Plasticity and Flow of Soft Materials

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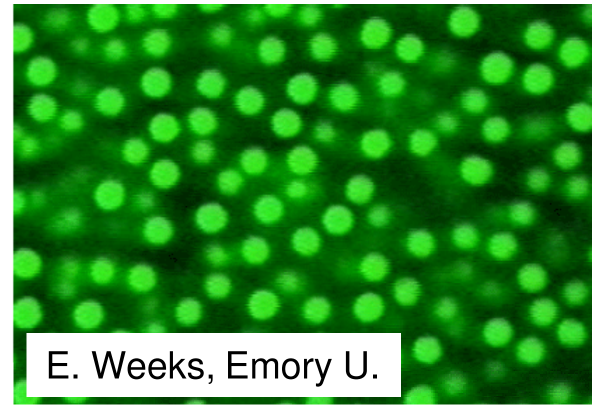
Complex Fluids under Mechanical Stress

From the process of industrial fluids ...... *to the flow of soft glasses*

http://mocoloco.com/art/archives/001001.php



- shear-induced transitions
- solid-liquid transition

Outline

I. Soft 2D columnar crystal

A) **Designing** a versatile self-assembled structured system

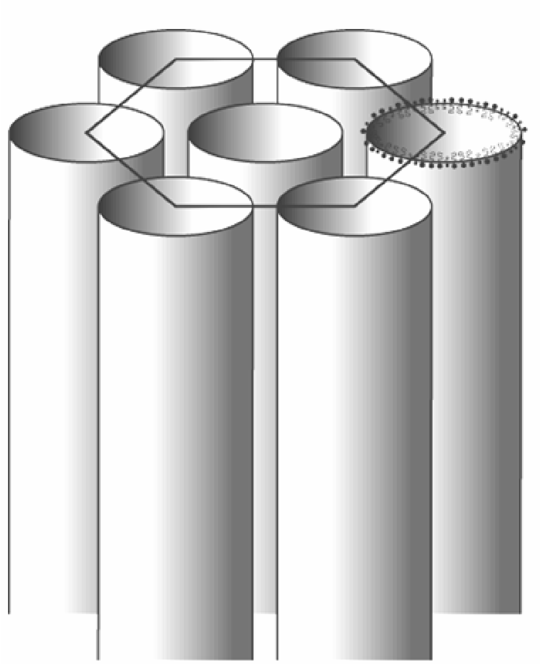
B) **Flow -** characterizing and modeling the shear-induced transition

C) **Plasticity -** Understanding the solid-liquid transition in complex fluids

II. Towards the plasticity of soft 3D polycrystals

III. Plasticity and spontaneous dynamics of soft glasses

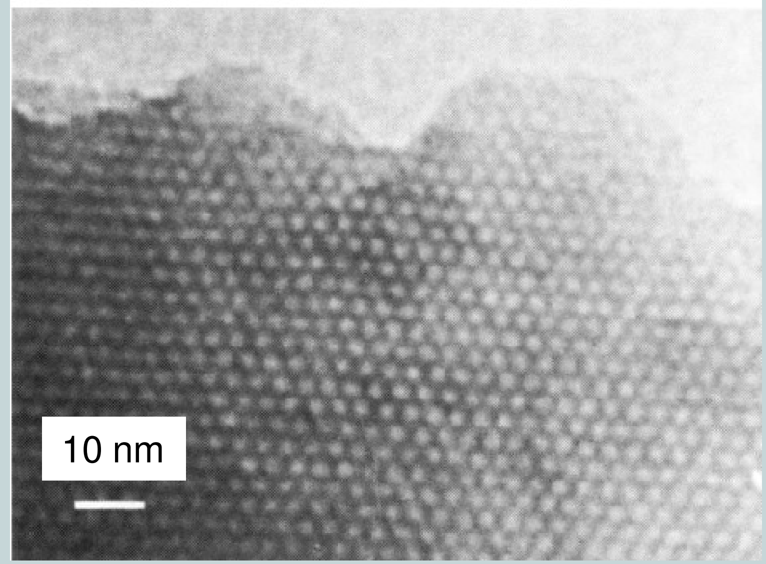
Self-Assembled Hexagonal Phases as Templates for Nanomaterials

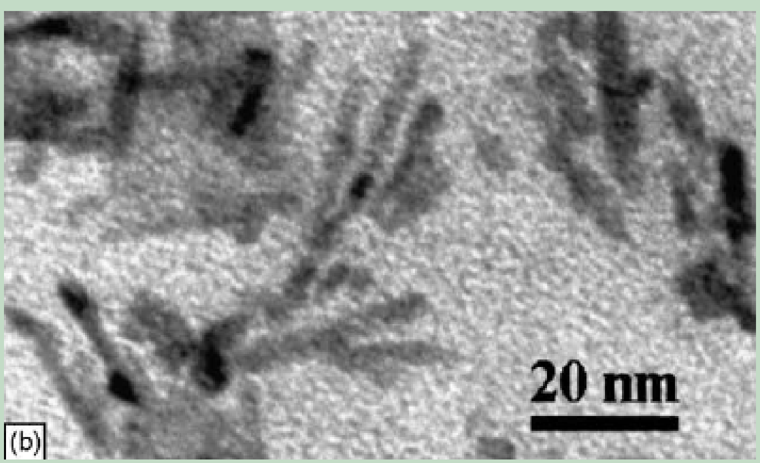


Liquid-crystalline phases as templates for the synthesis of mesoporous silica

George S. Attard, Joanna C. Glyde & Christine G. Göltner

NATURE · VOL 378 · 23 NOVEMBER 1995





In situ templating of PbS nanorods in reverse hexagonal liquid crystal

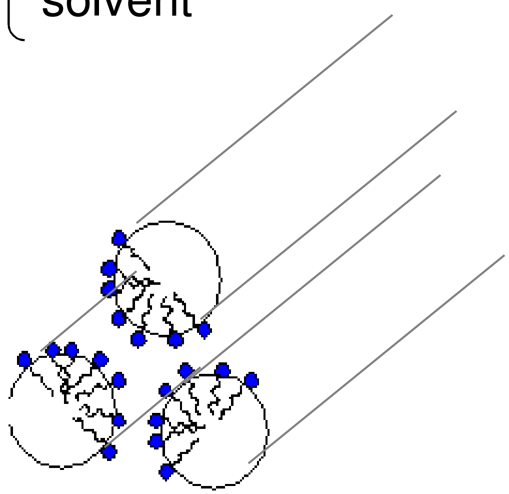
Huang et al. Colloids and Surf. A 2004

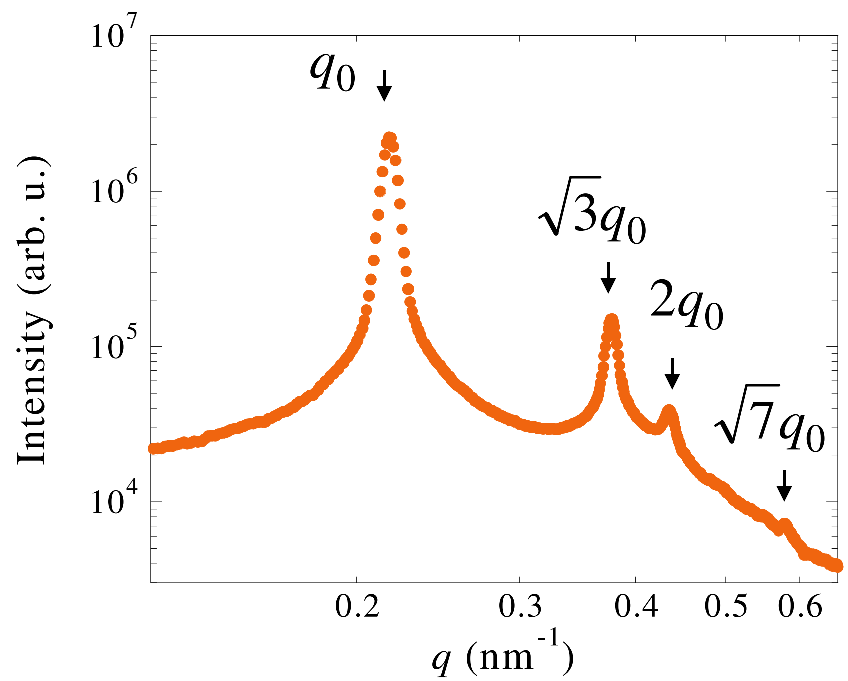
Experimental System

Soft columnar crystal

self-assembled system

- surfactant molecules 
- solvent





- triangular array of tubes
- 1D liquid, 2D solid

Experimental System

Soft columnar crystal

self-assembled system

- surfactant molecules 
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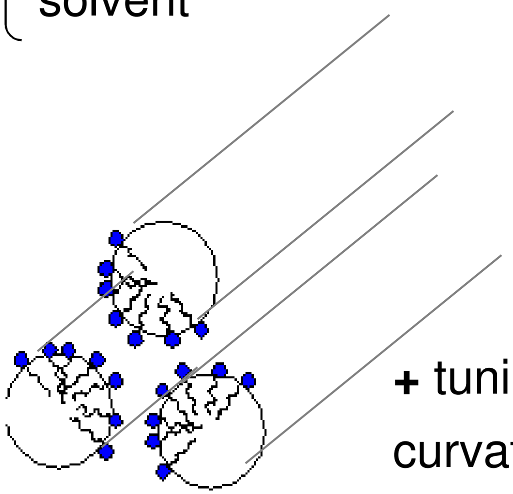
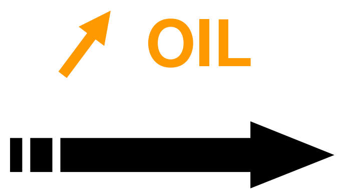
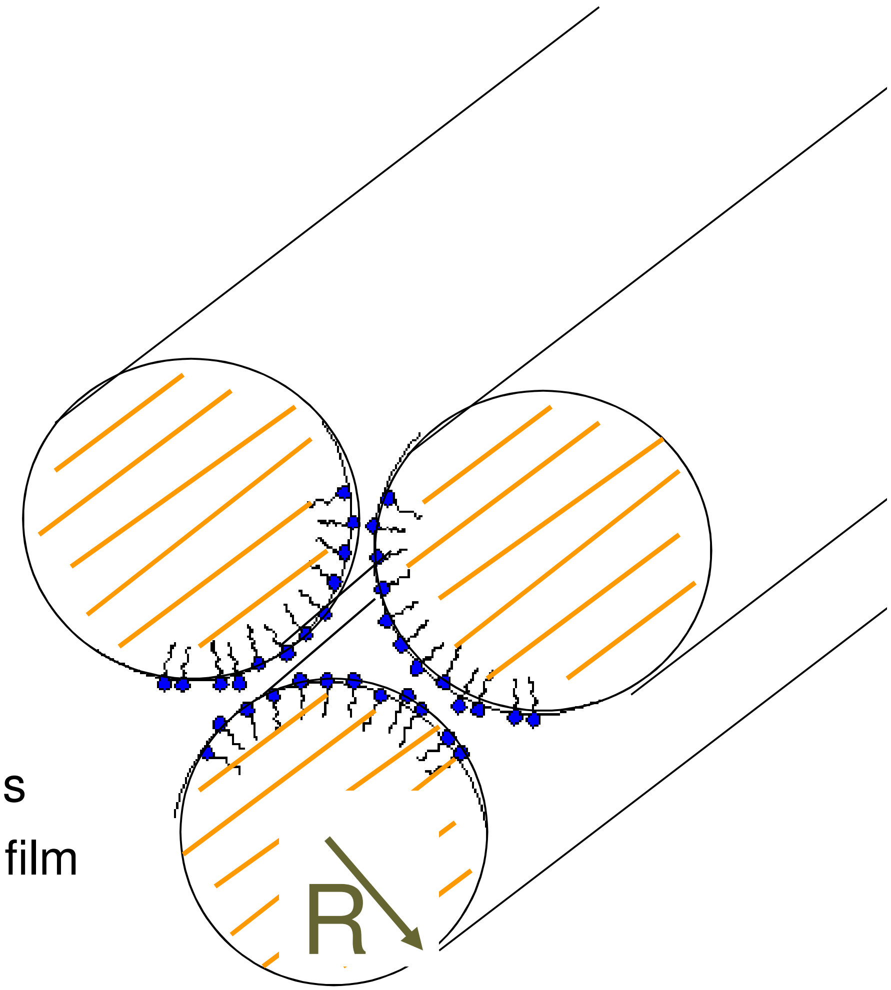




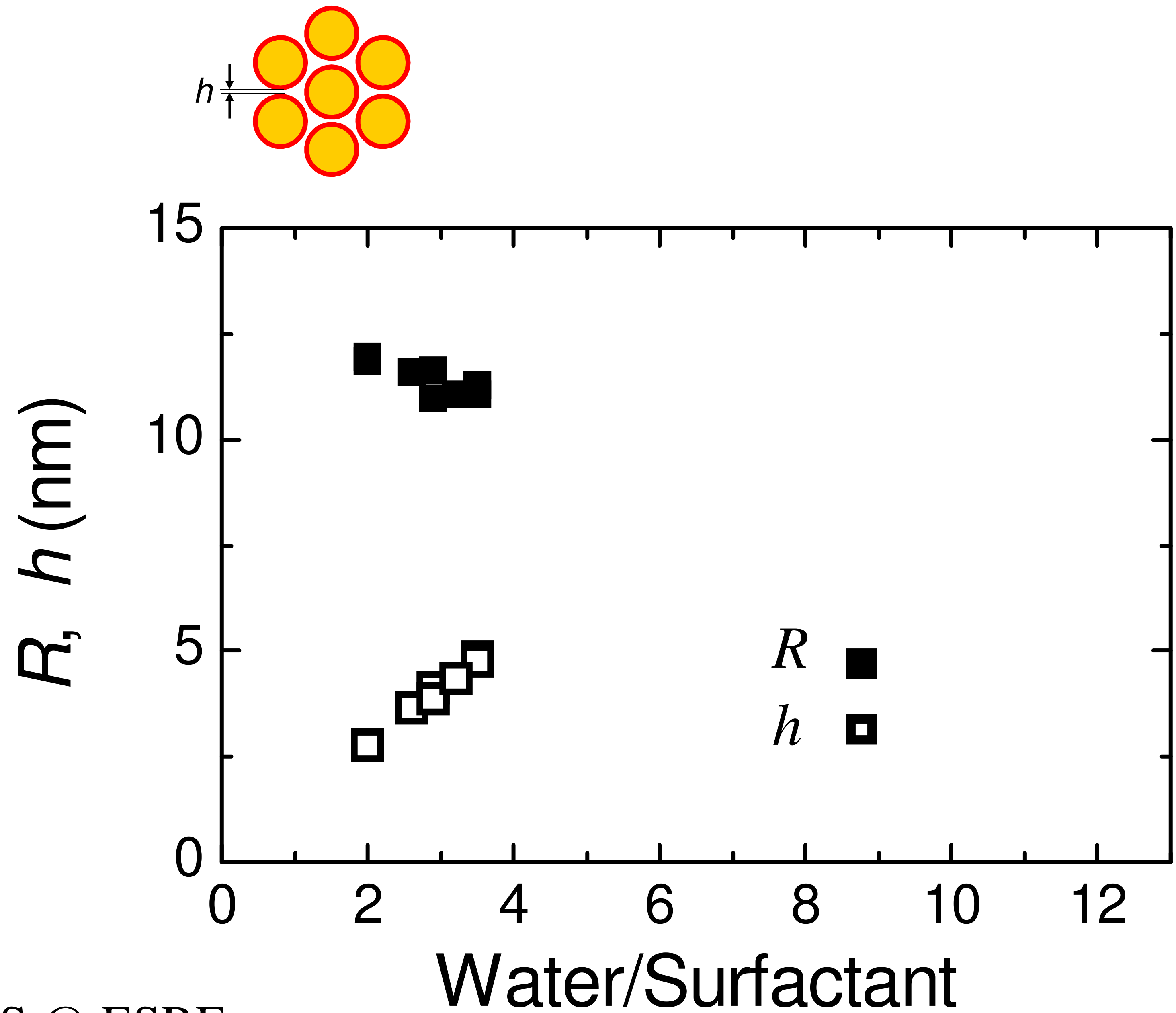
+ tuning of the spontaneous curvature of the surfactant film



1.5 -15 nm

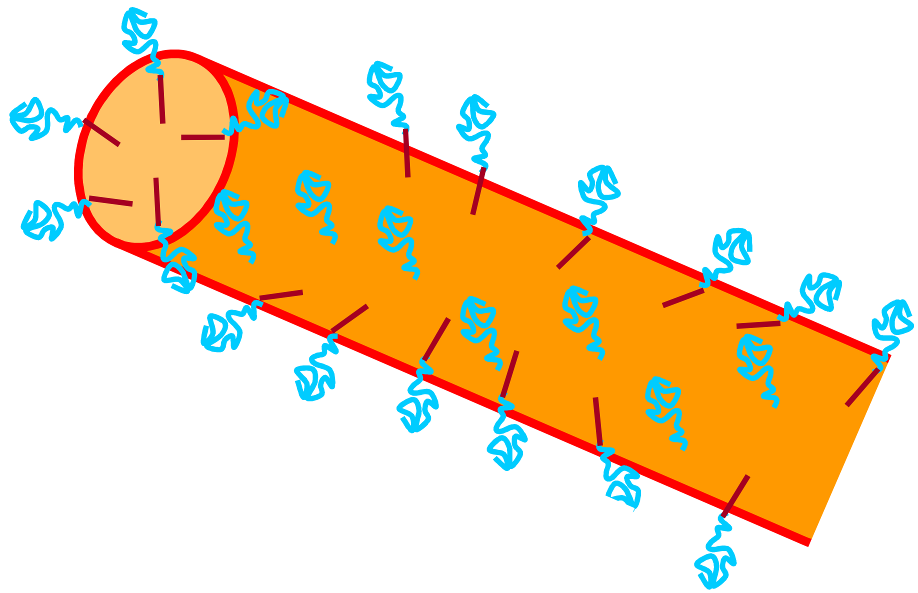
- triangular array of tubes
- 1D liquid, 2D crystal

LR and Fabre, Langmuir (1997)



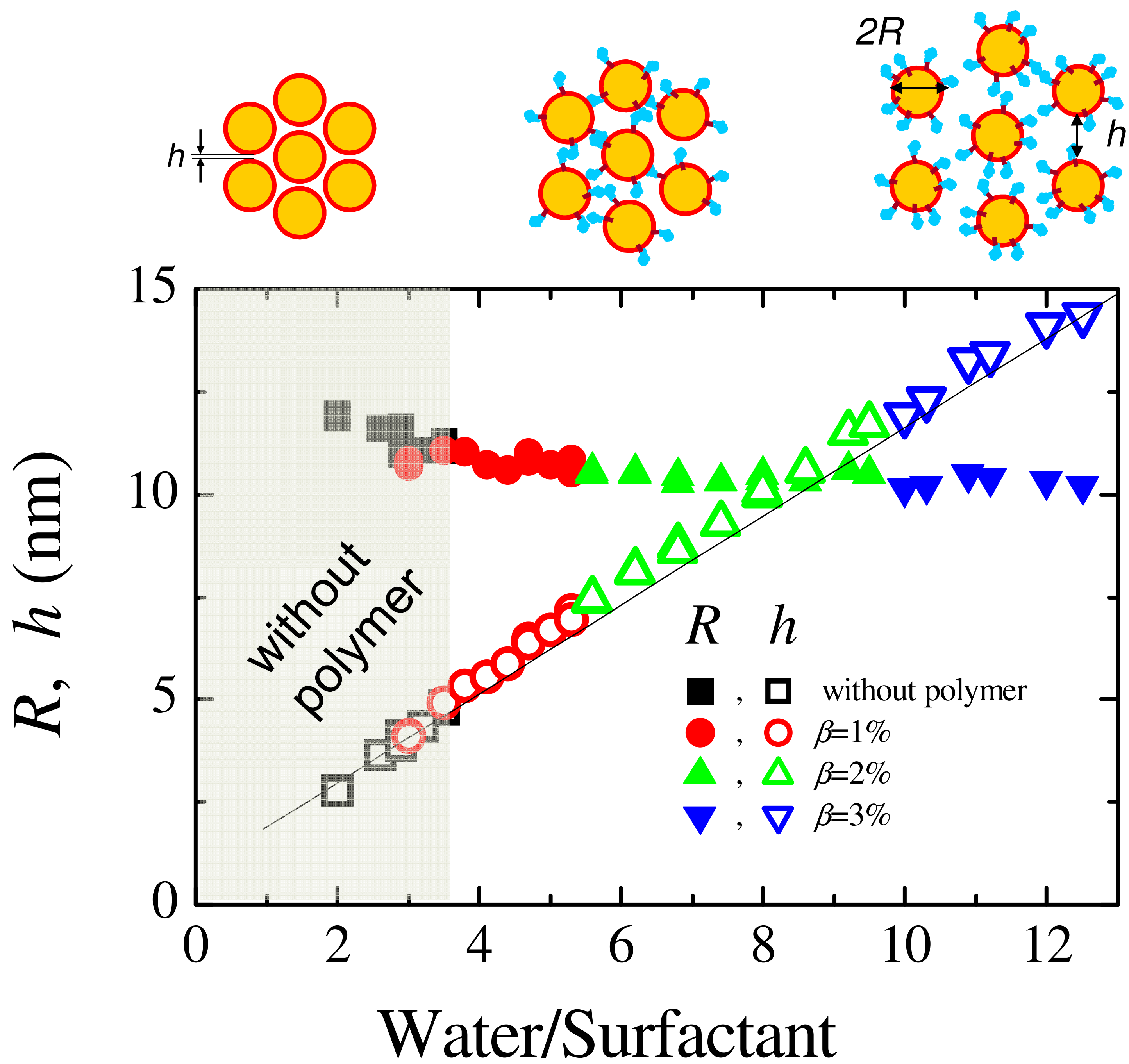
SAXS @ ESRF

Our strategy to Increase the Spacing between the Tubes



 *Amphiphilic di-block polymer (home-synthesized)*

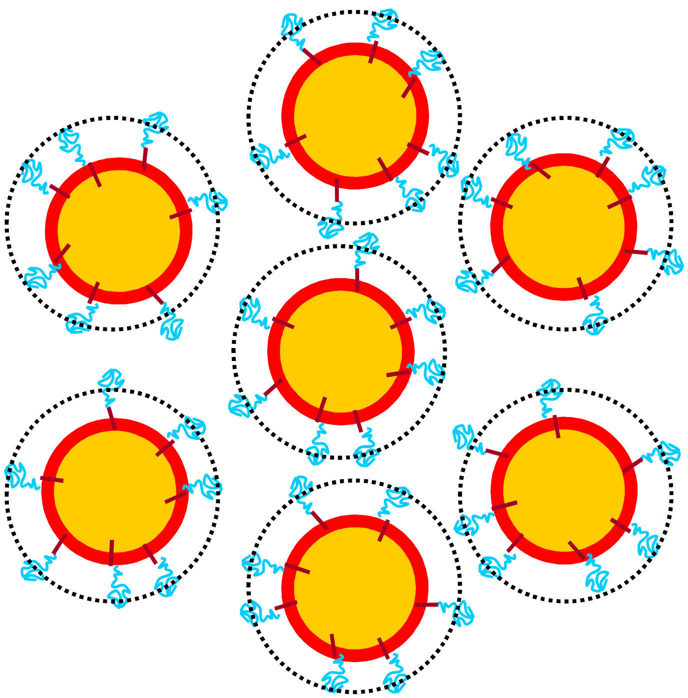
C_{18} - POE_{5K} (R_G = 2.4 nm)



