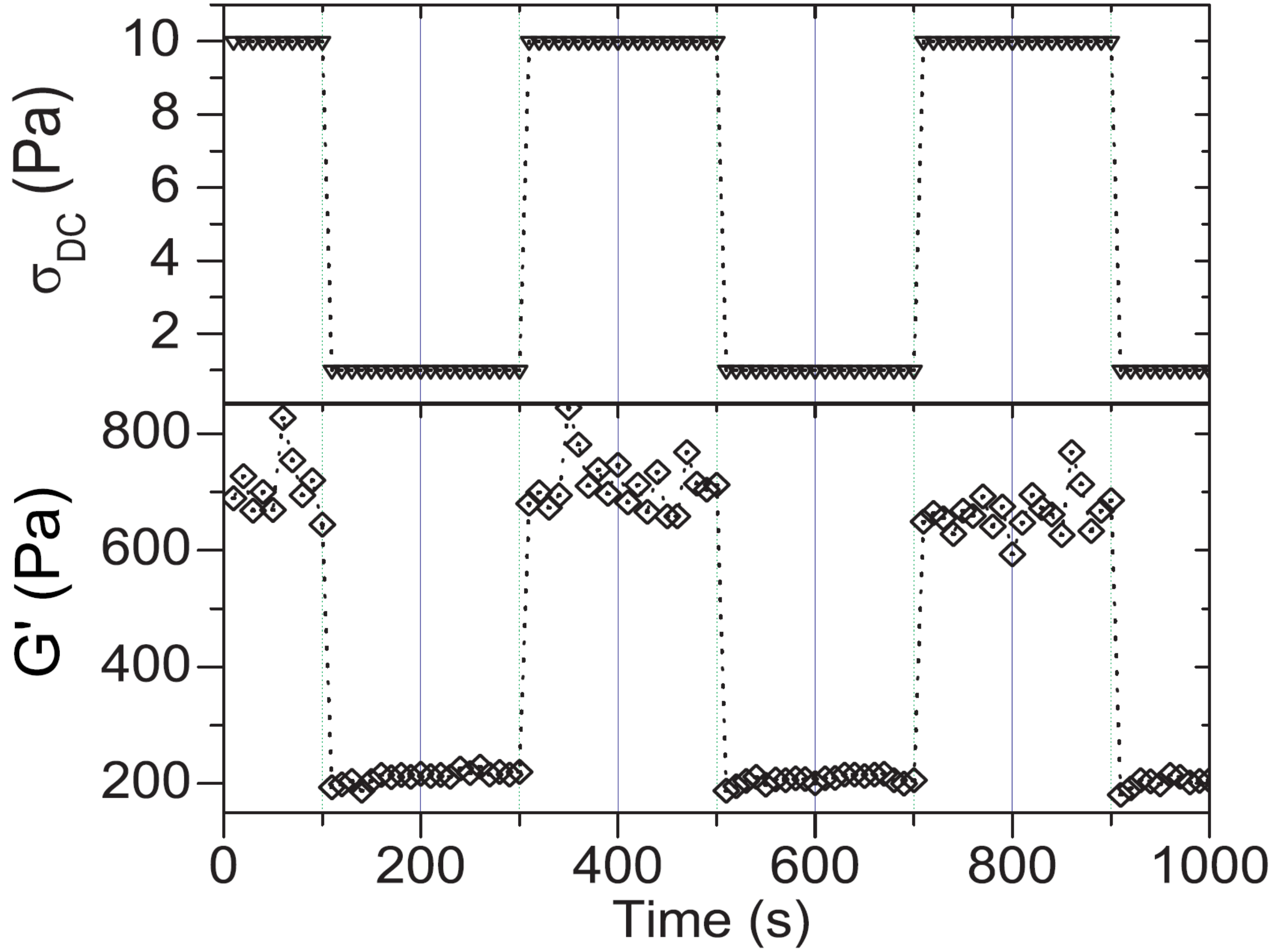


Initial state

Shear thickened state

TUNING OF ELASTICITY OF ST STATE

$$\sigma(t) = \sigma_{DC} + \sigma_0 \sin\omega t$$



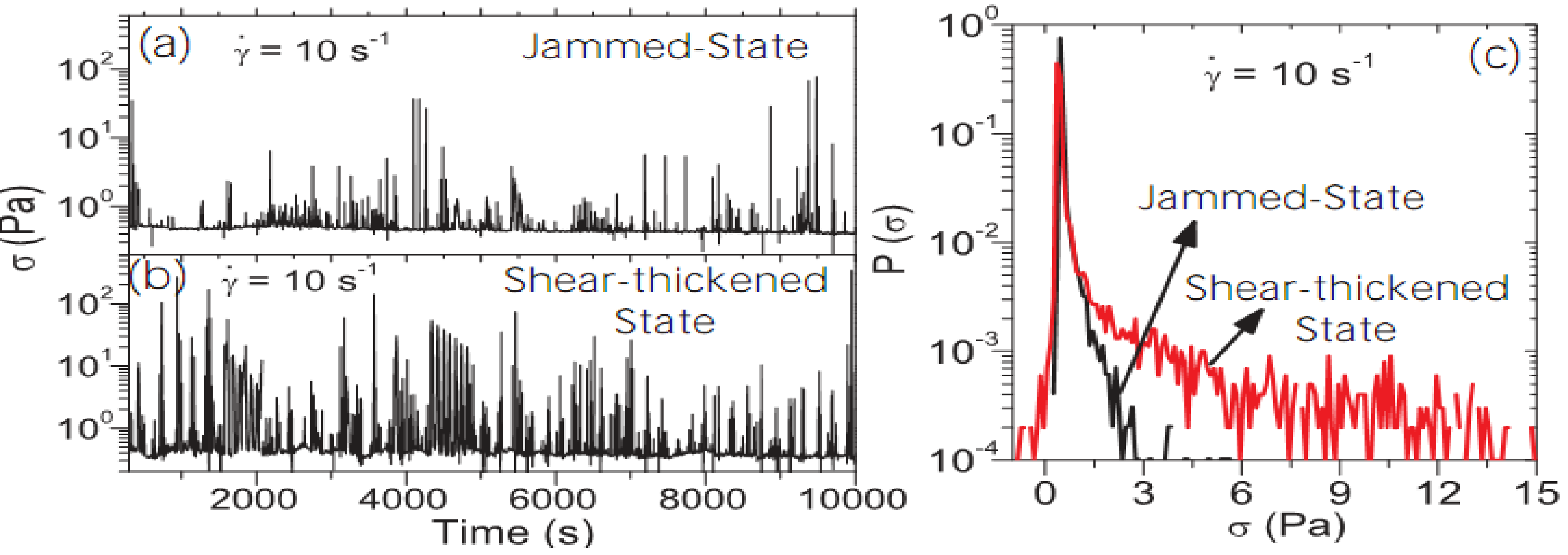
The response is instantaneous.

Applied A.C. amplitude for measuring G':

$\sigma_o = 0.5$ Pa

Increasing σ_{DC} enhances the cluster –cluster contacts and forms a stronger network.