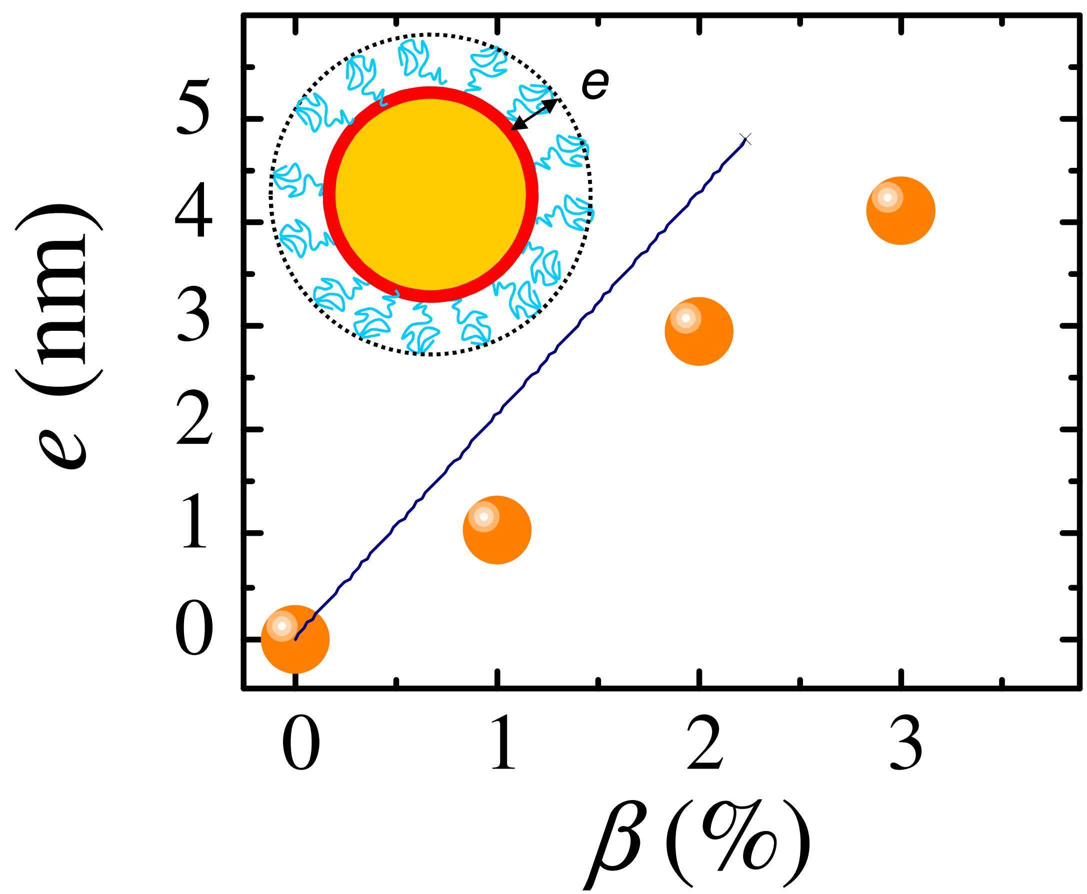
h
2R
h
15
10
5
0
0
2
4
6
8
10
12
R, h (nm)
Water/Surfactant
without polymer
R h
, without polymer
, β=1%
, β=2%
, β=3%

Effective Polymer Thickness

Excluded volume interaction between the tubes
Same effective surface density upon addition of polymer



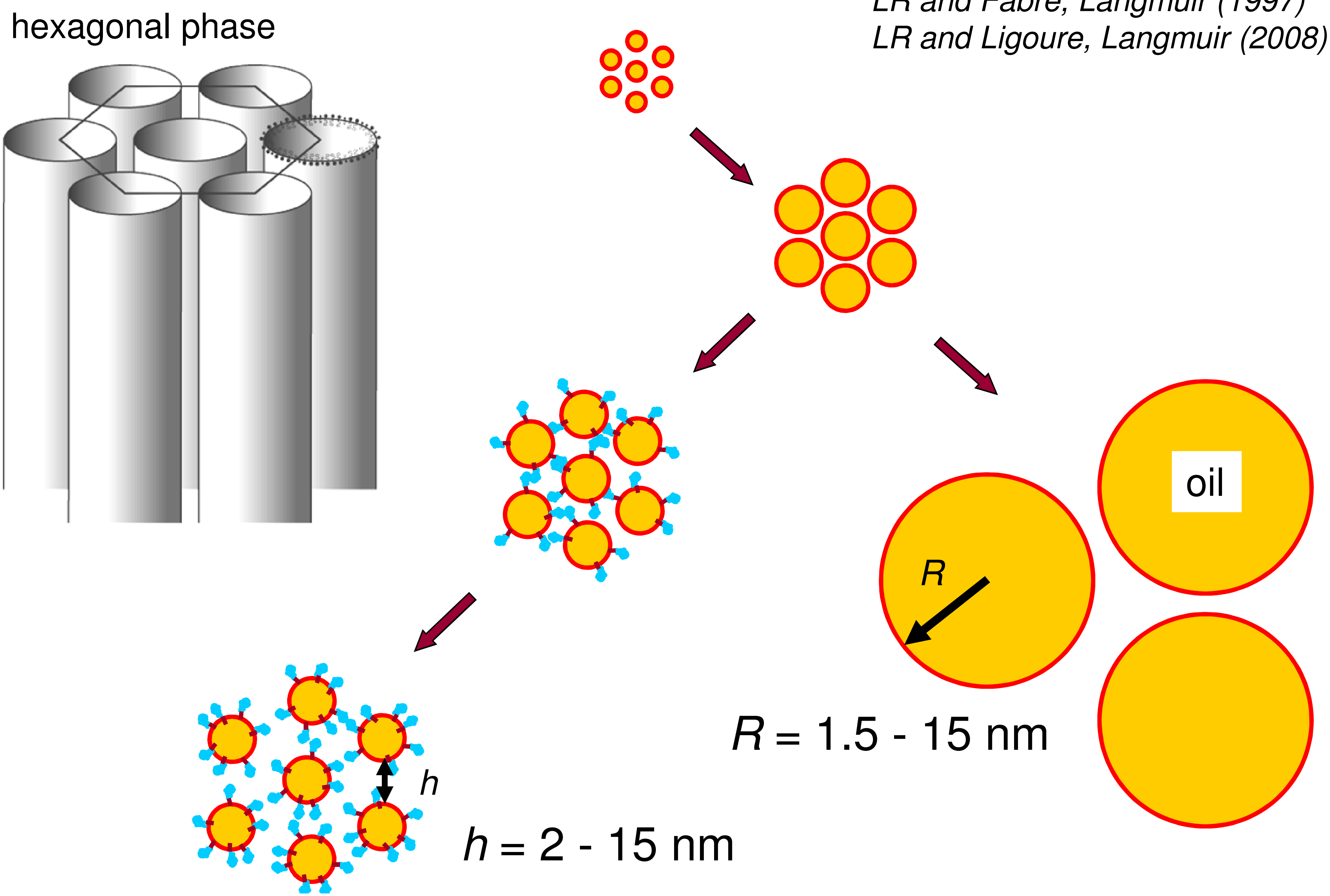
$$\rho_0 / \rho_{measur.} = (1 + e/R)^2$$



LR and Ligoure, Langmuir (2008)

A Versatile Soft Columnar Crystal

LR and Fabre, Langmuir (1997)
LR and Ligoure, Langmuir (2008)



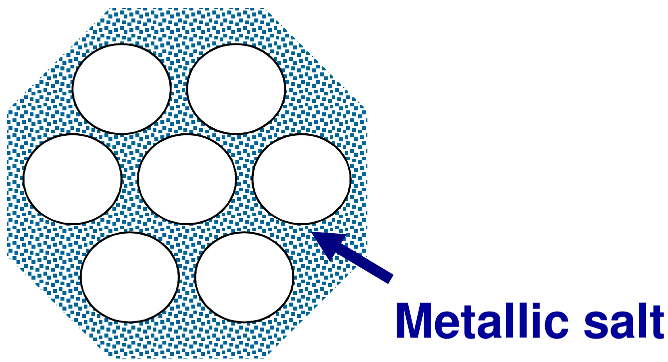
Specificities of the Soft Columnar Crystals

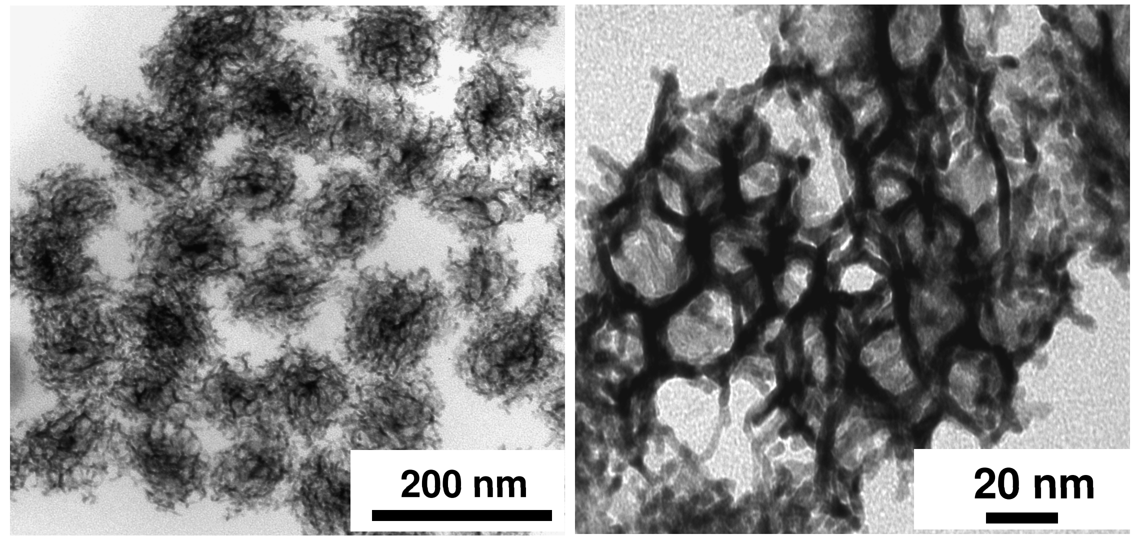
Soft hexagonal phase : a unique system

- Tunable characteristic sizes ⟹ *Template for nanomaterials*

… one example

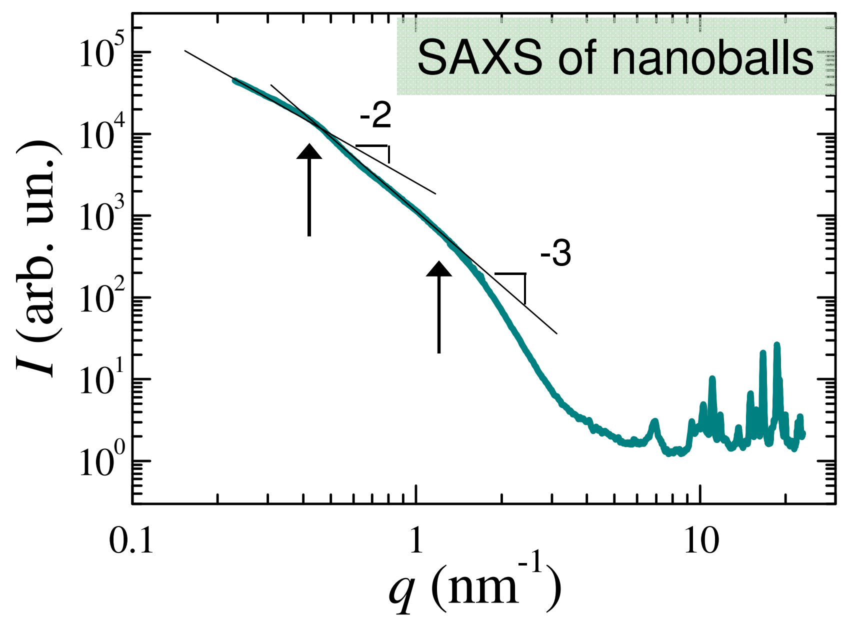
Chemistry Outside the Surfactant Tubes: Pt and Pd Porous Nanoballs





<u>2 required conditions</u>

- Confinement (in a hexagonal matrix)
- Slow and homogeneous reduction in the bulk (γ irradiation)



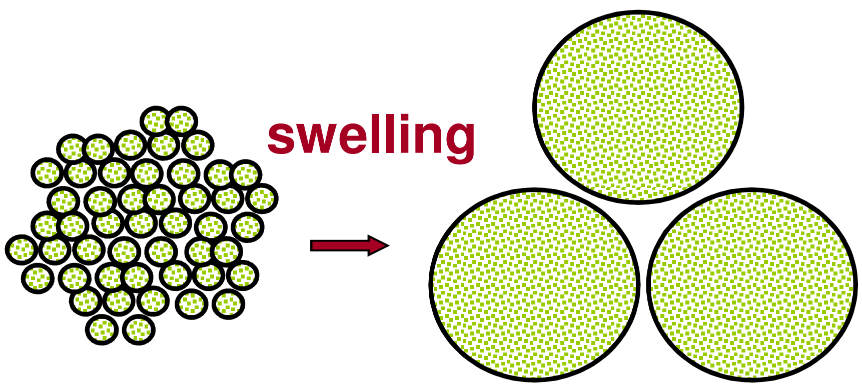
Surendran, LR et al. Chem. Mater (2007)
Surendran et al. J. Phys. Chem. C (2008)

Specificities of the Soft Columnar Crystals

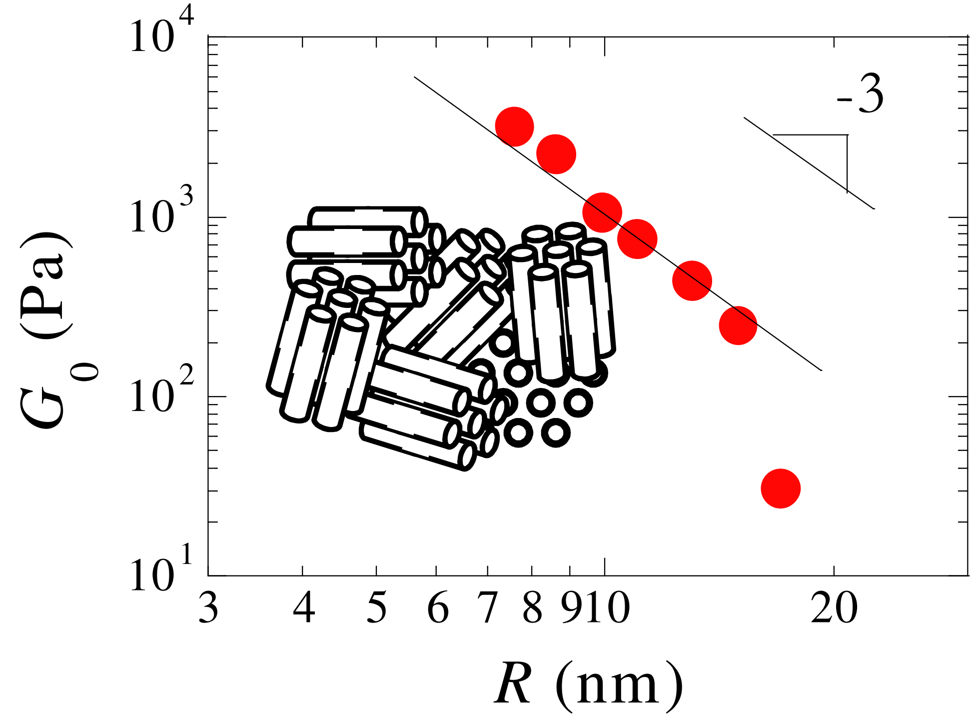
Soft hexagonal phase : a unique system

- Tunable characteristic sizes ⟹ *Template for nanomaterials*
- **Tunable elasticity**

Elasticity of Surfactant Hexagonal Phase



polycrystalline samples



$$G_0 \sim \frac{\kappa}{R^3}$$

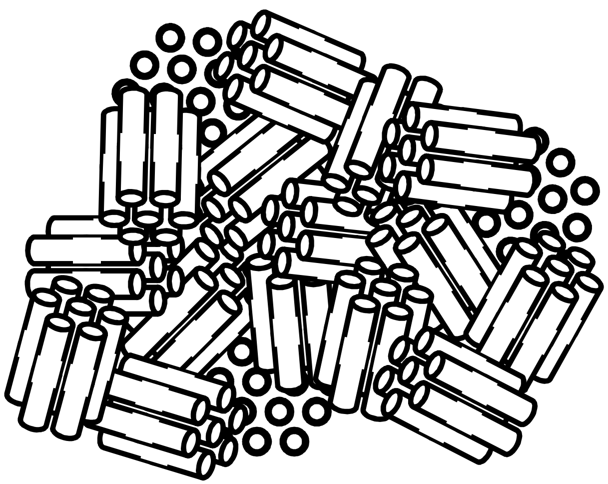
κ → bending constant of the surfactant film

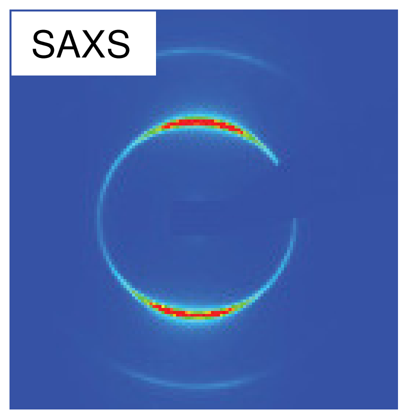
LR and Molino, EPL. (2000)

Specificities of the Soft 2D Crystals

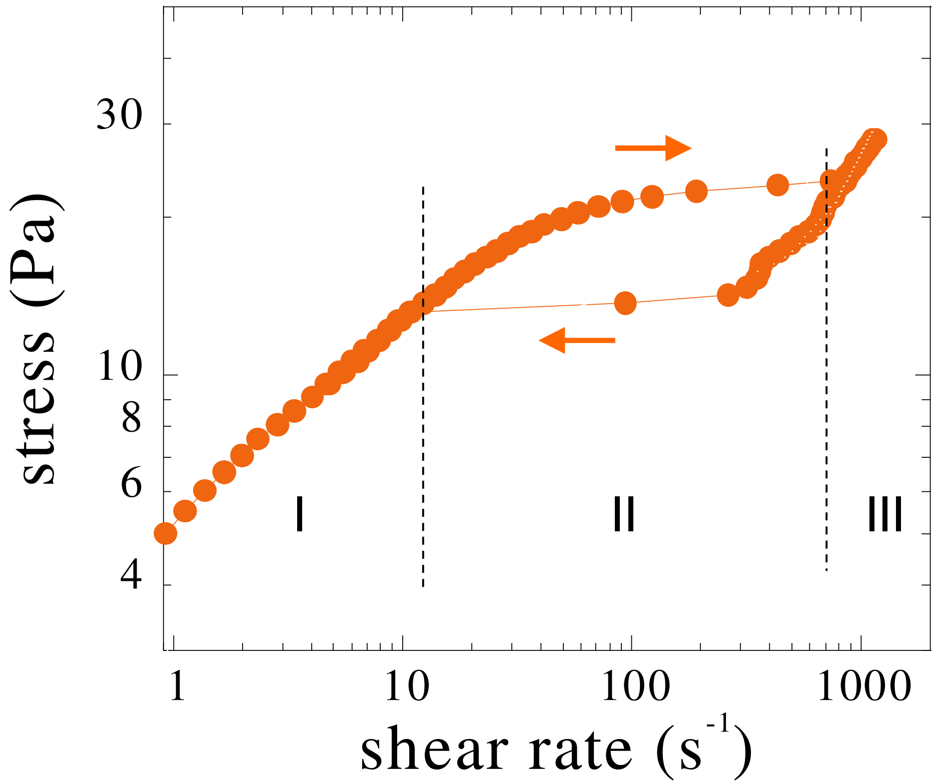
Soft hexagonal phase : a unique system

- Tunable characteristic sizes
- **Tunable elasticity**
- **Structural signature**