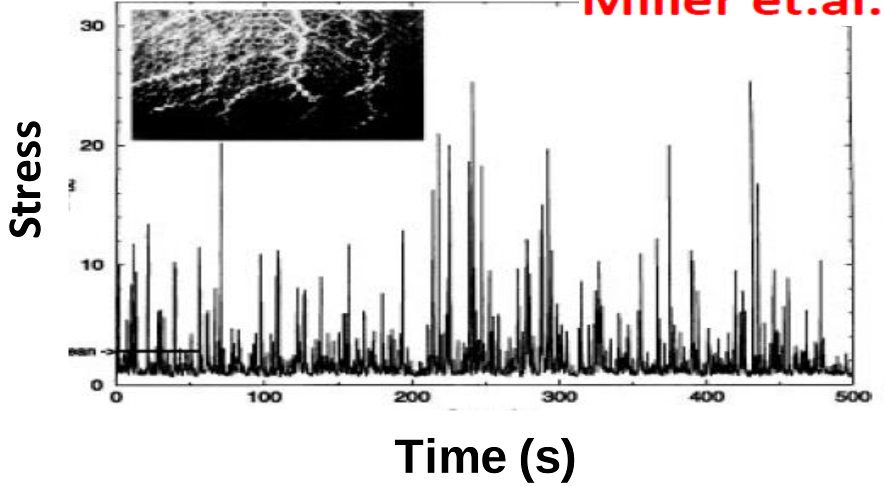
STRESS FLUCTUATIONS AT CONSTANT SHEAR-RATE



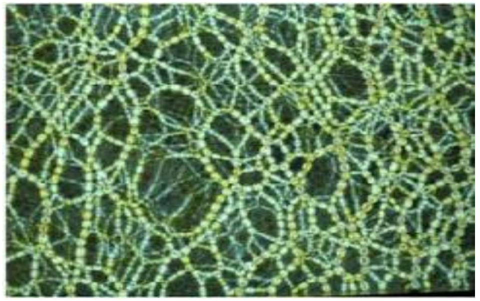
Percolated structures are connected network due to floc-floc contacts spanning system size.

Similar stress fluctuations have been observed in dense granular flows

Miller et.al. PRL (1996)

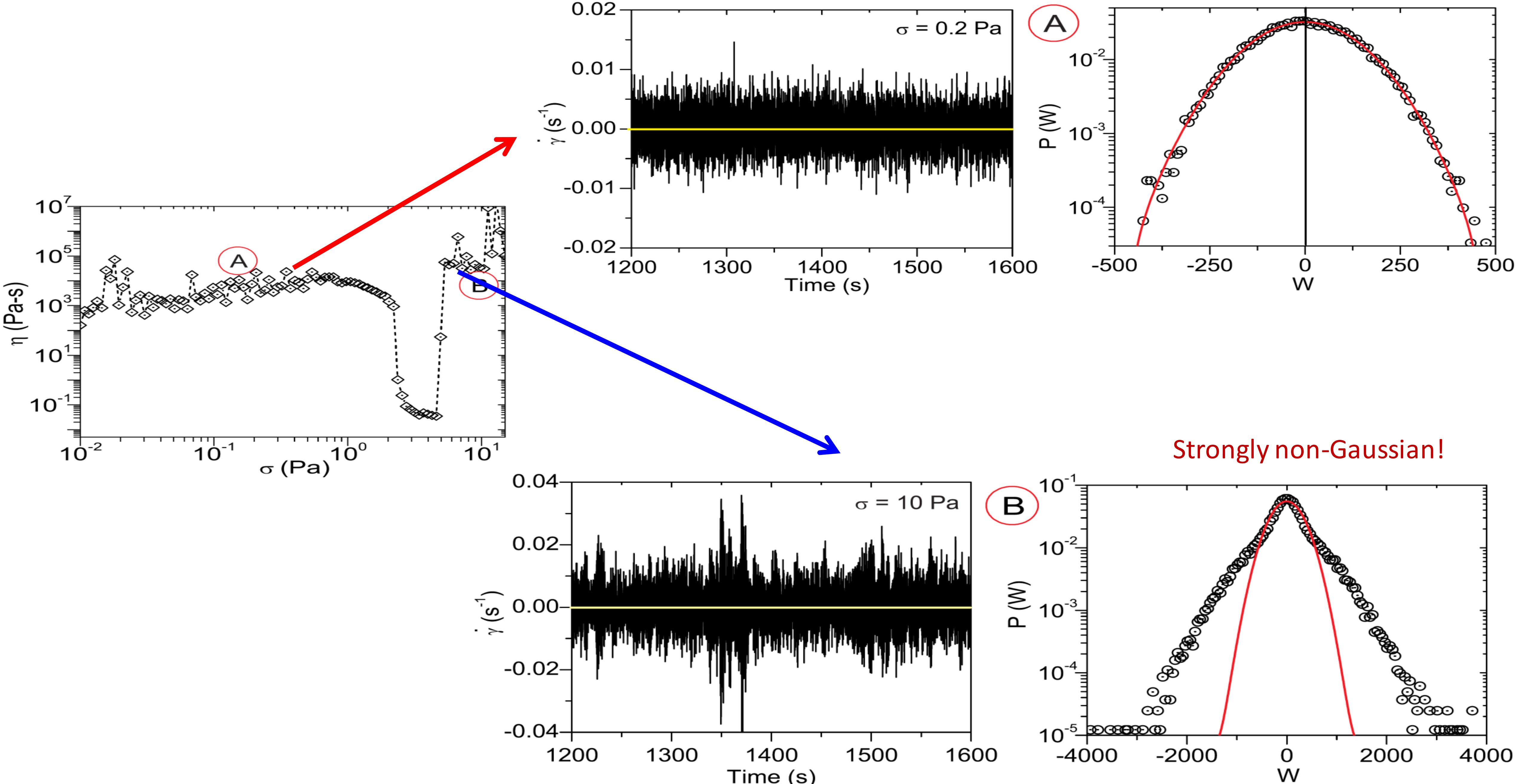


Percolated structures are stress bearing chains forming a network due to bead-bead contacts spanning system size.