Flow Curves

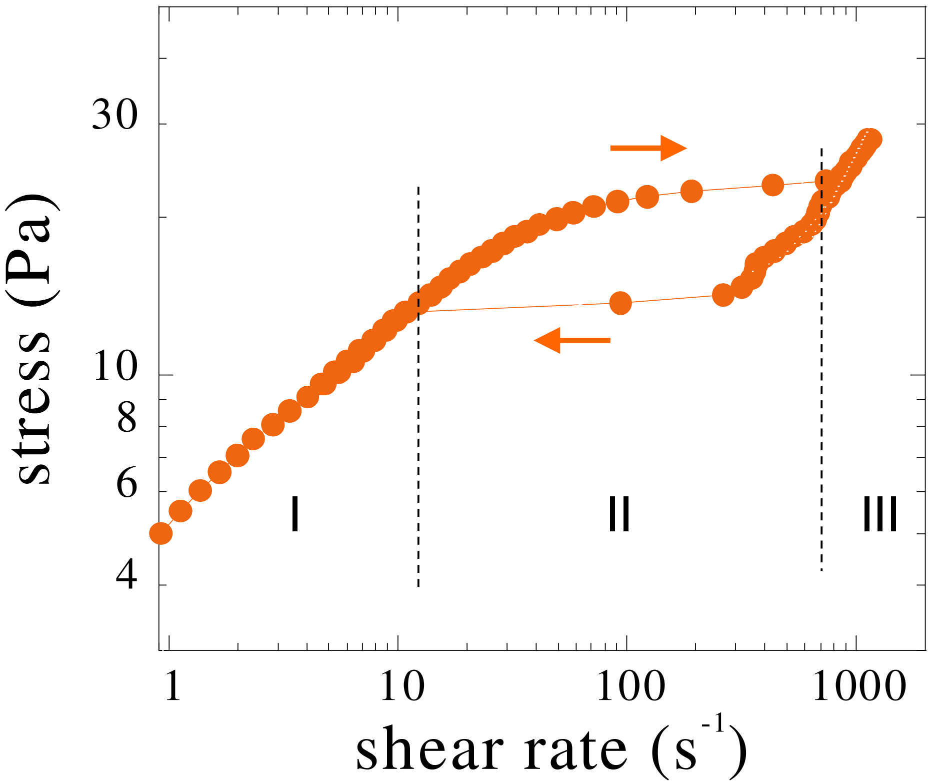


I shear-thinning

II stress plateau and hysteretic loop

III low viscosity Newtonian fluid

Flow Curves



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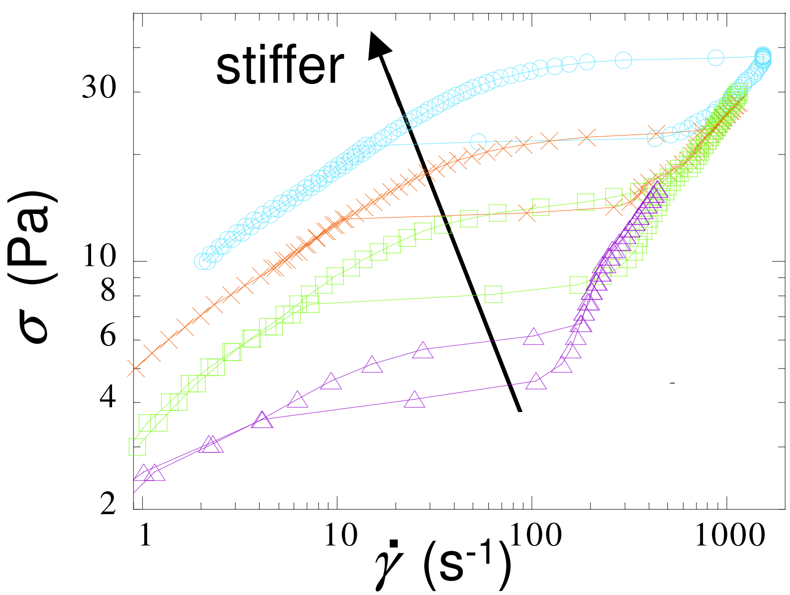
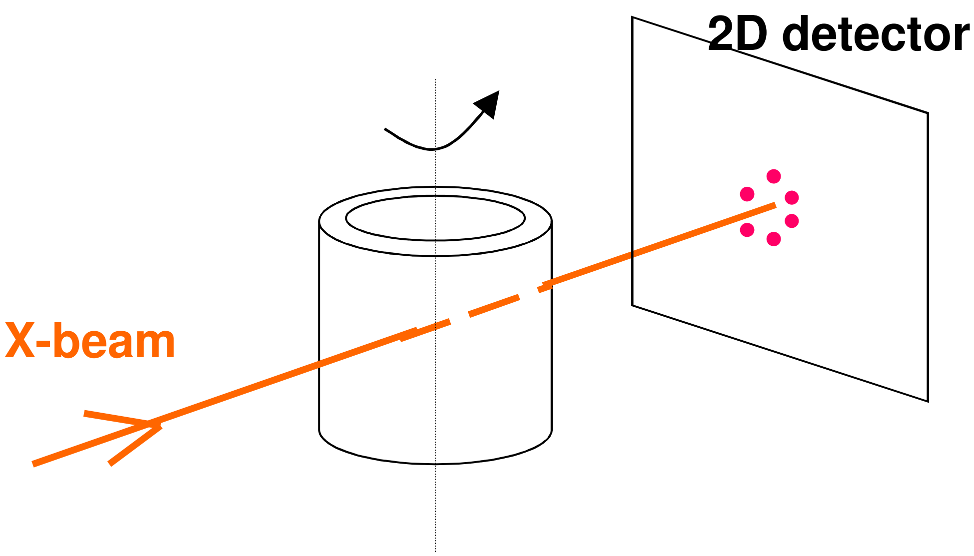
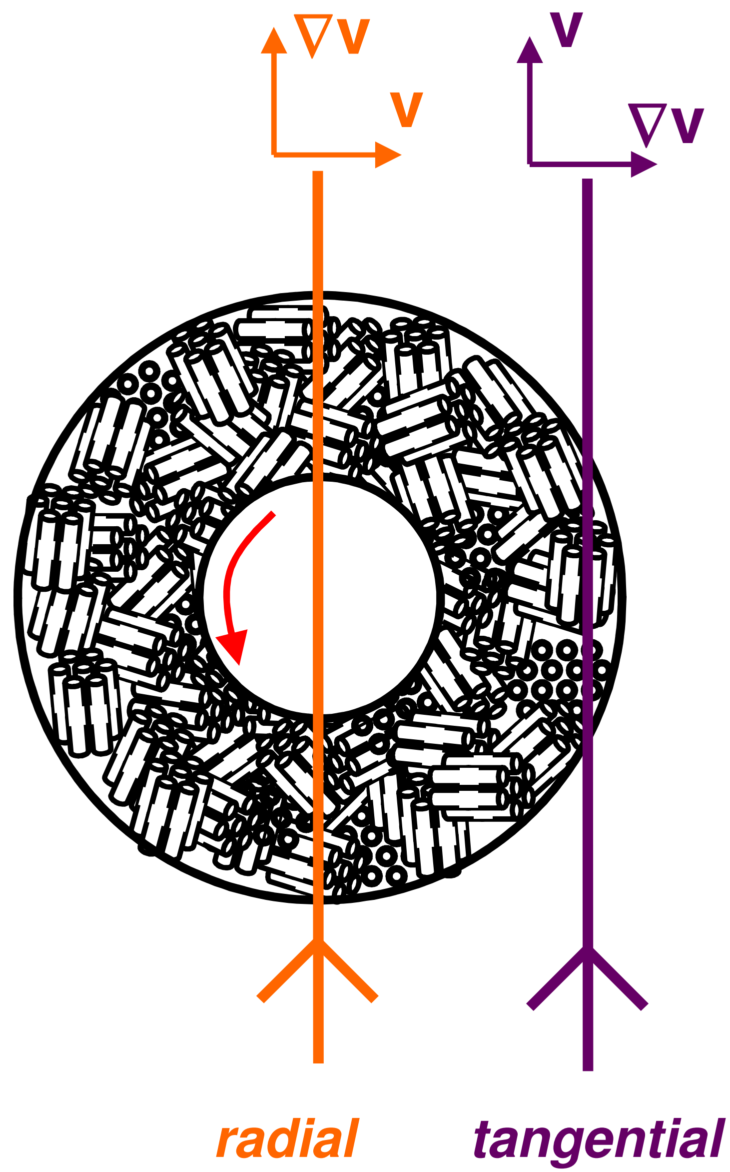


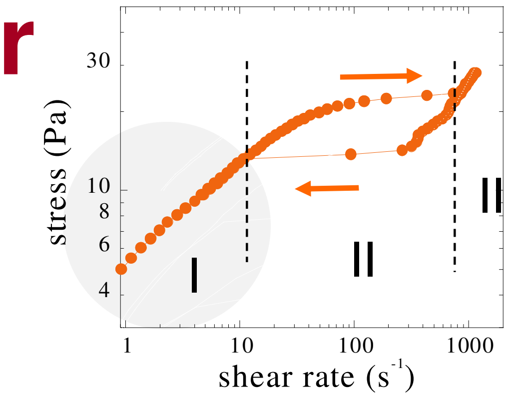
SAXS under Shear

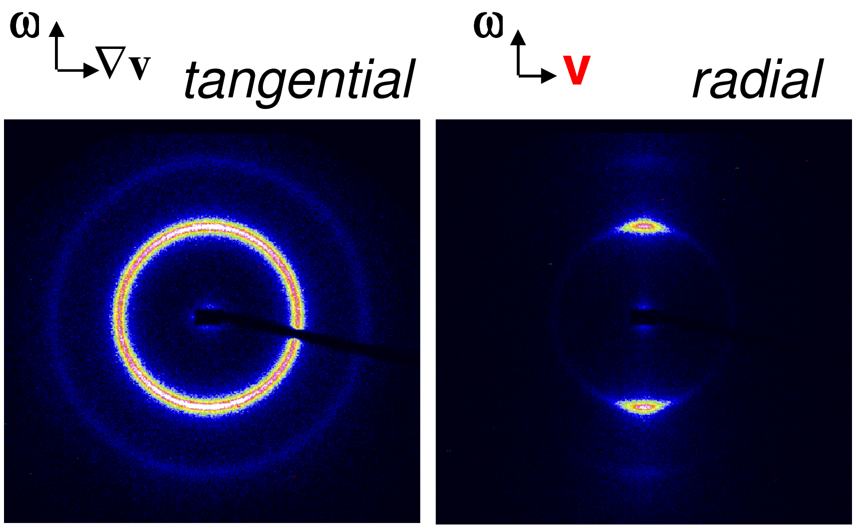




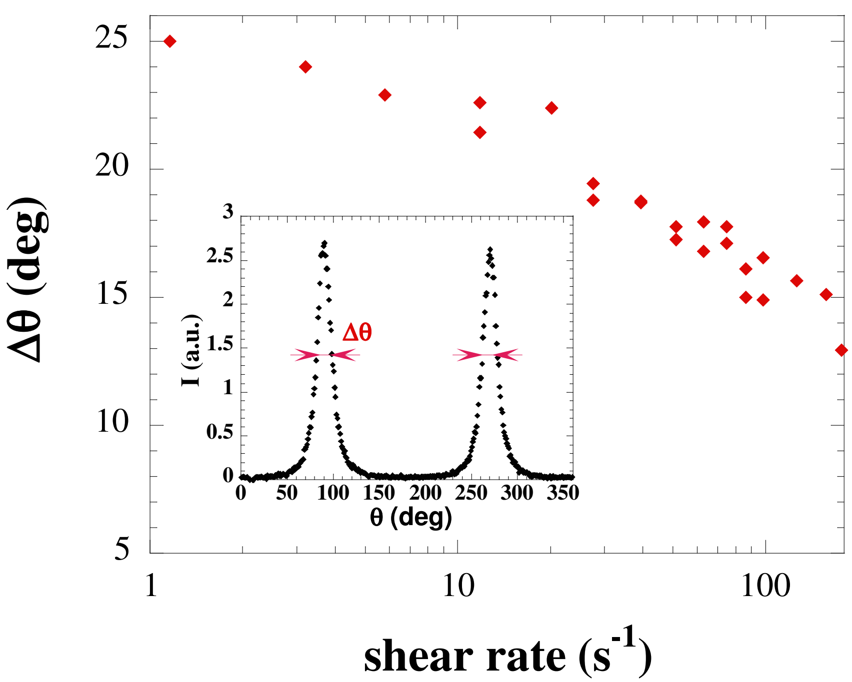
Structure under controlled shear rate

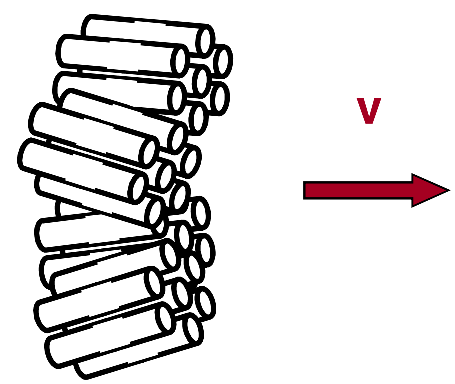
SAXS under Low Shear





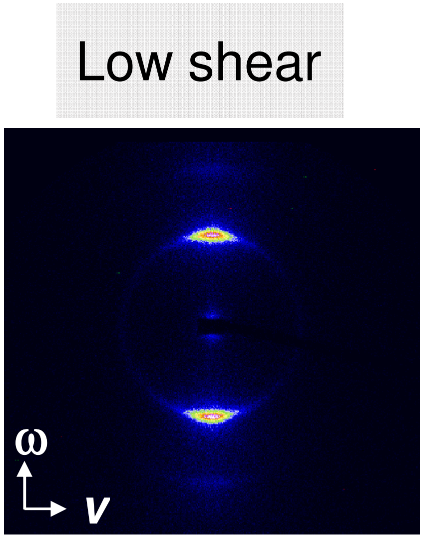
- Polydomain
- Preferential orientation of the tubes along **v**

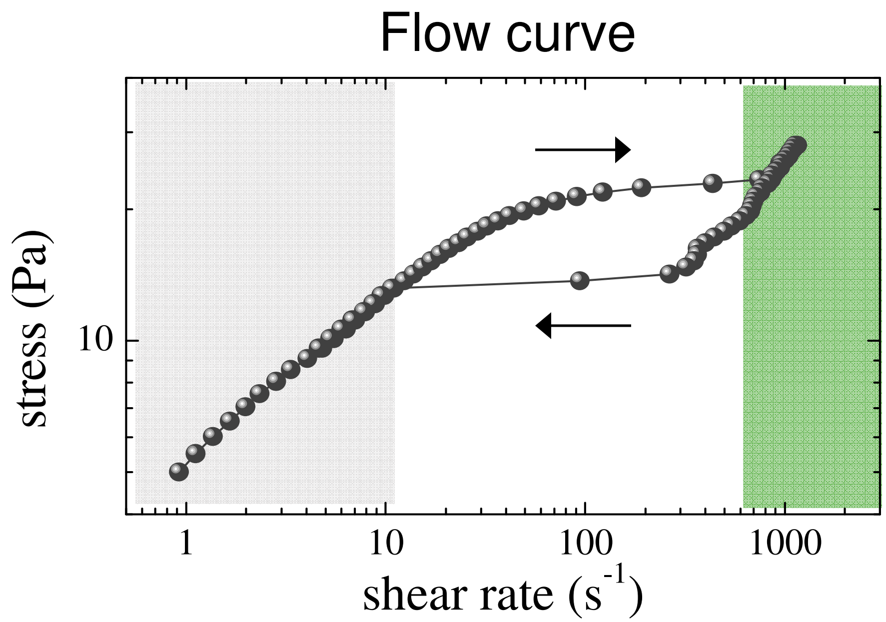


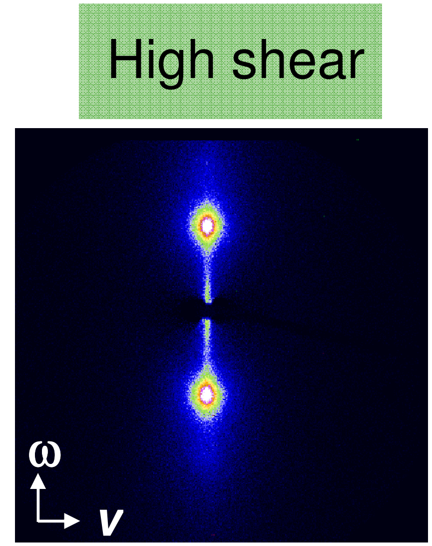


Progressive alignment of the tubes along v

Structural Transition under Shear

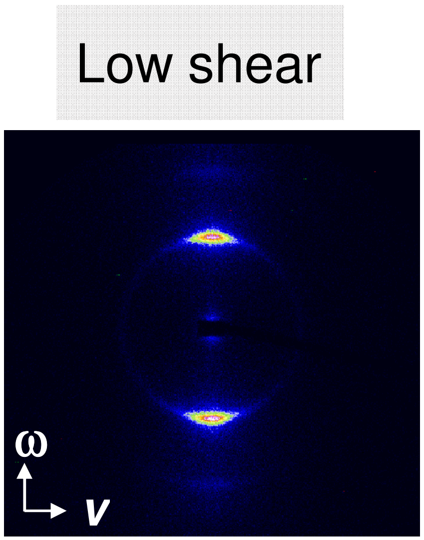


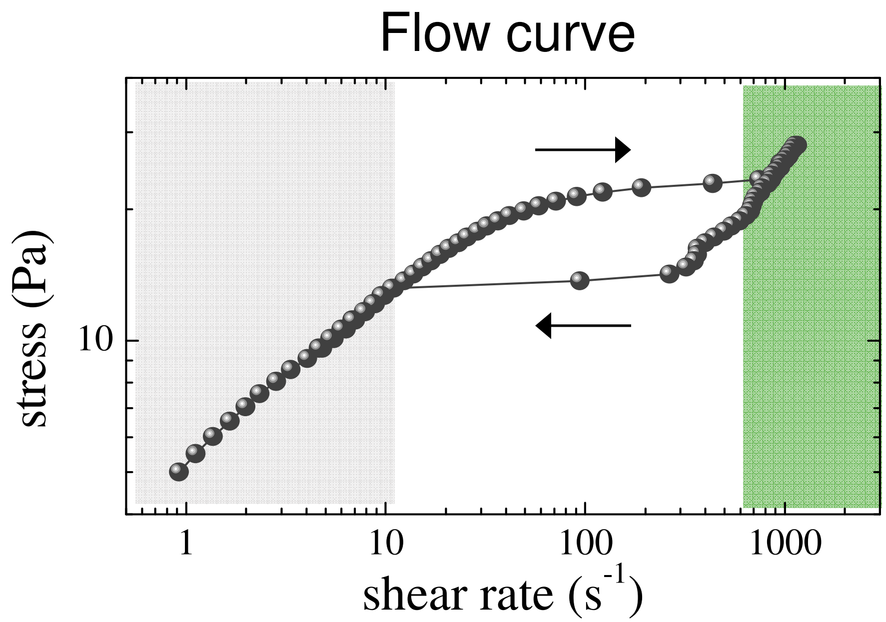


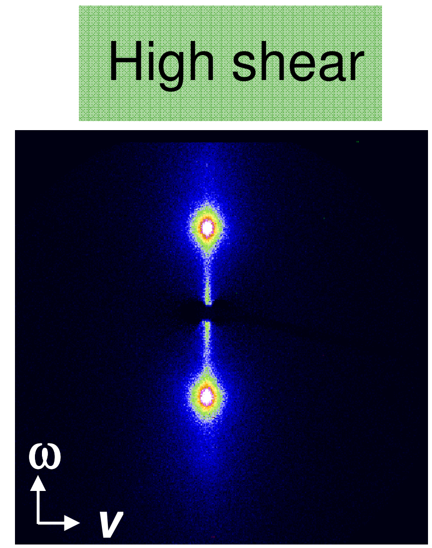


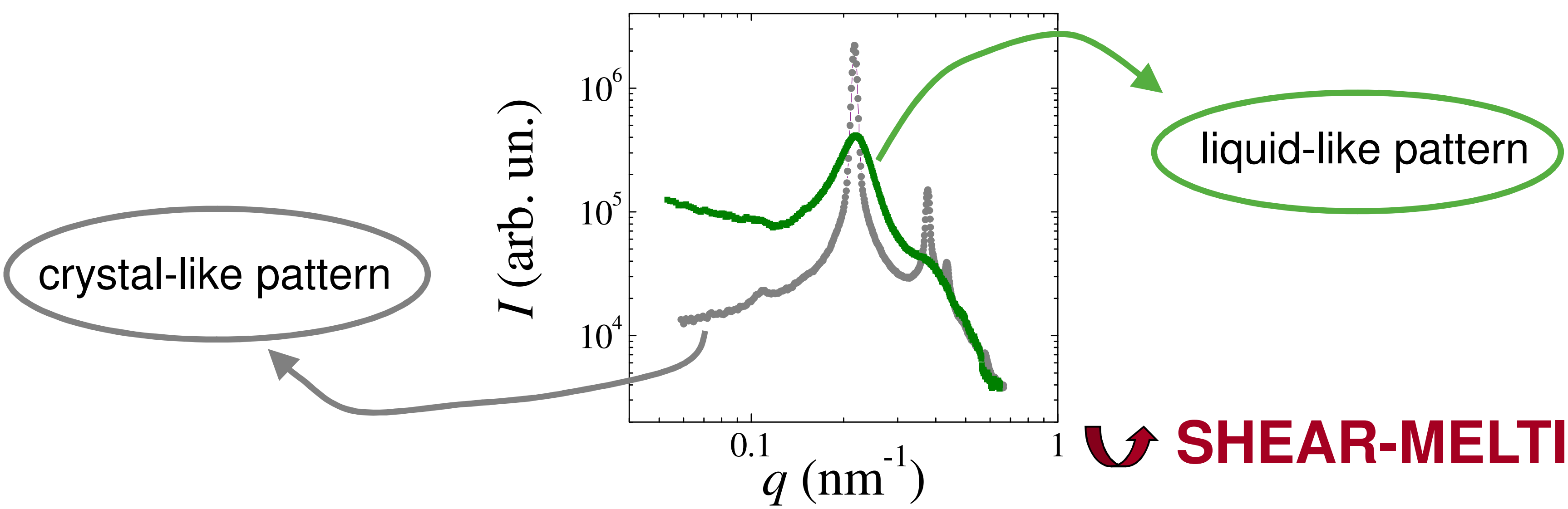
Perfect alignment of the tubes along **v**

Structural Transition under Shear



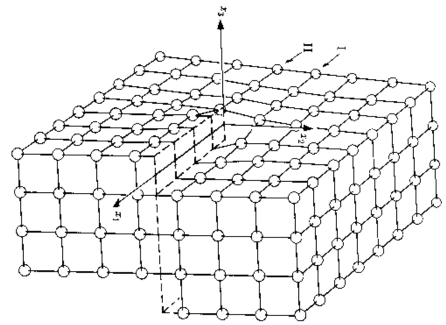






SHEAR-MELTING

Role of Dislocations



Nabarro *et al.* (1964)

<u>Work-hardening of crystals</u>

dimensional arguments

$\sigma / G_0 = f(\boldsymbol{b}\,\rho^{1/2})$

G_0 : shear modulus
$\boldsymbol{b}$: Burgers vector
ρ :density of dislocations

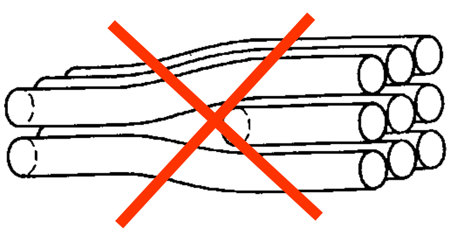
Driving force $F_1 \sim \boldsymbol{b}\sigma$ (Peach-Kohler)