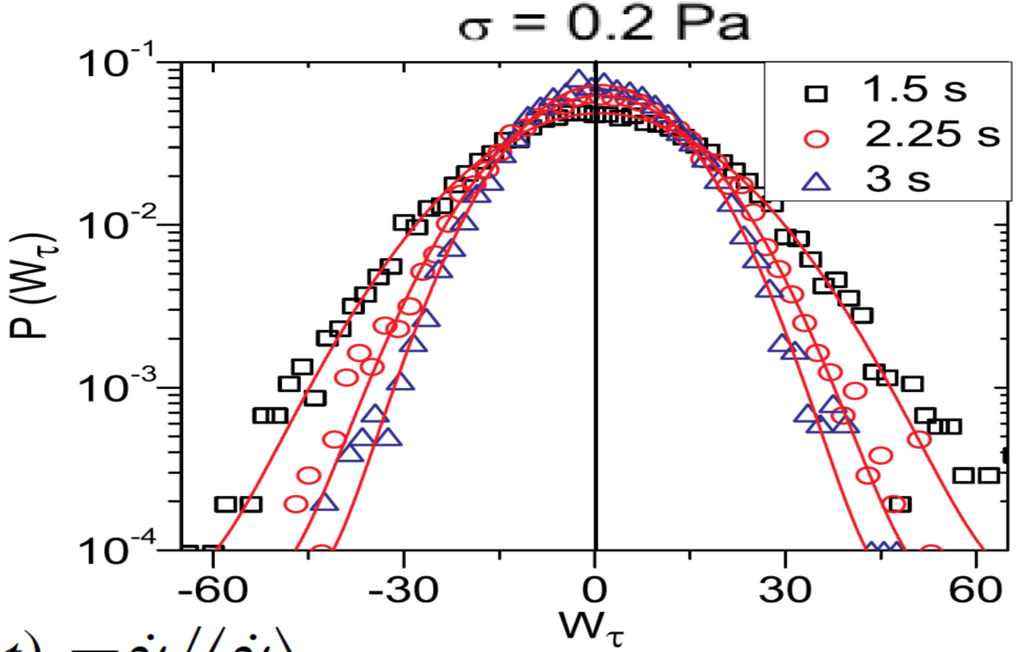
R.P. Behringer group website

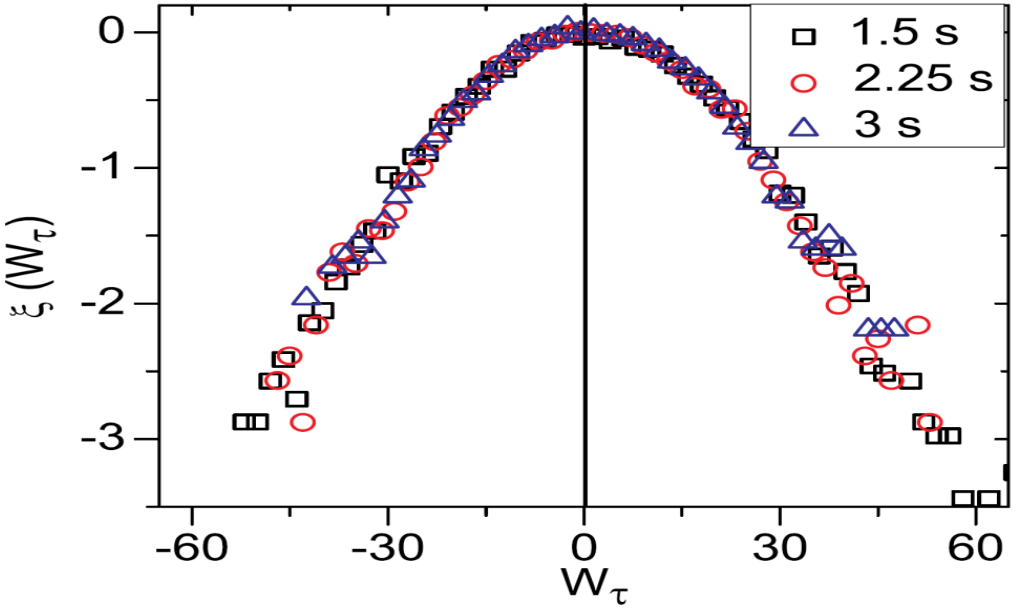
STRAIN-RATE FLUCTUATIONS AT CONSTANT SHEAR STRESS



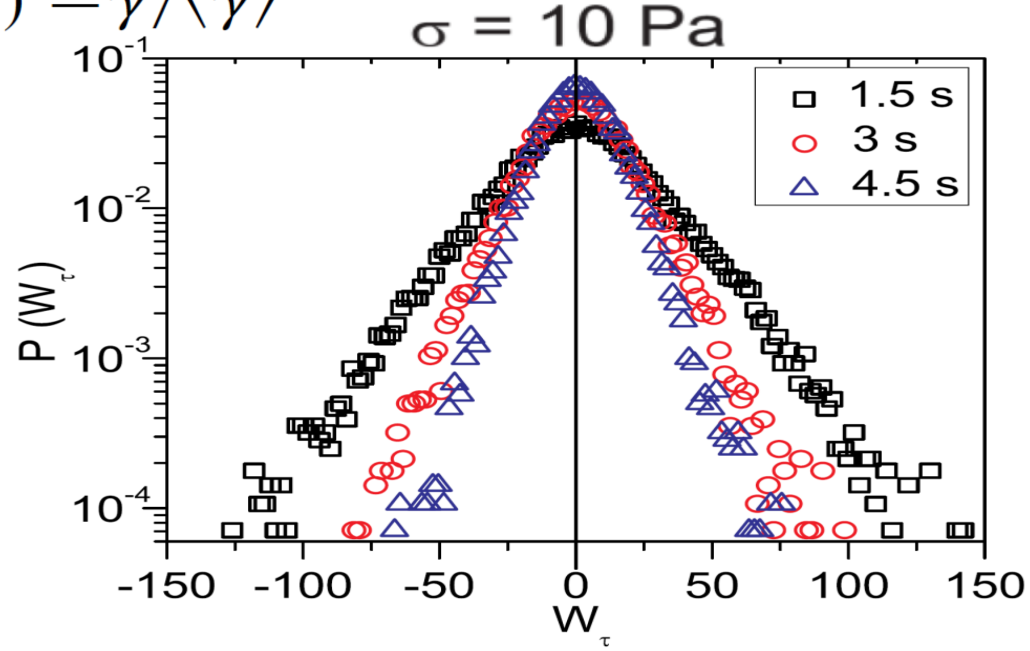
Strongly non-Gaussian!

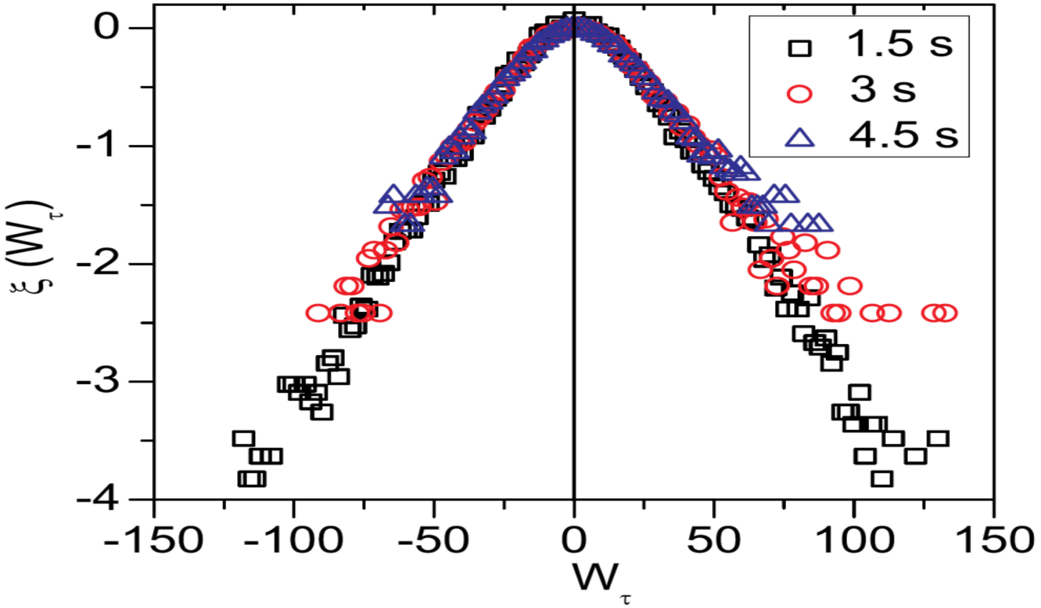
SCALING OF PDFS





$$W(t) = \dot{\gamma}/\langle\dot{\gamma}\rangle$$





Nonequilibrium Fluctuation Theorem………

On an average heat flows from hot to cold

Average heat flux direction

(Entropy production)

$\Delta S>0$

T_H

T_C

Rare event

$\Delta S<0$

(Entropy consumption)

- **Fluctuations in heat current flowing from cold to hot can be observed for a short time.**

What is the probability of such rare events ?

. ***Source of fluctuations is coupling with the heat bath.***

How do we analyze negative shear rate events??

$$W_\tau = \frac{S_\tau}{< S_\tau >} = \frac{\int_t^{t+\tau} S(t)dt}{< S_\tau >}$$

$S(t)$ is instantaneous
Entropy production rate.

- For large τ :