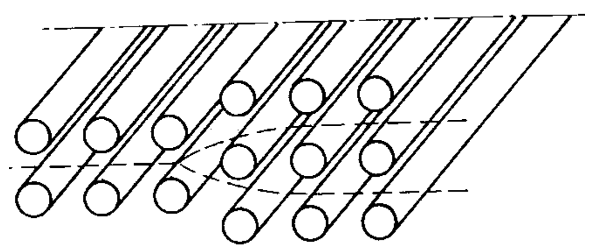
Resistive force $F_2 \sim \boldsymbol{b}^2$ (line tension of a dislocation)

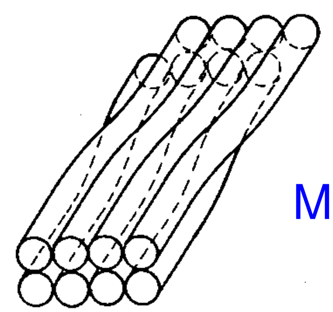
$\sigma \sim \boldsymbol{b}$

$\sigma \sim G_0\, \boldsymbol{b}\, \rho^{1/2}$

3 types of dislocations in columnar crystal





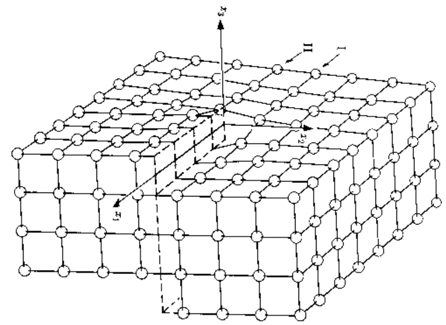


Marchetti and Nelson (1990)

Role of Dislocations

Nabarro *et al.* (1964)

Work-hardening of crystals



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Resistive force $F_2 \sim b^2$ (line tension of a dislocation)

$\sigma \sim b$

$\sigma \sim G_0\, b\, \rho^{1/2}$

Orowan

$\dot{\gamma} = \rho\, b\, v$

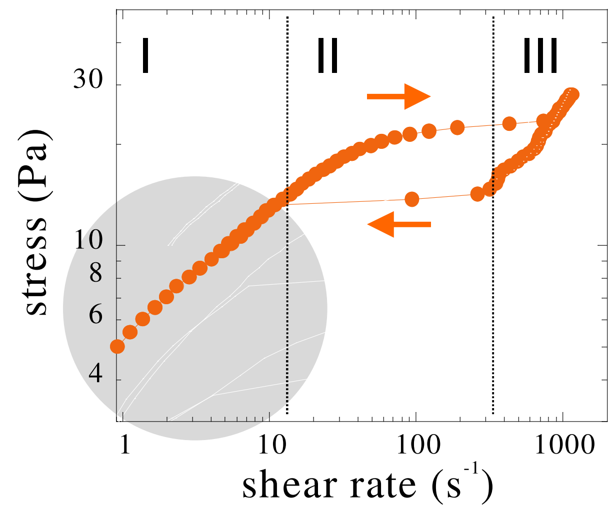
$v \sim \sigma$

(geometrical argument)

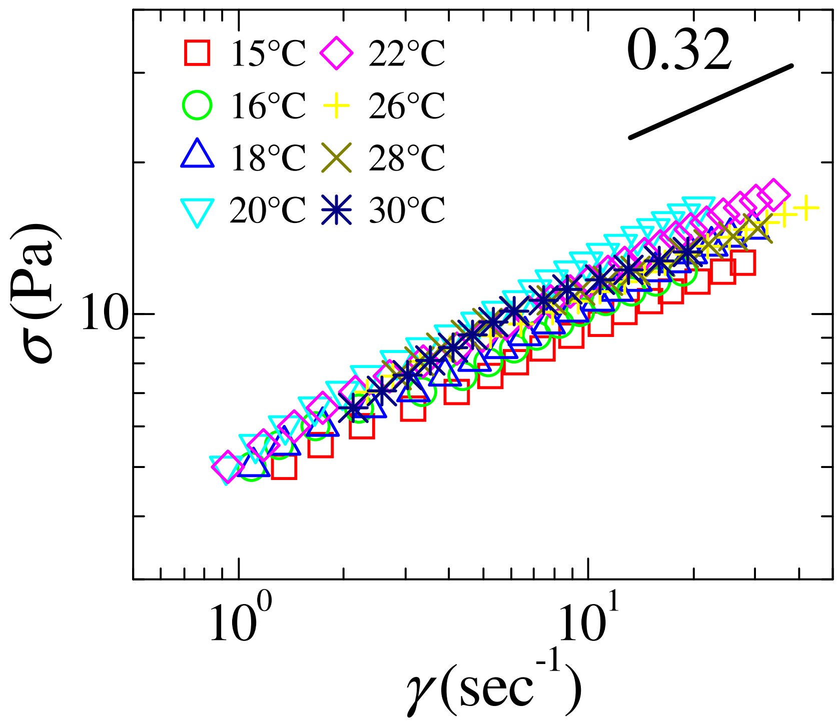
$\sigma \sim \dot{\gamma}^{1/3}$

$\rho \sim \sigma^2 \sim \dot{\gamma}^{2/3}$

Determination of $\rho = f(\dot{\gamma})$ from Rheology Data



low $\dot{\gamma}$ regime

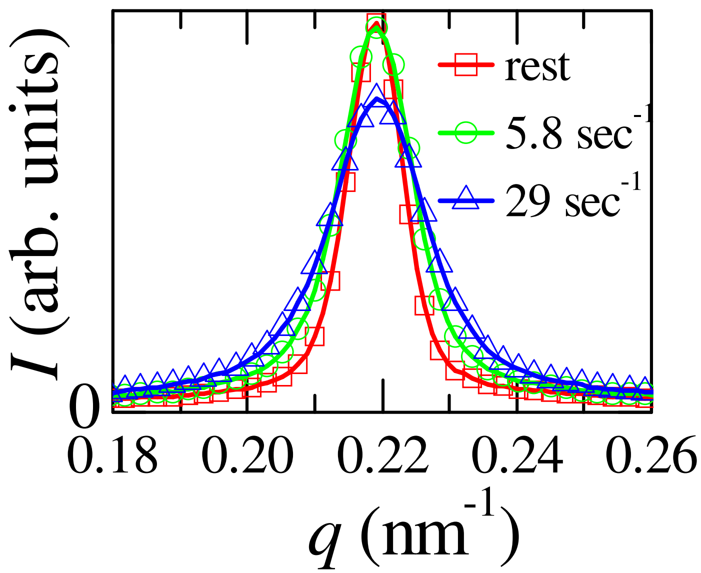


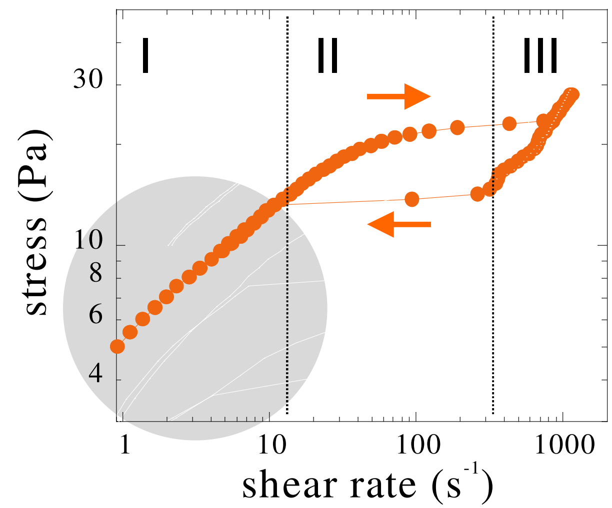
shear-thinning regime

$$\sigma \propto \dot{\gamma}^{1/3} \quad \rho \propto \dot{\gamma}^{2/3}$$

Determination of $\rho = f(\dot{\gamma})$ from SAXS Data

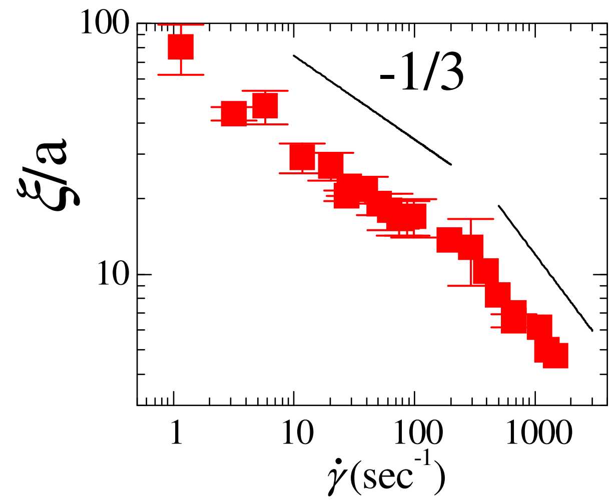
Broadening of the diffraction peaks





correlation length $\xi = \dfrac{2\pi}{\Delta q}$

$\xi \equiv$ mean distance between dislocations



$\rho \equiv 1/\xi^2$ $\rho \propto \dot{\gamma}^{2/3}$

Broadening of the diffraction peaks

Shear-thinning regime

$$\rho \propto \dot{\gamma}^{2/3}$$

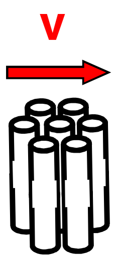
- **Scaling in agreement with simple theory of work-hardening of crystals**
- **Shear-melting due to a proliferation of dislocations**

LR and F Molino, PRL (2004)

Analogies with Flux Line Lattices in Superconductors

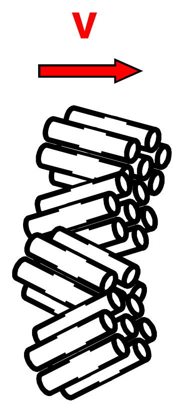
FFL | **soft hexagonal phase**

Shear-melting due to a proliferation of dislocations



Corbino disk geometry

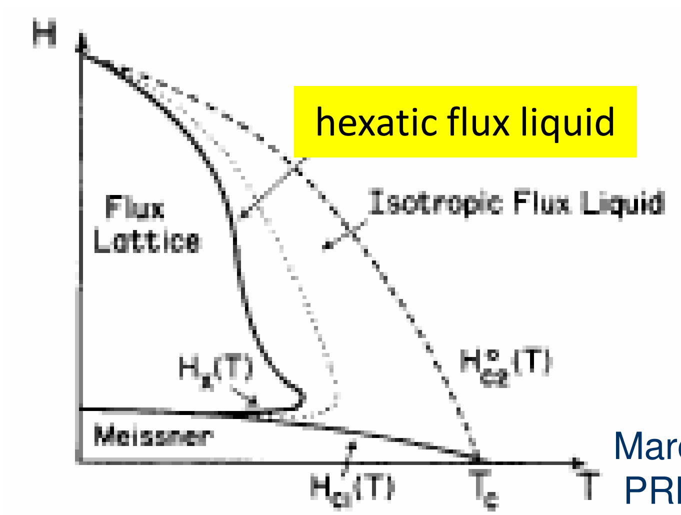
Benetatos and Marchetti PRB (2002)



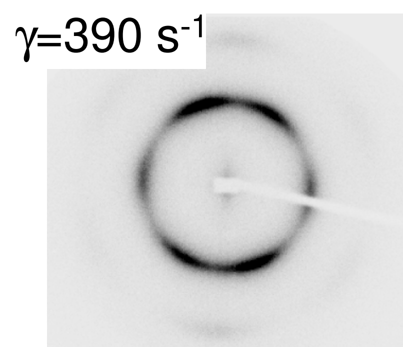
HOWEVER

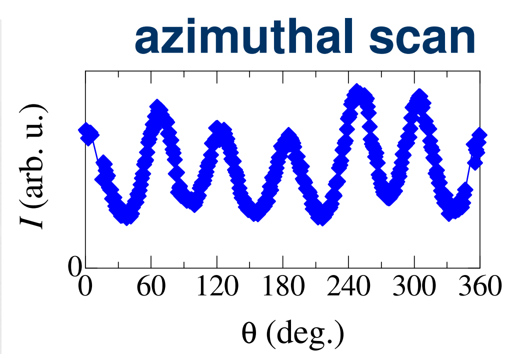
coupling between orientation of the tubes and density of dislocations

Intermediate hexatic phase ?

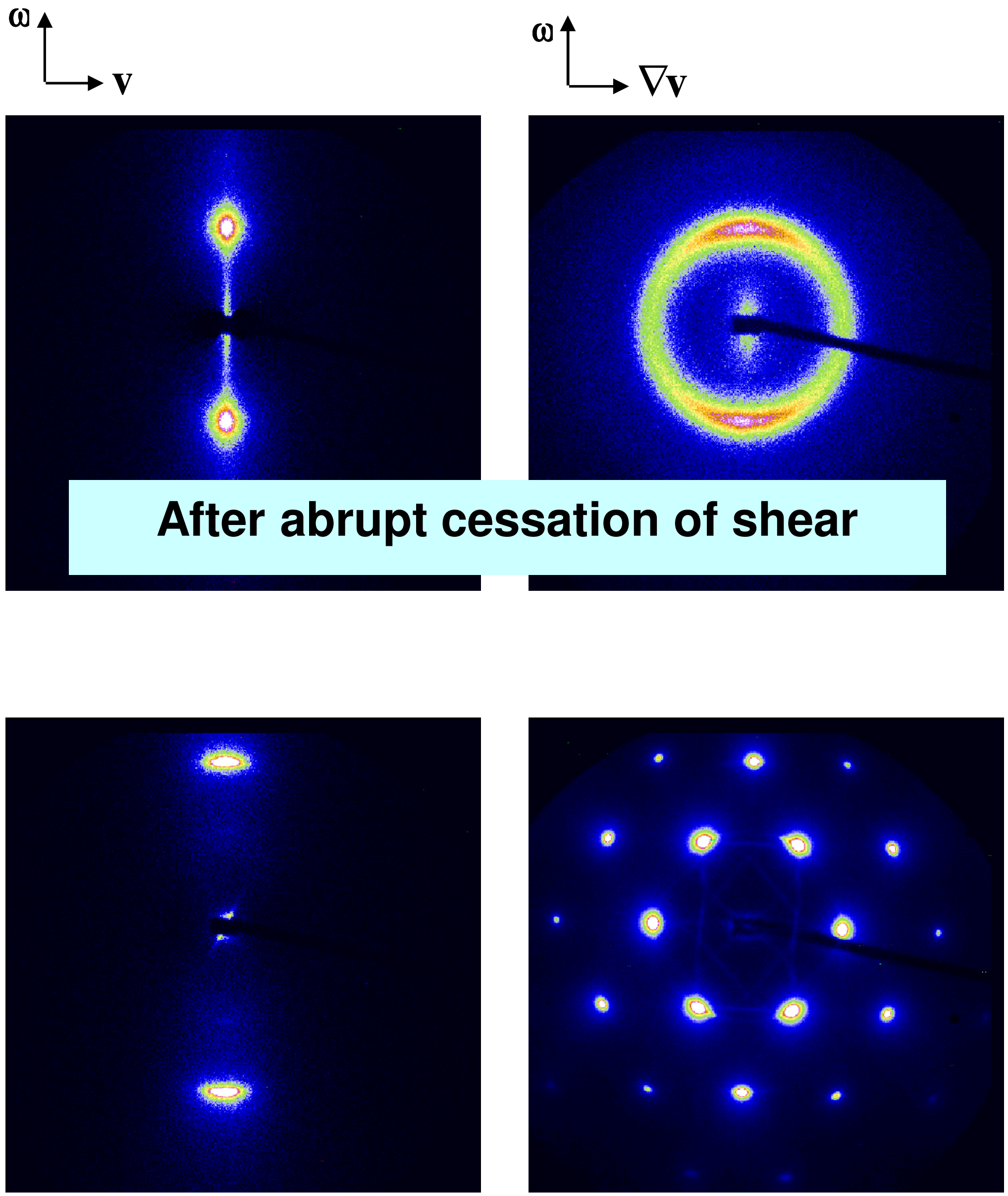


Marchetti and Nelson PRB (1990)





Shear-Melting… and Re-Crystallization



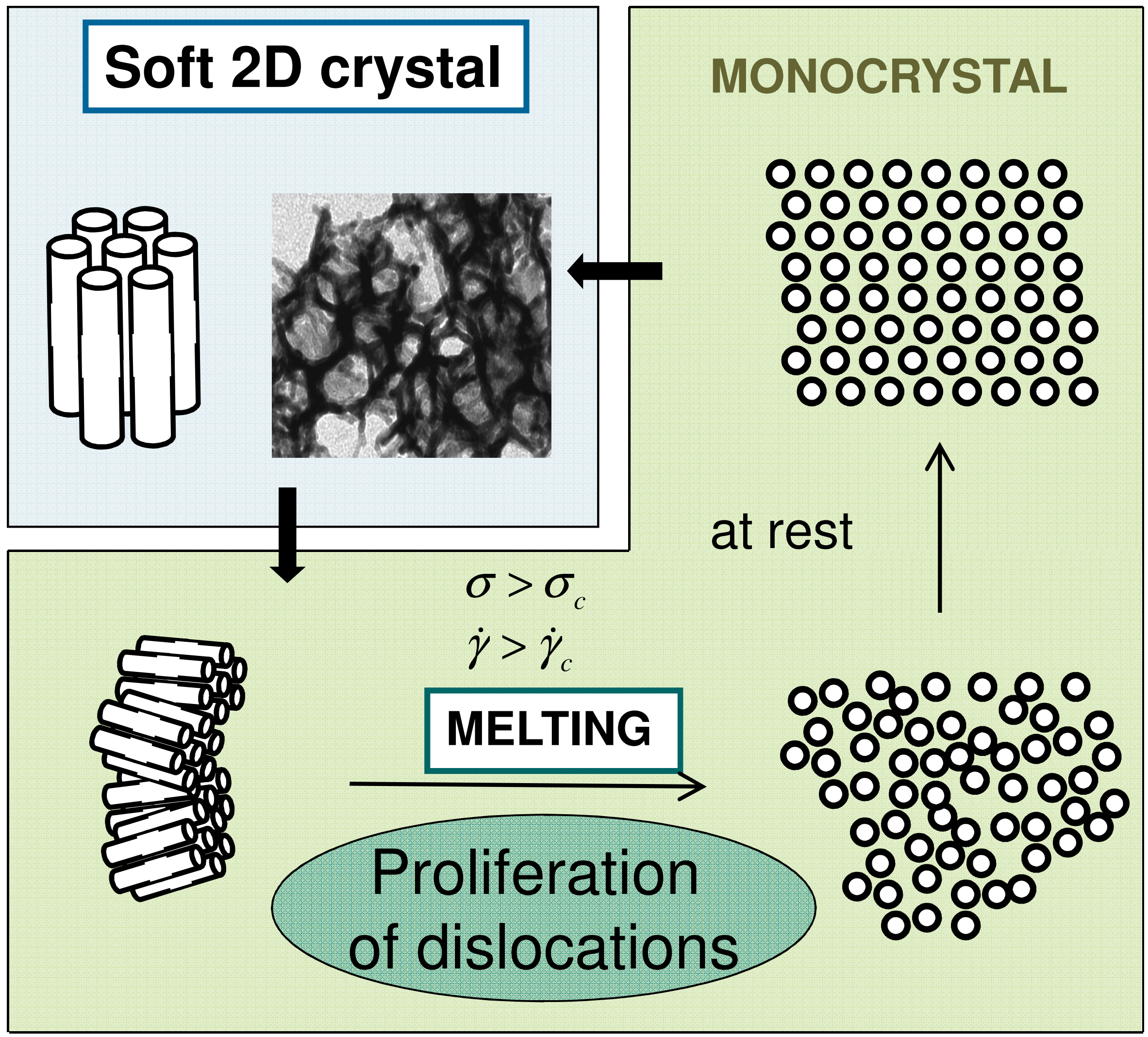
$$\dot{\gamma} = 1400\ s^{-1}$$

MONOCRYSTAL

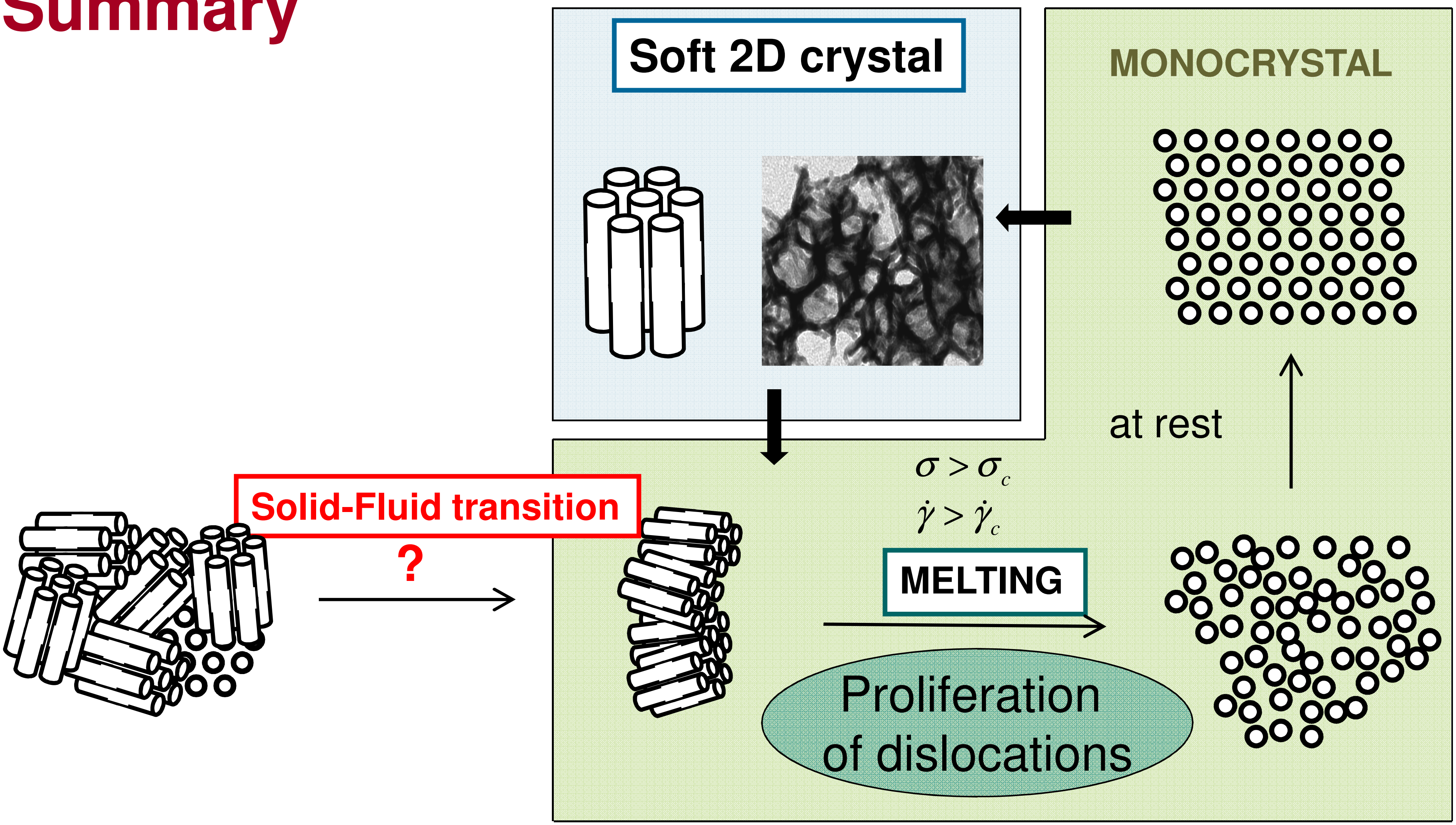
•Time scale ~ 100 sec
•Stable at rest

Nanostructured materials !!

Summary

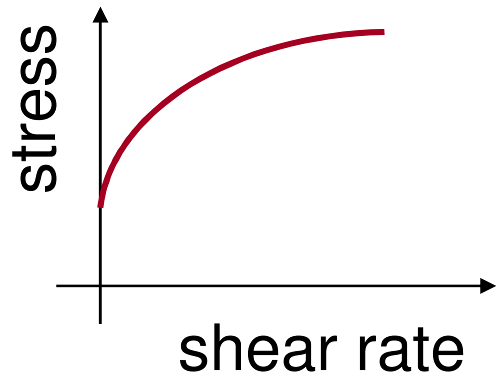

Soft 2D crystal
MONOCRYSTAL
at rest
$\sigma > \sigma_c$
$\dot{\gamma} > \dot{\gamma}_c$
MELTING
Proliferation of dislocations

Summary


Soft 2D crystal
MONOCRYSTAL
at rest
$\sigma > \sigma_c$
$\dot{\gamma} > \dot{\gamma}_c$
MELTING
Proliferation of dislocations
Solid-Fluid transition
?

Solid-Fluid Transition

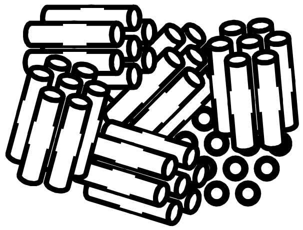
Yield Stress Fluids



- Nature of the solid to fluid transition?
- Prediction whether and when a material will flow
- Structural modifications at the onset of flow?
- ...

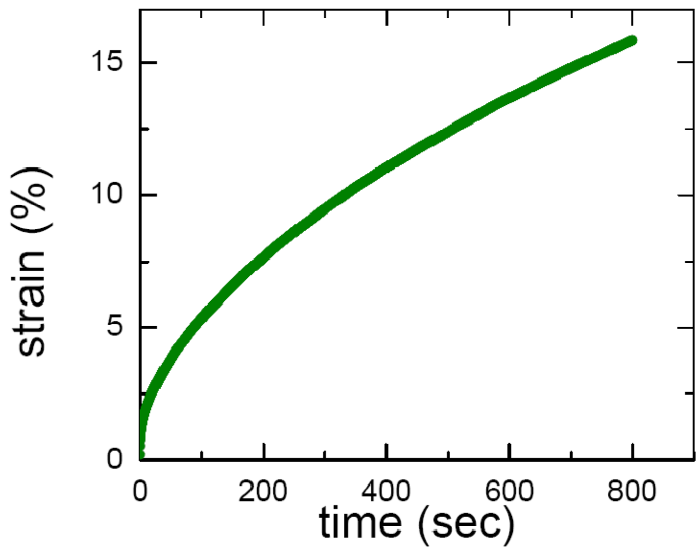


Behavior under Low Stress



Low stress

$\sigma = 2$ Pa



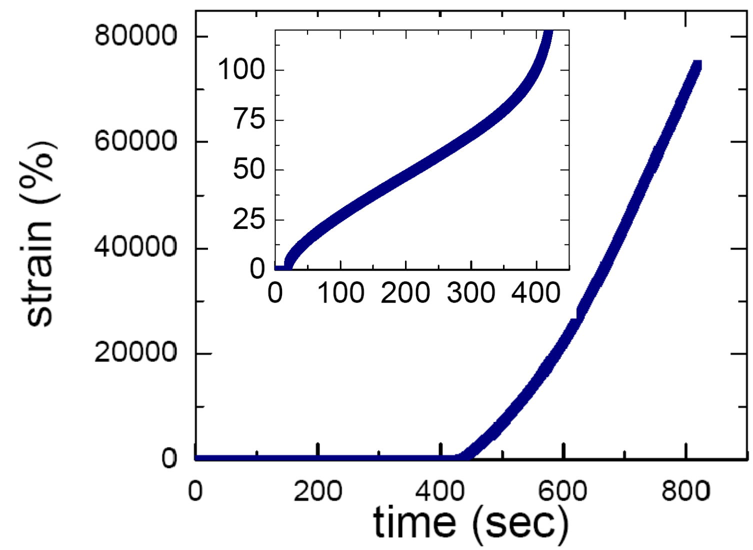
$\gamma \sim t^m \quad (m < 1)$

No steady state

"creep"

Higher stress

$\sigma = 5$ Pa

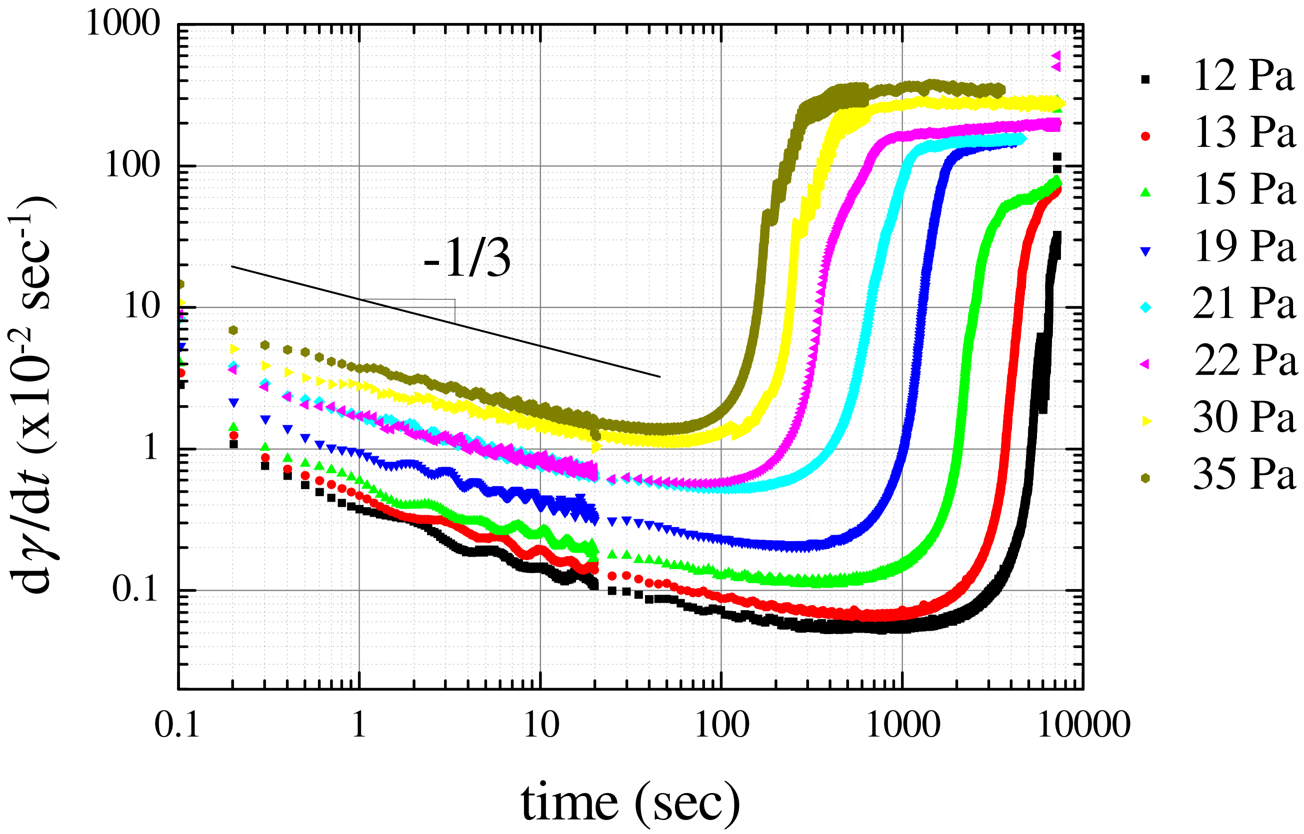


$\gamma \sim t$

Stationary regime

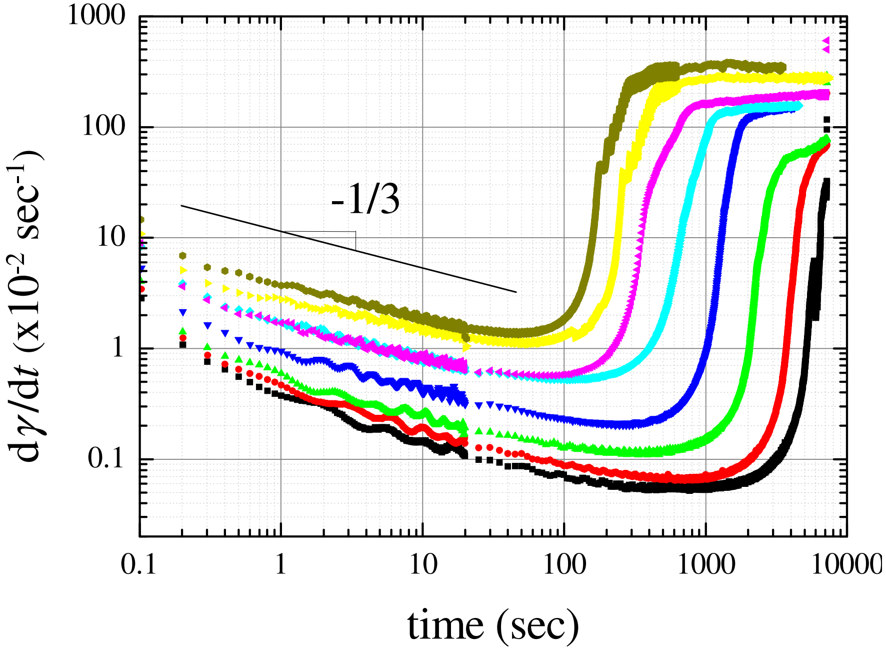
"flow"

Behavior under Low Stress

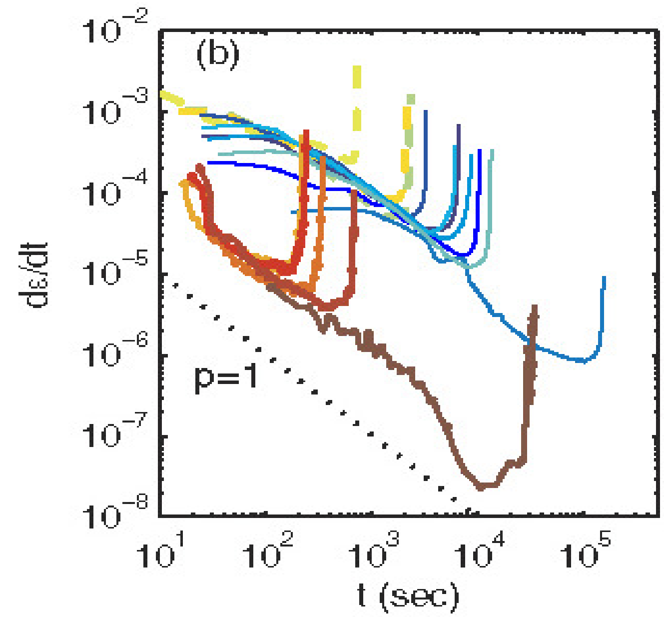


Behavior under Low Stress

surfactant hexagonal phase



polymer composite



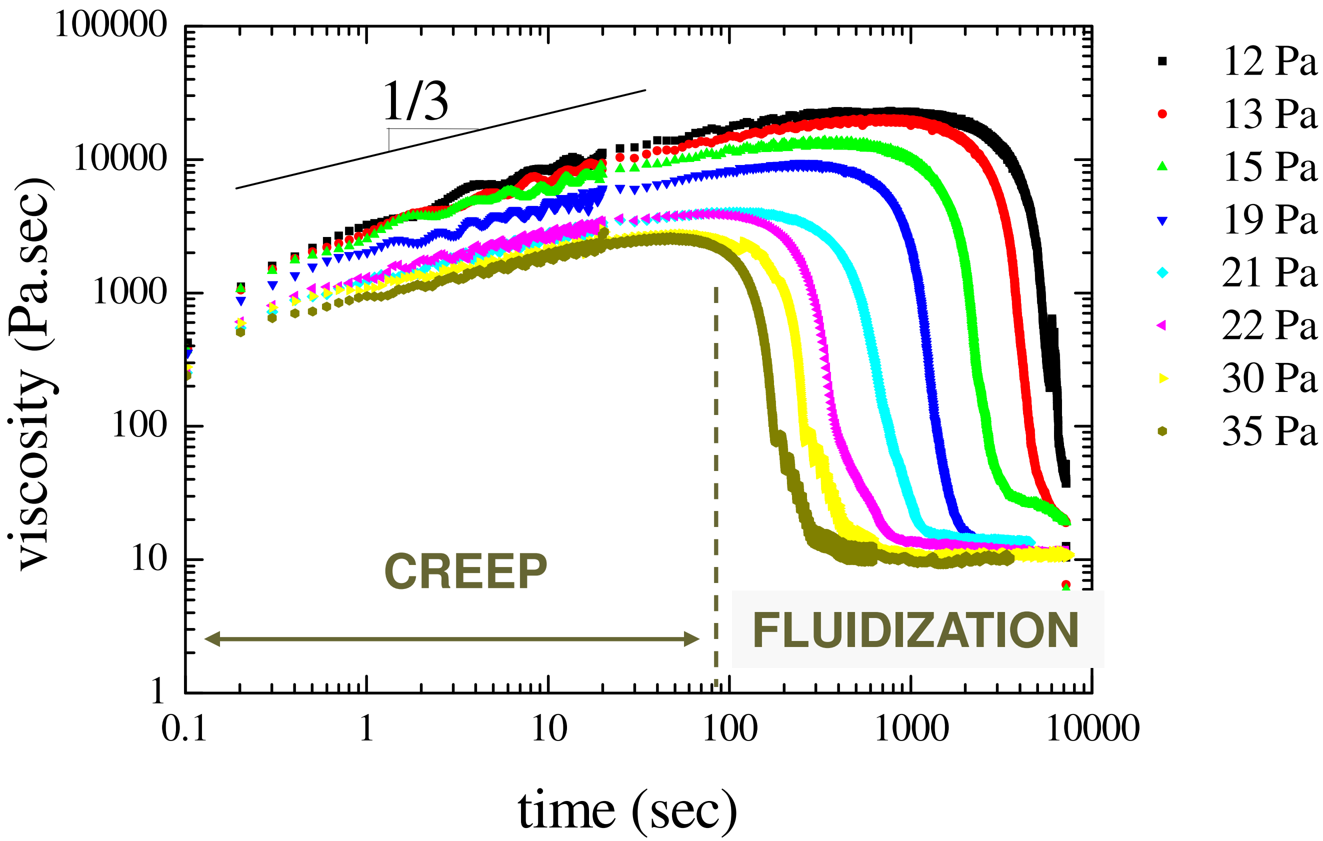
Nechad, PRL (2005)

Analogies with

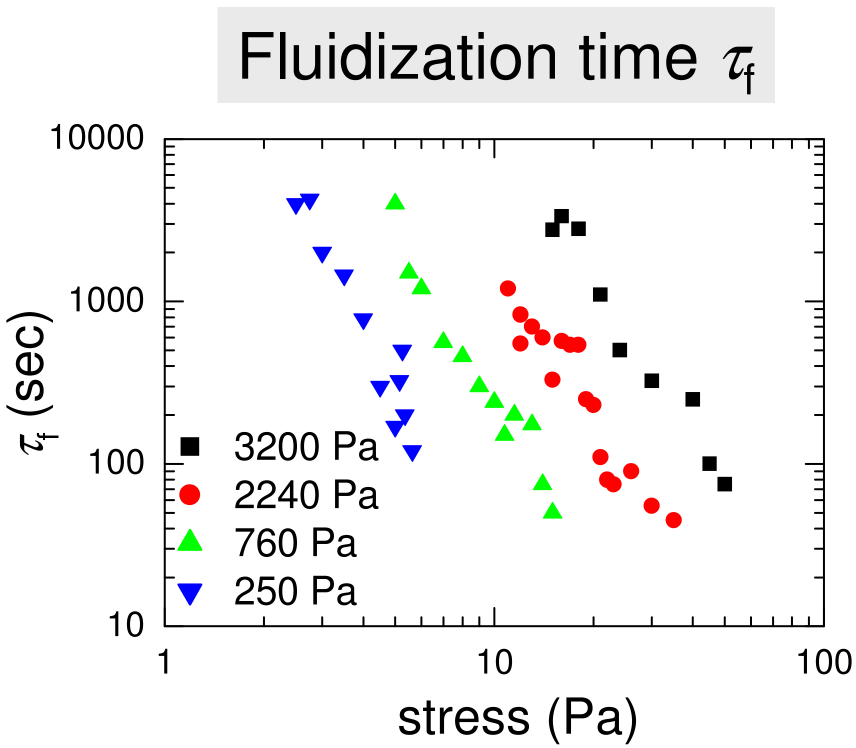
heterogeneous composite polymer materials
EXCEPT **flow with low viscosity** instead of **rupture**

Behavior under Low Stress

$$\eta = \sigma / \dot{\gamma}$$



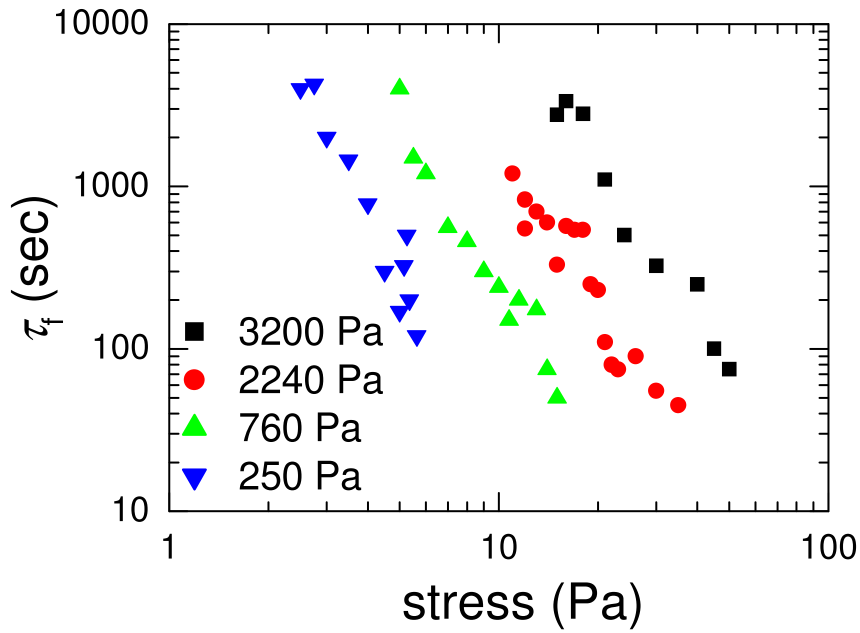
Onset of Flow



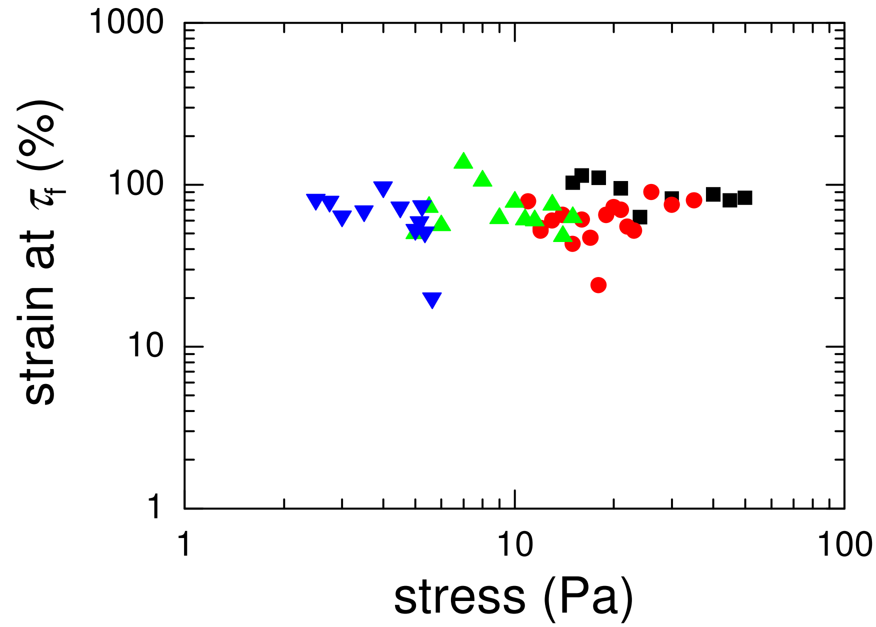
- τ_f ↘ when σ ↗
- τ_f *vs* σ shifted towards smaller stresses for softer materials