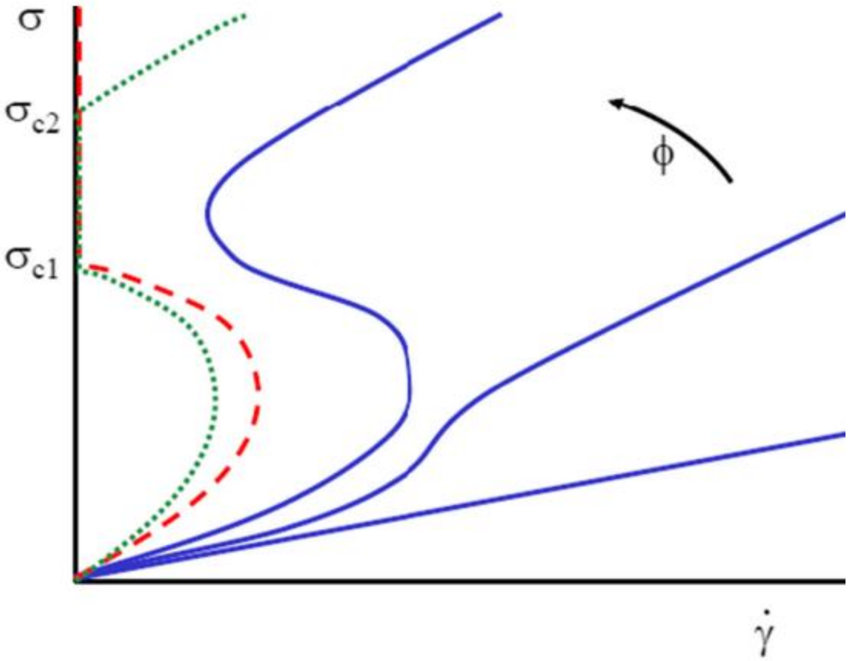
<S> : Mean phase space
contraction rate

$$\frac{P(W_\tau)}{P(-W_\tau)} = \exp[\tau W_\tau < S >]$$

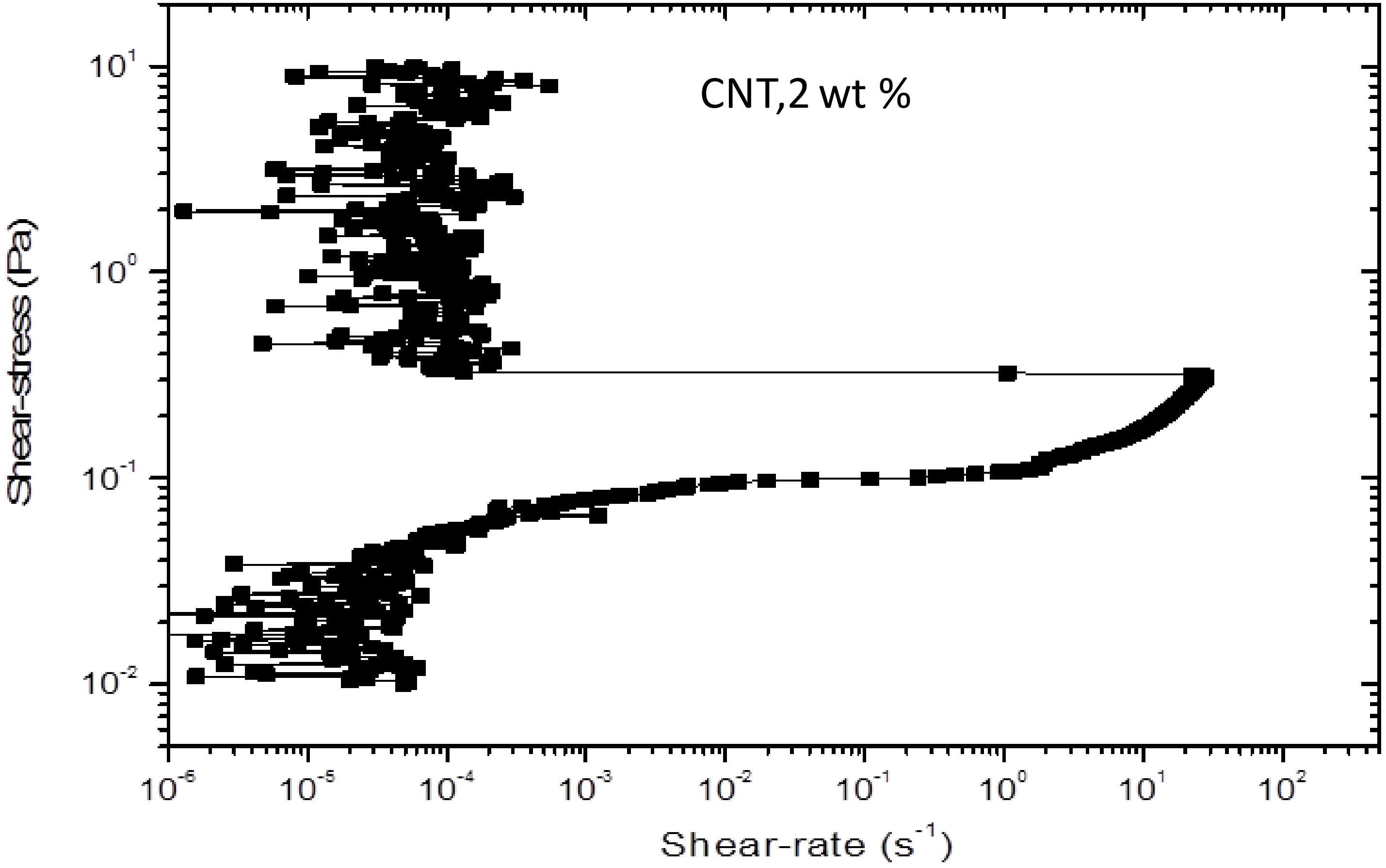
Fluctuation Theorem

Gallavotti & Cohen: PRL (1995) & JSP (1995)

“Shear thickened” state is unusual…
Perhaps the Shear Jammed state?



M. Cates and M. Wyart, Rheol Acta (2014) 53:755–764



Conclusions

Need to redefine "dense" suspensions which show ST.

Observed gigantic effect of fractal nature of participating entities on flow behavior.

The final state at higher stress following the shear-thinned state is likely a shear jammed state.

Thank you