Onset of Flow

Fluidization time τ_f

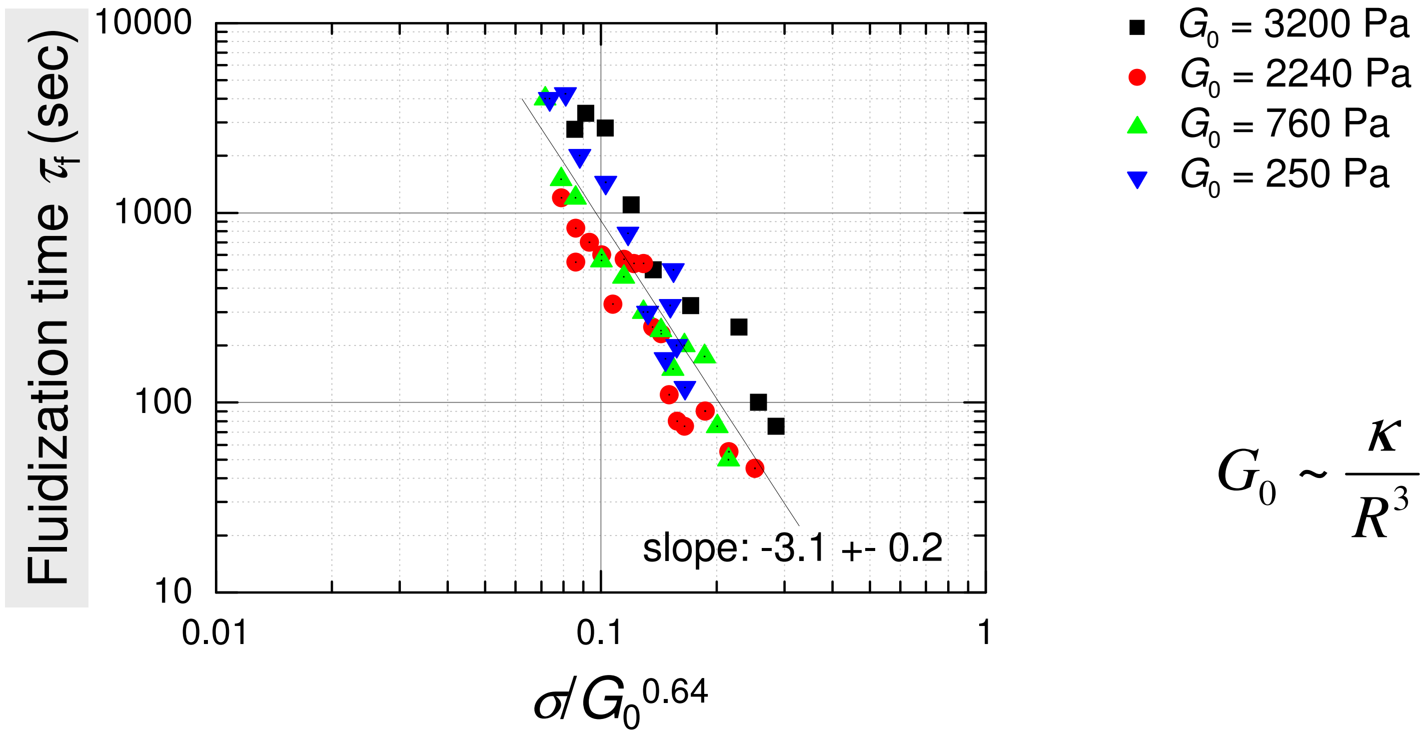


Strain at τ_f



- τ_f ↘ when σ ↗
- τ_f *vs* σ shifted towards smaller stresses for softer materials
- γ_c ~ 70 %
  independent of σ and G_0

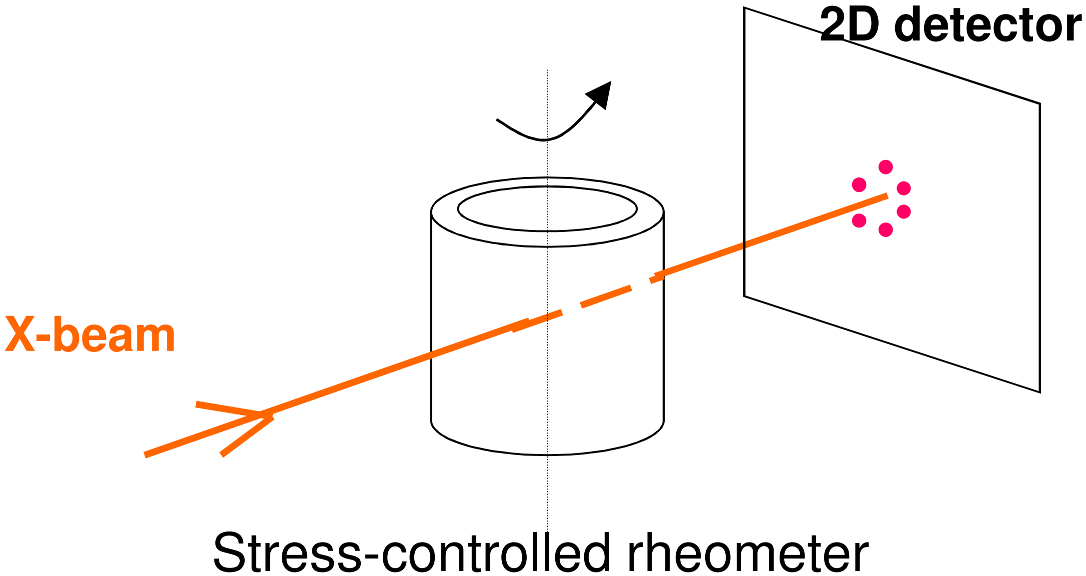
Onset of Flow

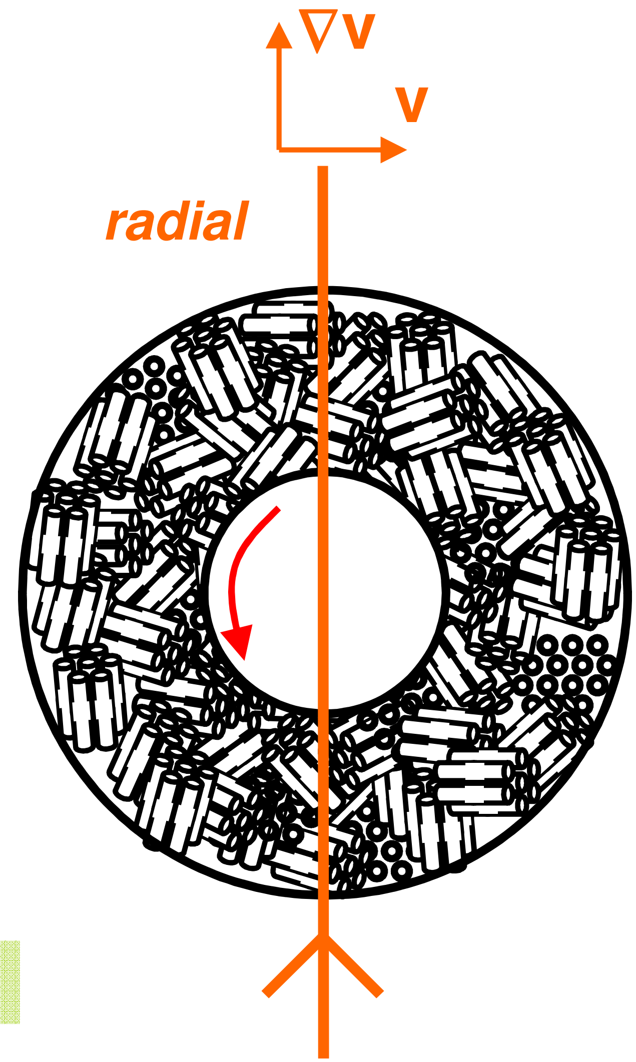


$$G_0 \sim \frac{\kappa}{R^3}$$

- **Powerlaw variation of the time with stress**
  - ➡ ***N**o yield stress?*
- **Collapse when stress normalized by $G_0^{2/3}$**
  - ➡ ***F**luidization time depends only on the force applied per tube*
  - ➡ ***B**ulk properties?*

SAXS under Controlled Stress

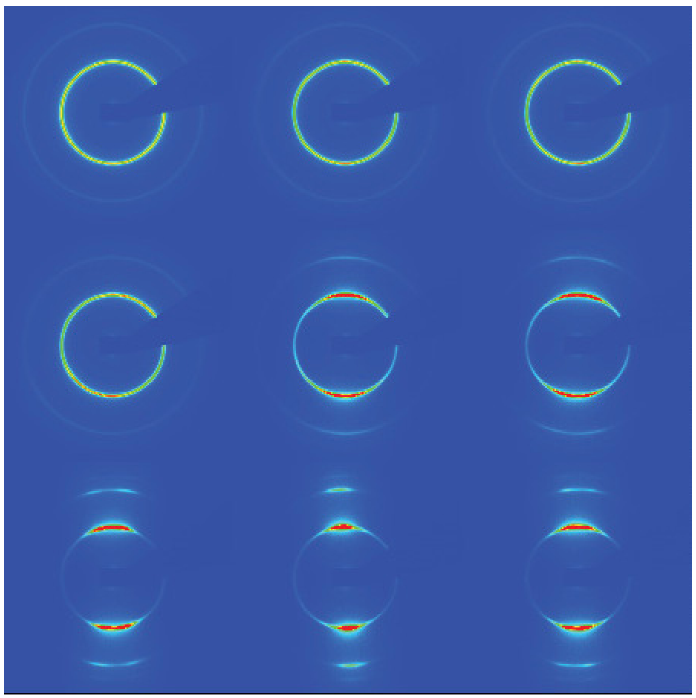


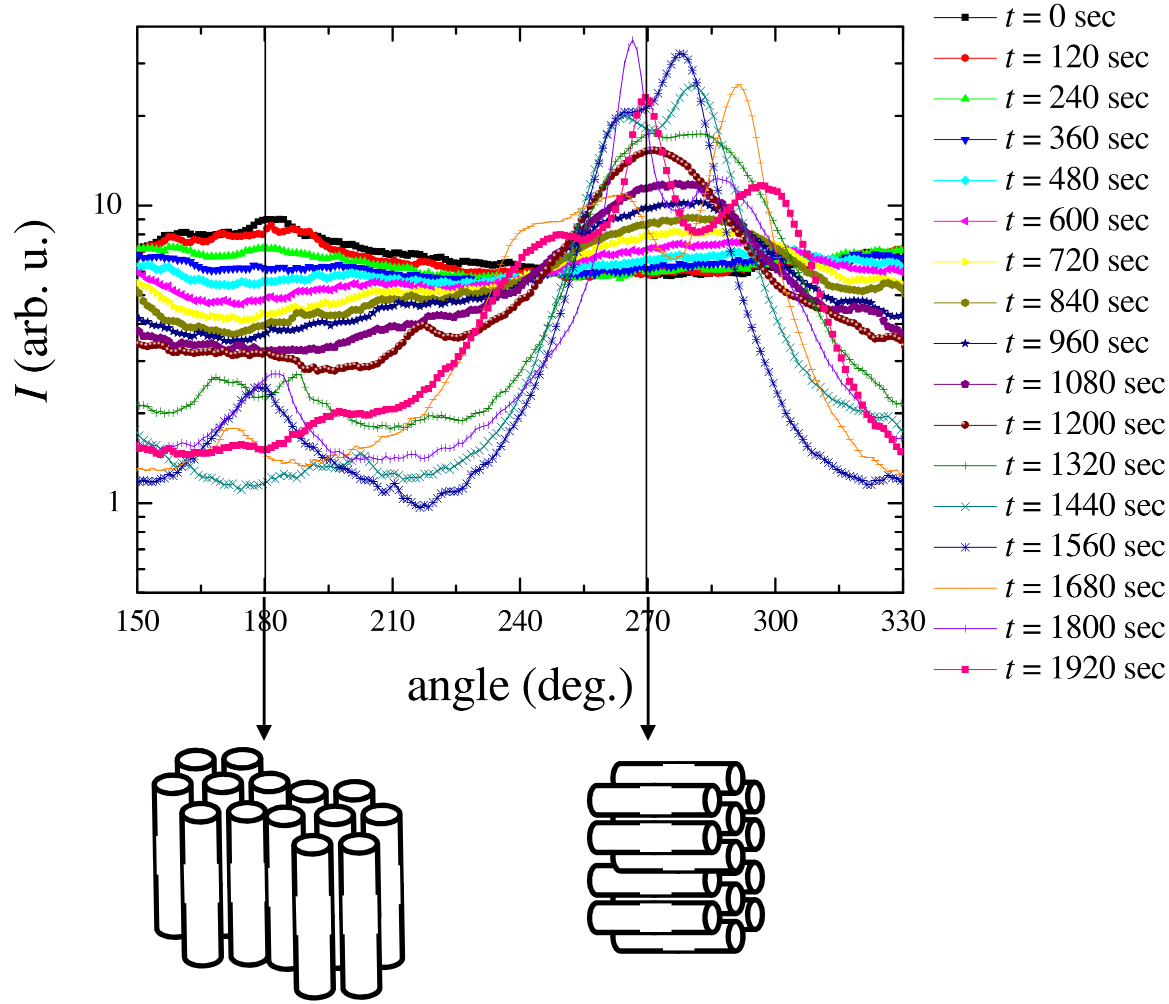


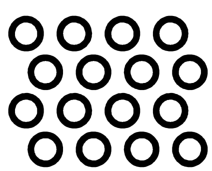
concomitant measurements of SAXS and rheology

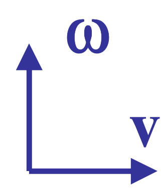
Structures in the creep regime and at the onset of flow?

Time Evolution of the Angular Scan

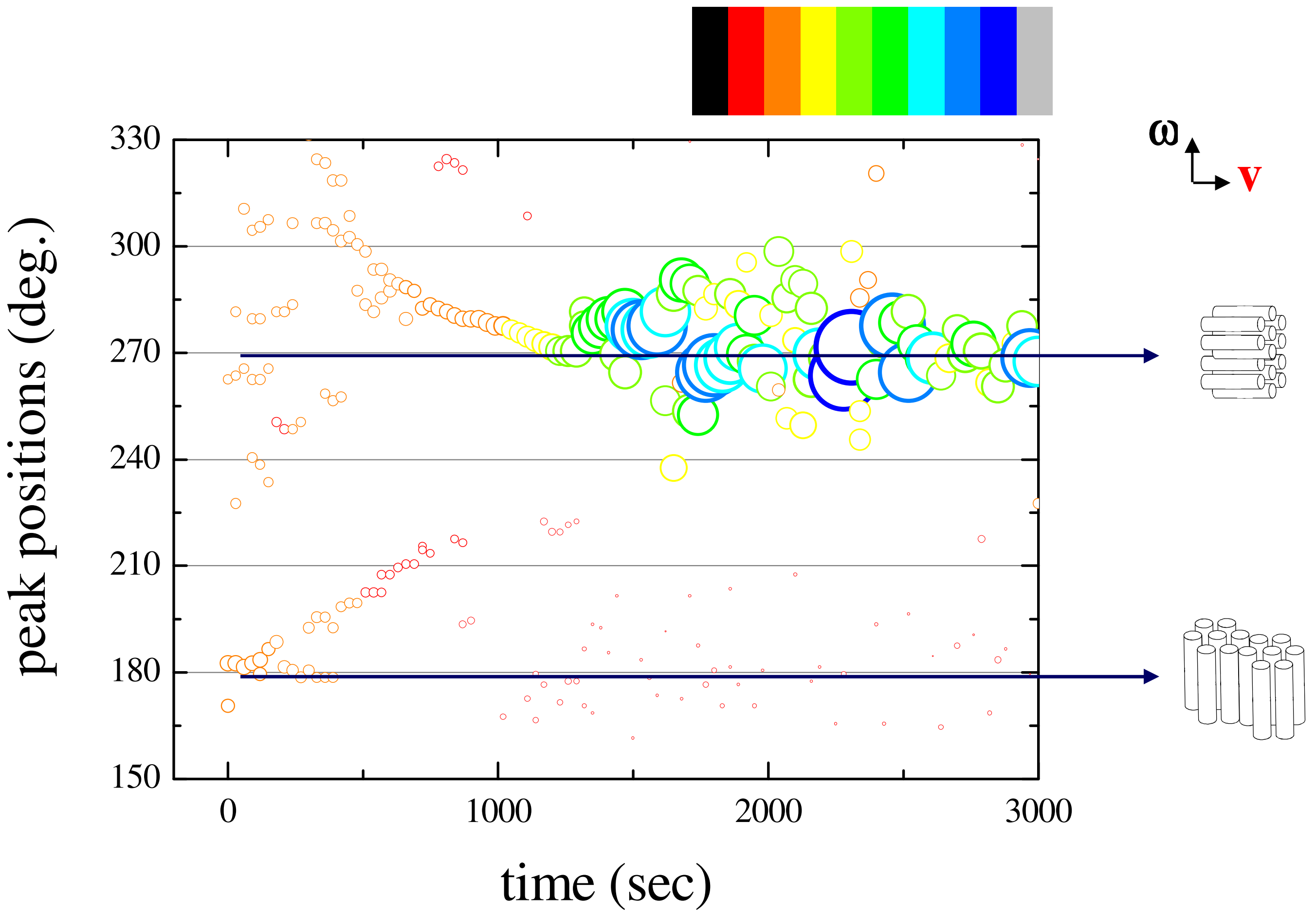


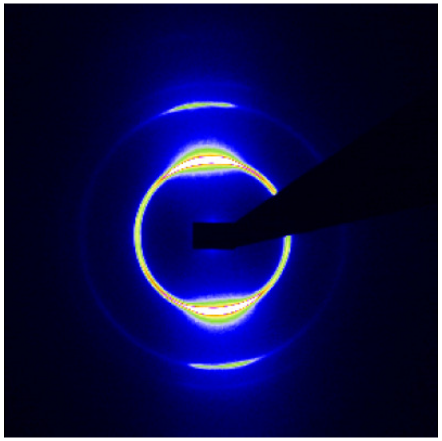




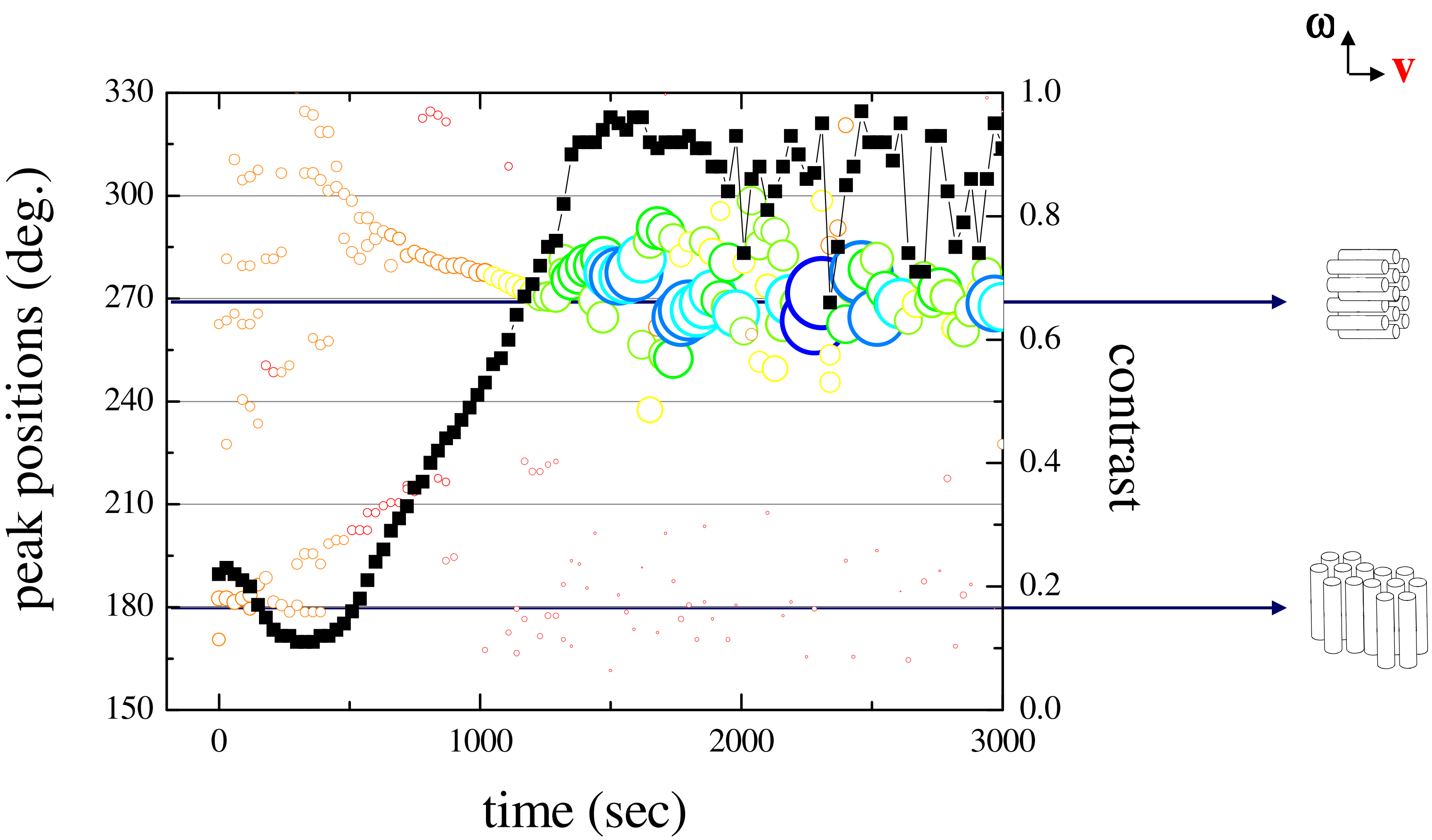


Time Evolution of the Peaks' Positions and Intensity



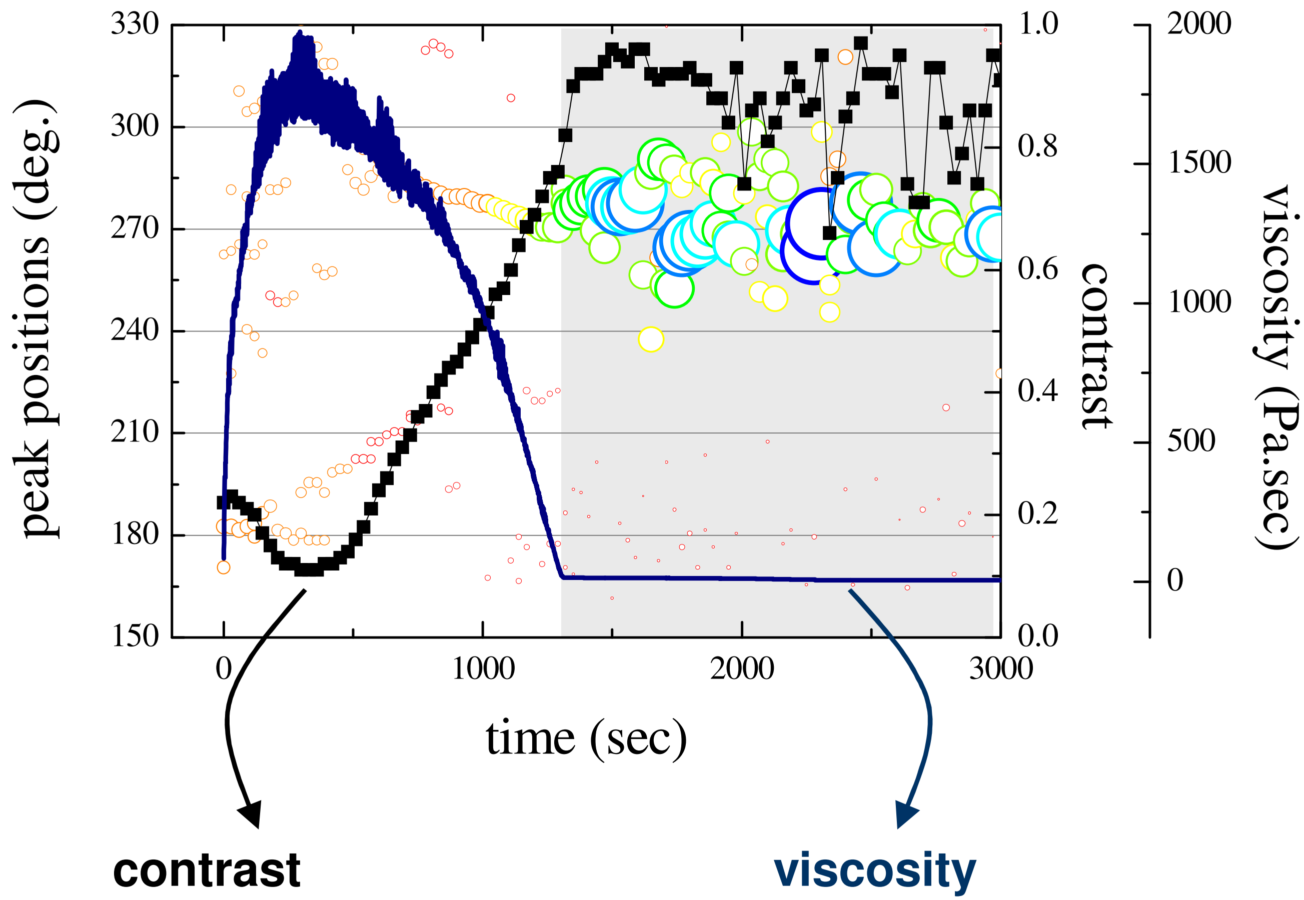


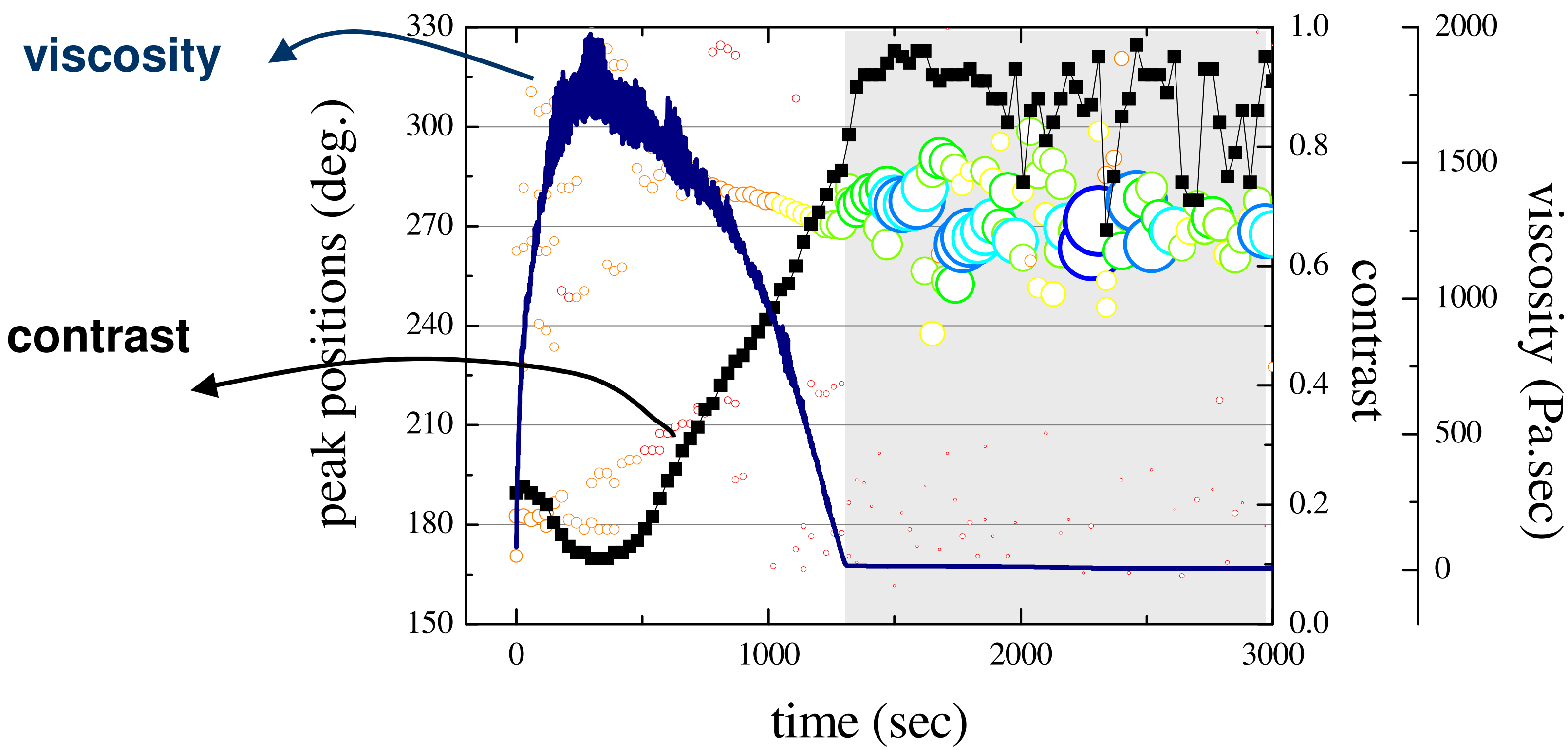
Time Evolution of the Peaks' Positions and Intensity



Contrast = ($I_{max} - I_{min}$) / ($I_{max} + I_{min}$)

Correlation Structure / Rheological Behavior





At the onset of flow:

Collective rearrangements of all crystallites

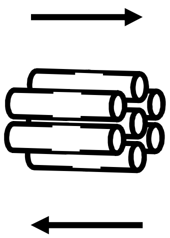
- *All oriented along the flow (90 deg) but wide angular distribution (35 deg)*

- In agreement with the scaling for fluidization time

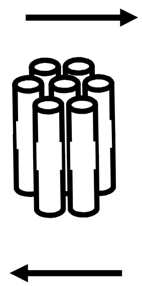
Not due to wall slip !!

What happens in the solid regime?

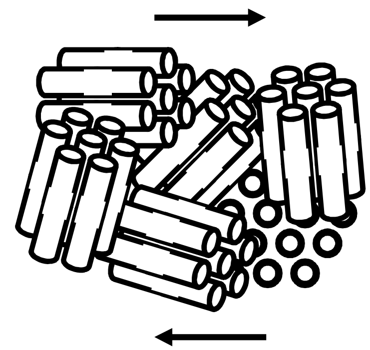
~~resistance to flow~~



resistance to flow



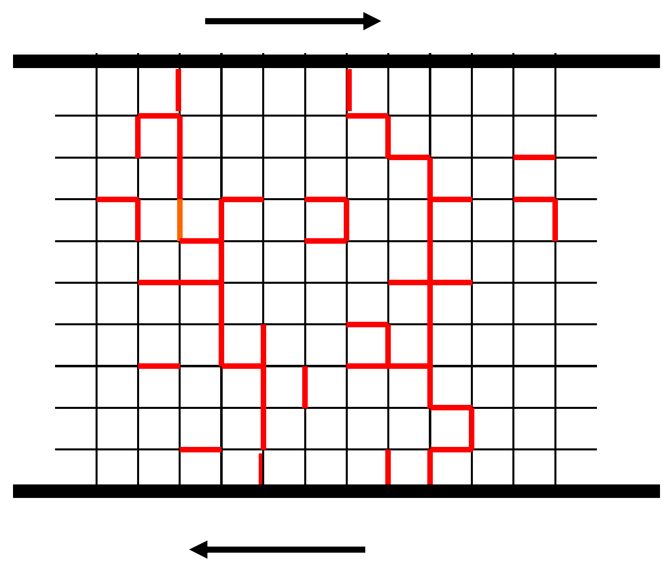
resistance to flow



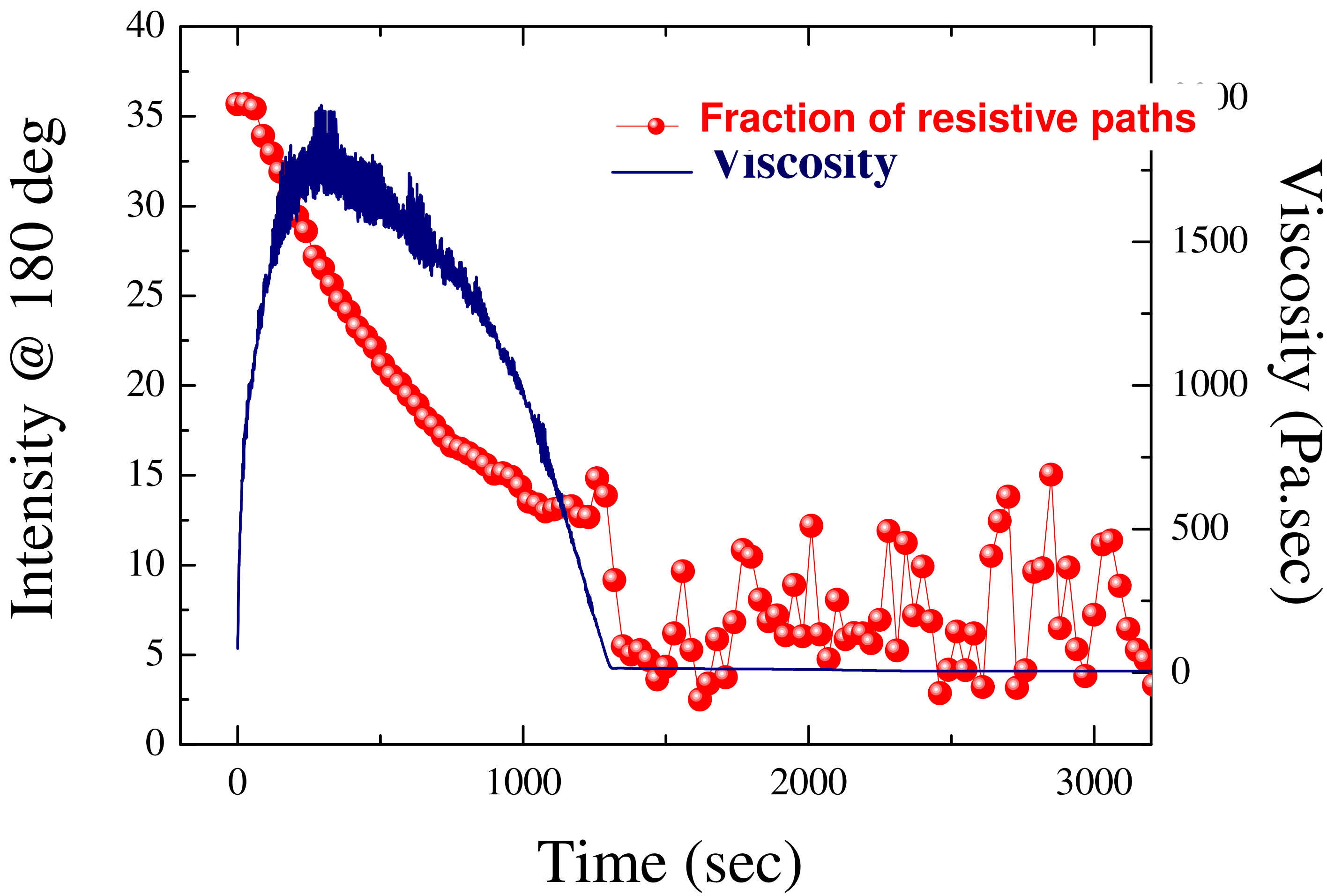
Bulk 3D polycrystalline sample

=

Percolated network of resistive paths



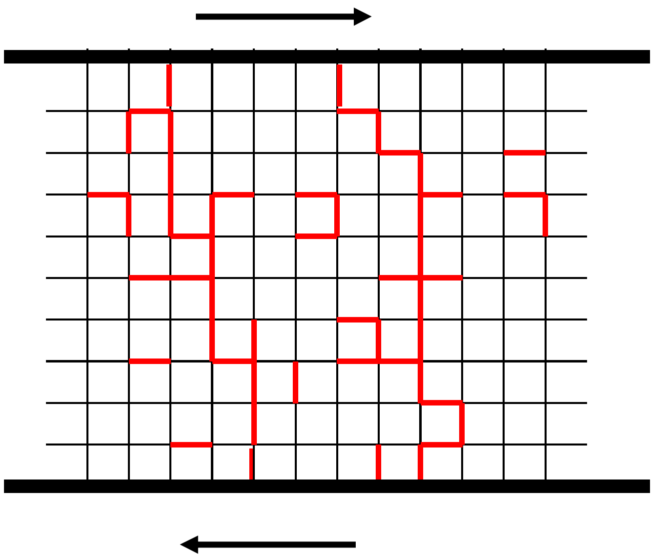
What happens in the solid regime?



Before onset of flow:

slow rearrangements to remove « most unfavorable » grain orientation (180 deg)

Correlation Structure / Rheological Behavior
A NAIVE PICTURE



De-percolation

FLUIDIZATION

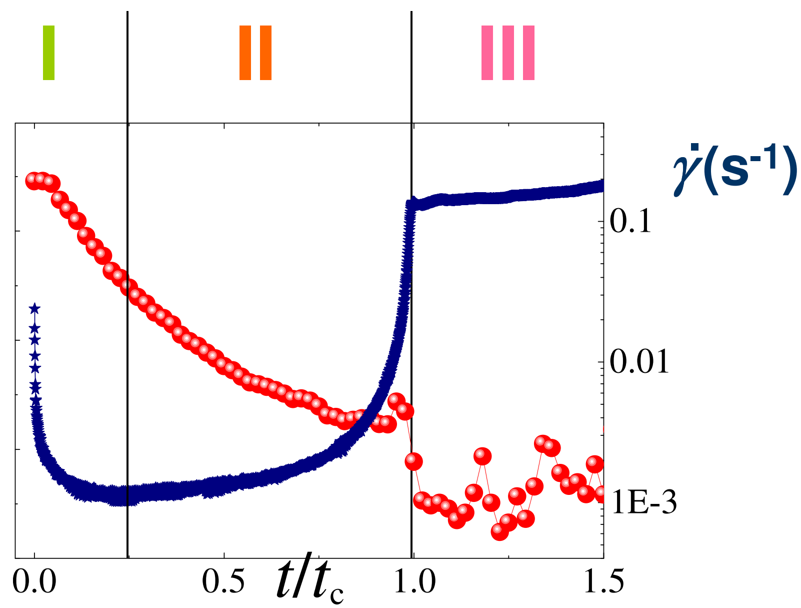
Percolated network

CREEP

No resistive paths

FLOW
stationary state

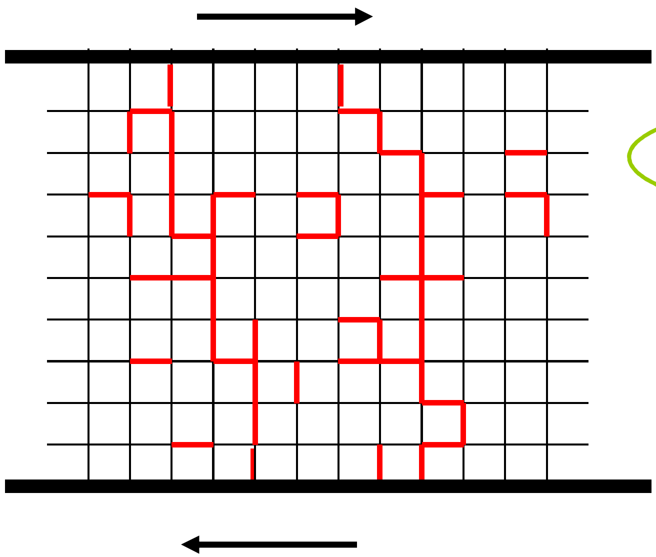
Fraction of resistive paths



General mechanism?

Bauer, Oberdisse and LR, PRL (2006)

Correlation Structure / Rheological Behavior
A NAIVE PICTURE

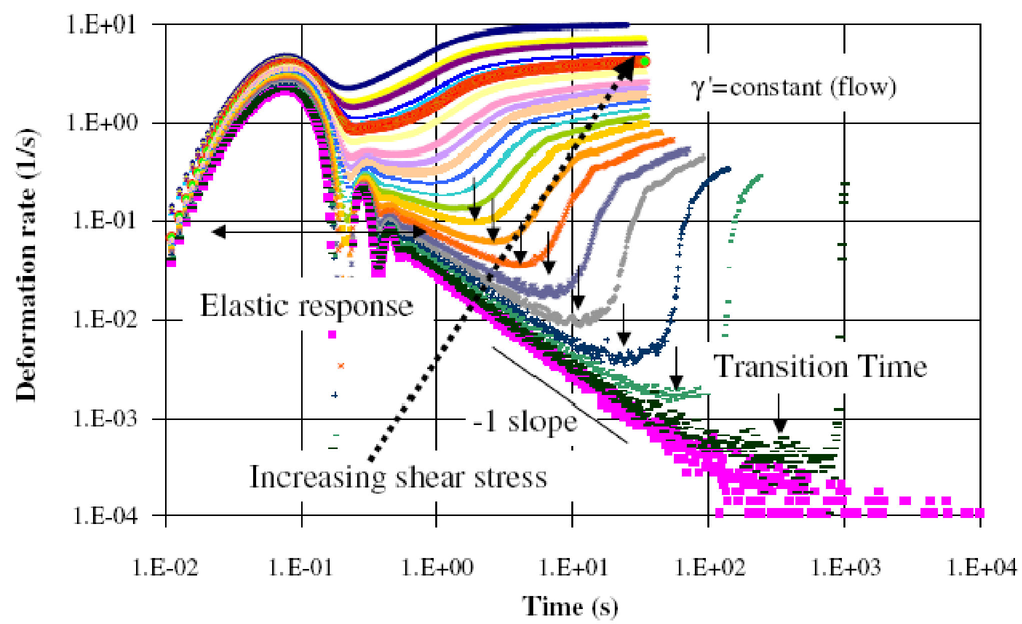


Percolated network — CREEP

De-percolation — FLUIDIZATION

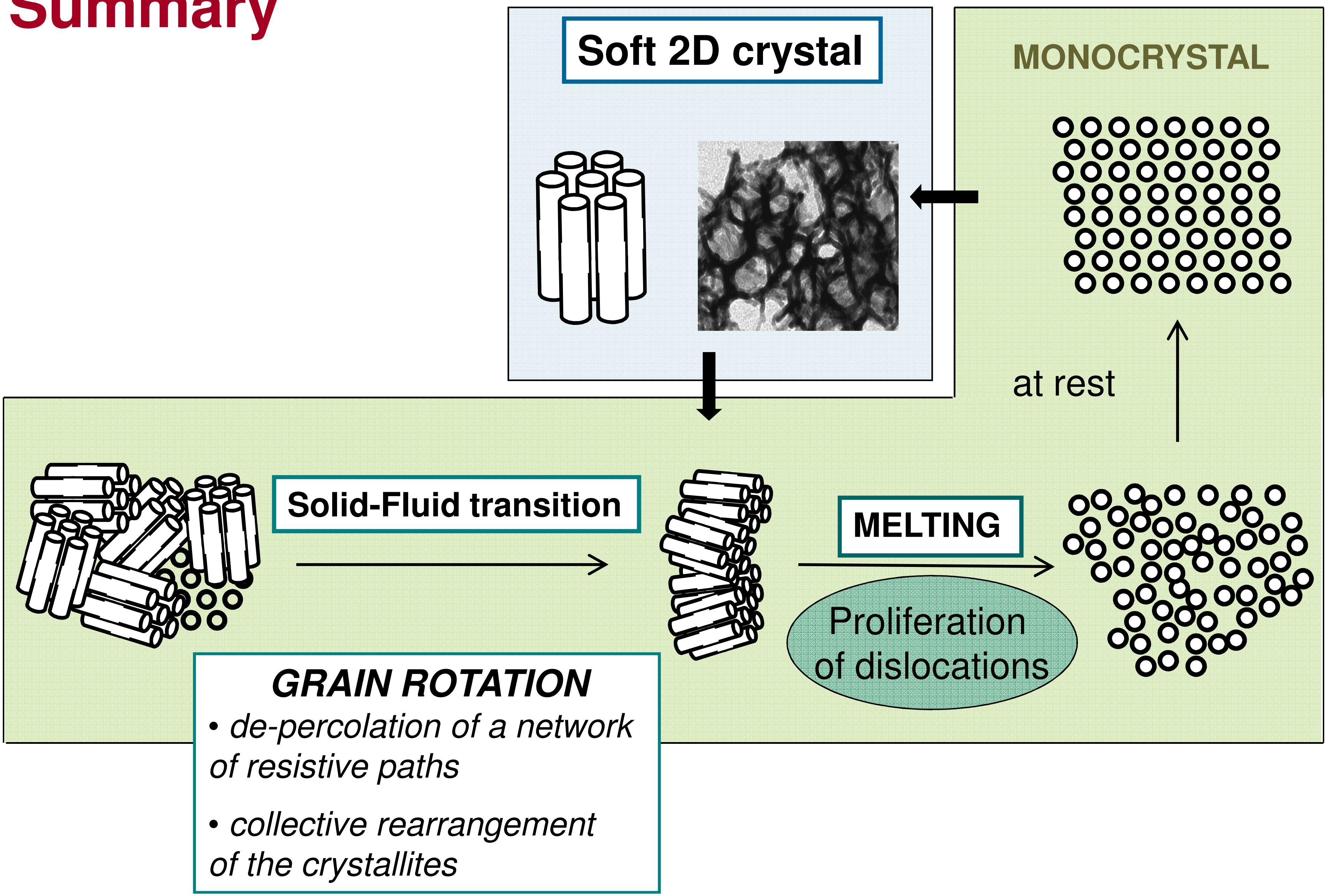
No resistive paths — FLOW stationary state

General mechanism?



F. Caton, Rheologica Acta (2008)

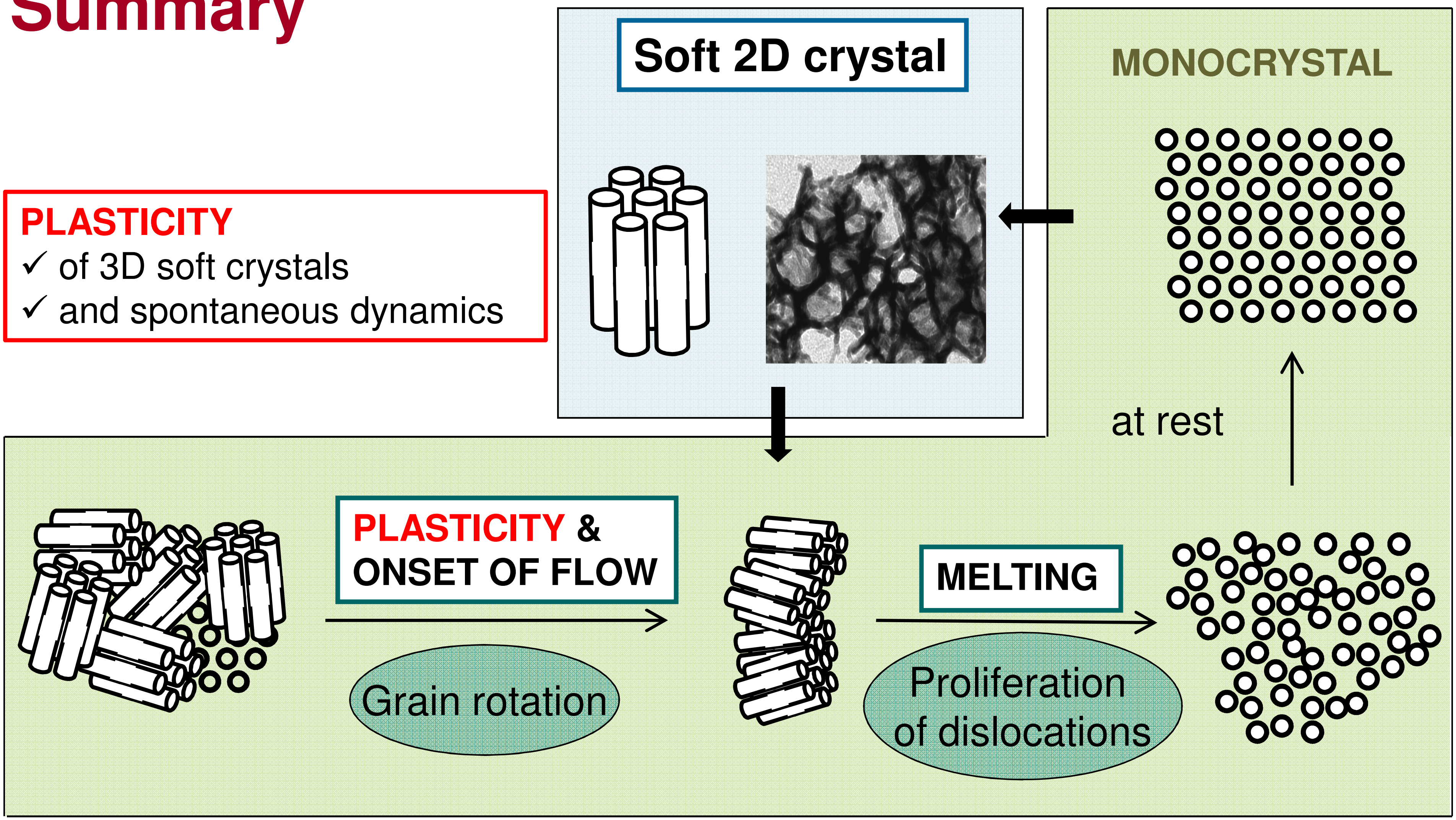
Summary


Soft 2D crystal
MONOCRYSTAL
at rest
Solid-Fluid transition
MELTING
Proliferation
of dislocations
GRAIN ROTATION
• de-percolation of a network of resistive paths
• collective rearrangement of the crystallites

Summary

PLASTICITY

✓ of 3D soft crystals
✓ and spontaneous dynamics



Outline

I. Soft 2D columnar crystal

A) **Designing** a versatile self-assembled structured system

B) **Flow -** characterizing and modeling the shear-induced transition

C) **Plasticity -** Understanding the solid-liquid transition in complex fluids

II. Towards the plasticity of soft 3D polycrystals

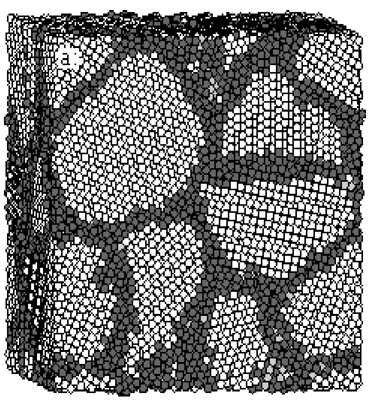
III. Plasticity and spontaneous dynamics of soft glasses

Plasticity of Polycrystals

DYNAMICS and PLASTICITY of ATOMIC POLYCRYSTALS

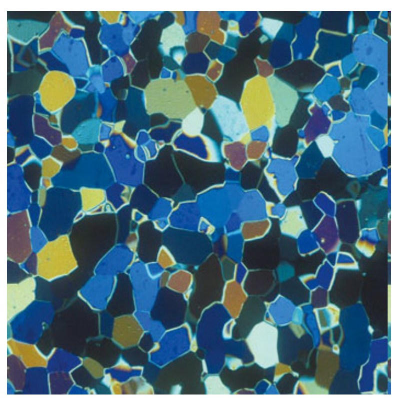
- Original mechanical properties of polycrystals (e. g. superplasticity)
- Physical mechanisms at the origin of plasticity?
- Role of grain boundaries?

Simulation



Schiotz, 1998

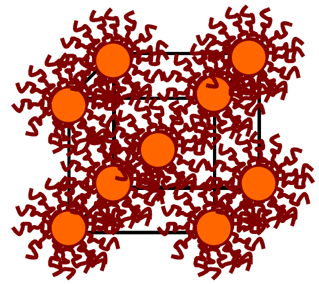
Experiment



J. Weiss, LGGE/CNRS

OUR APPROACH: USE of a COLLOIDAL ANALOGUE

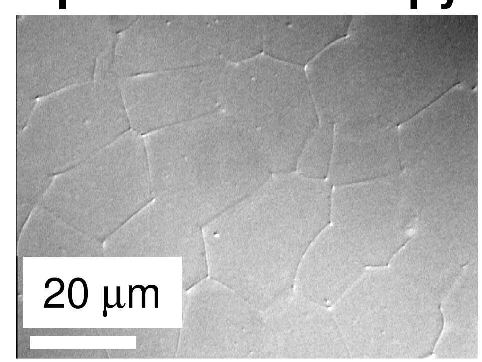
block-copolymer  + nanoparticles



cubic phase (fcc)

segregation in the grain-boundaries

optical microscopy



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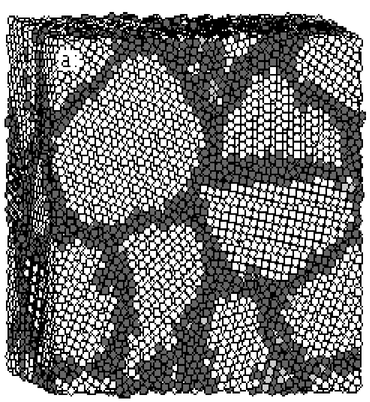
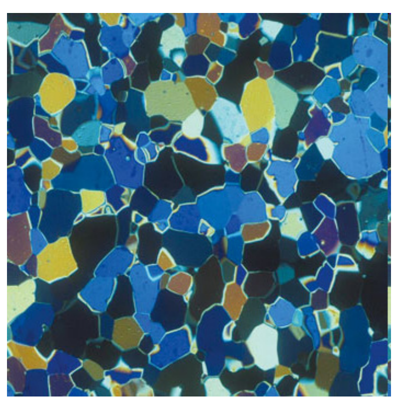


Schiotz, 1998

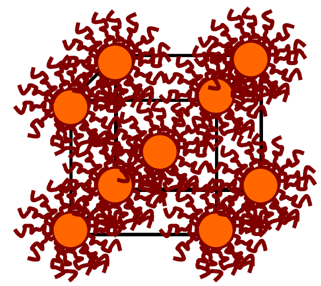
Experiment



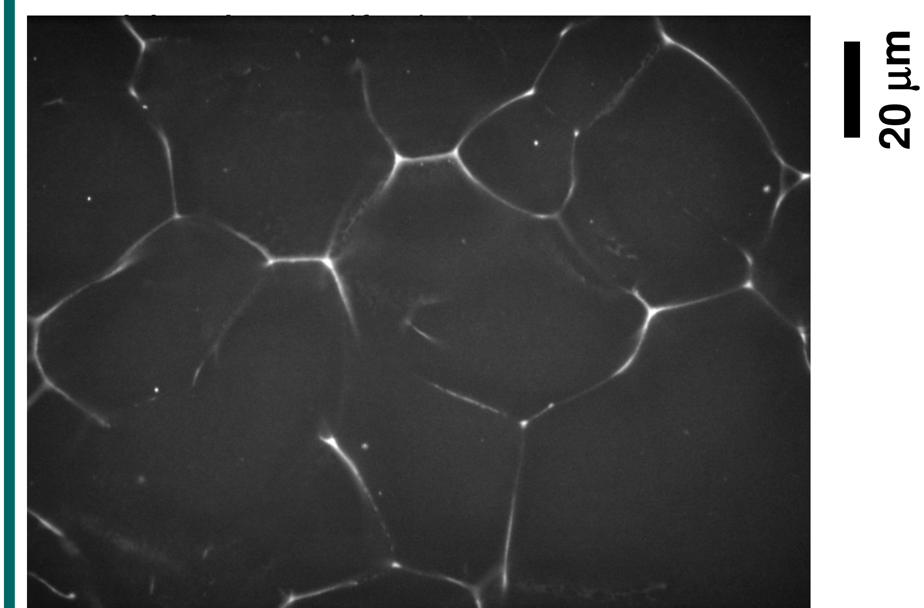
J. Weiss, LGGE/CNRS

OUR APPROACH: USE of a COLLOIDAL ANALOGUE

<u>block-copolymer</u>  + <u>nanoparticles</u>



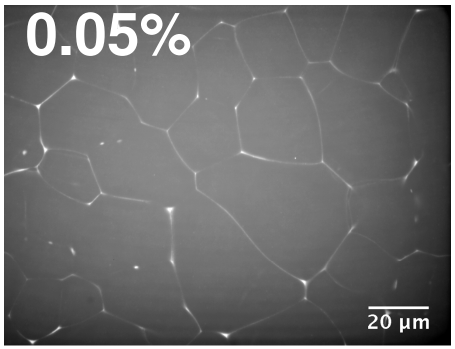
segregation in the grain-boundaries

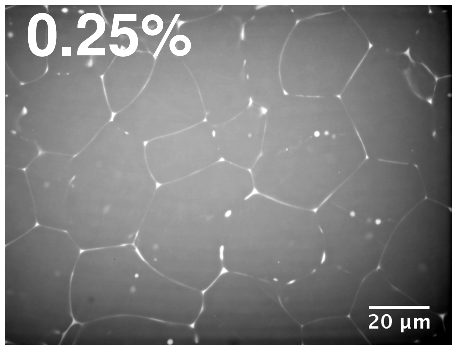


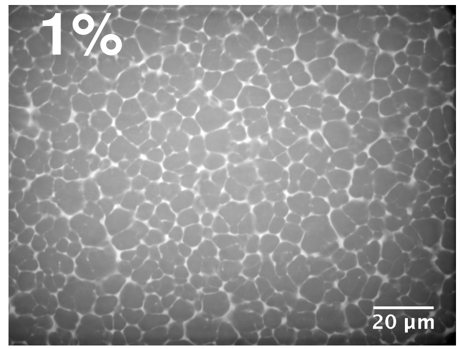
Direct Visualization of Grain Refinement

2 control parameters

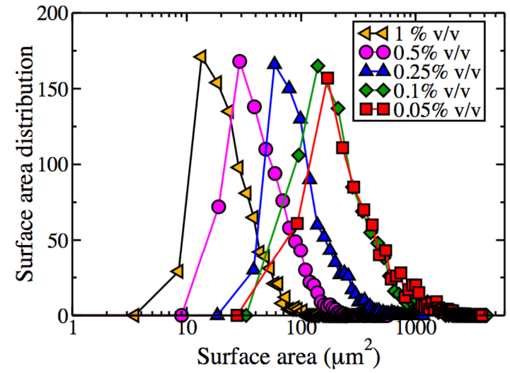
- Φ, volume fraction of « impurities »
- R, speed of the crystallization ramp

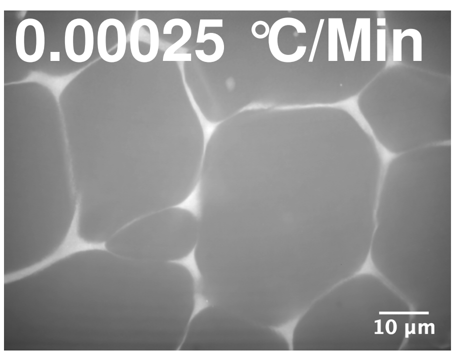


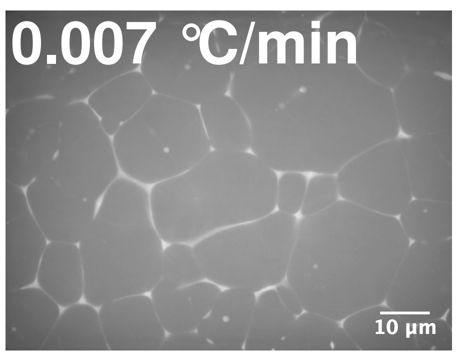


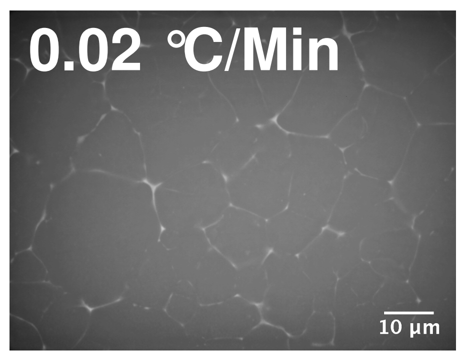


R = 0.007 ℃/min

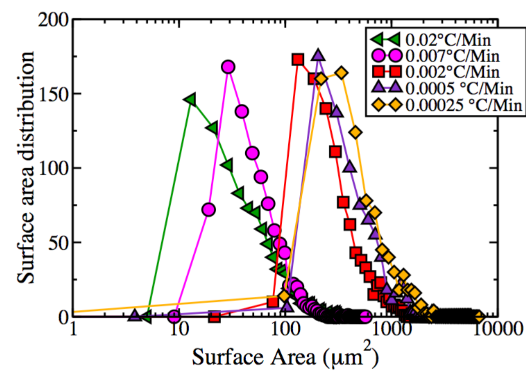




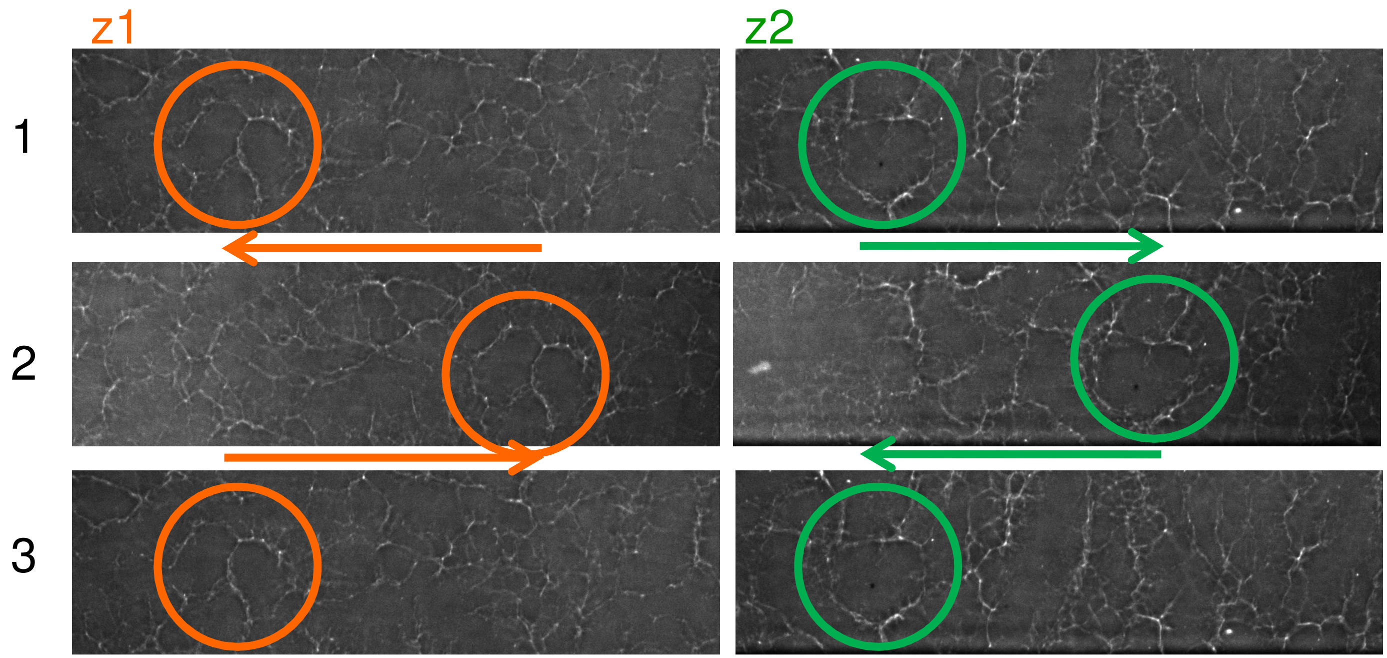


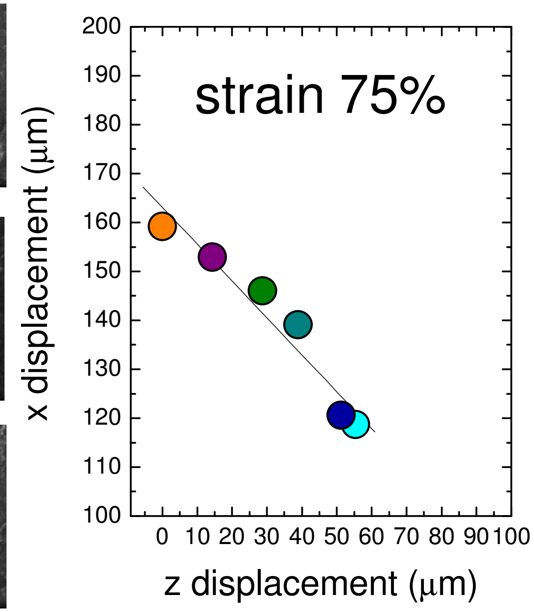


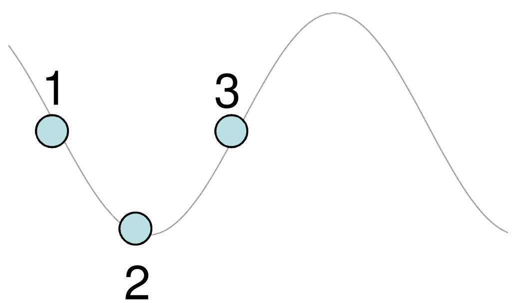
Φ = 0.5%

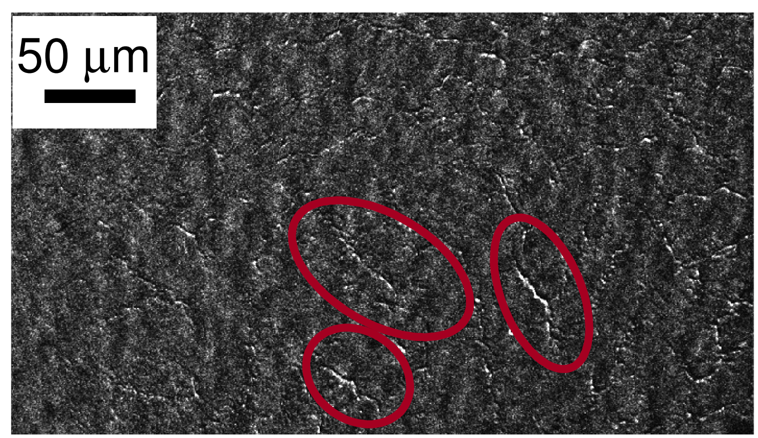


Super Preliminary Shear Experiments









on-going work …

Cf. simulations Shiba & Onuki (Poster 108)

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Slow Dynamics of Soft Glasses

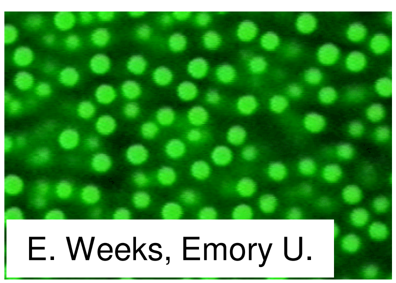
SLOW DYNAMICS of JAMMED MATTER

still poorly understood

- Associated with aging & dynamical heterogeneities
- Key role of elasticity & relaxation of internal stresses

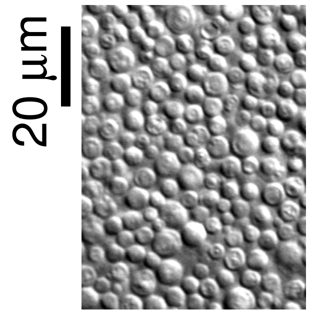
Origin? Driving force?

colloids



grains

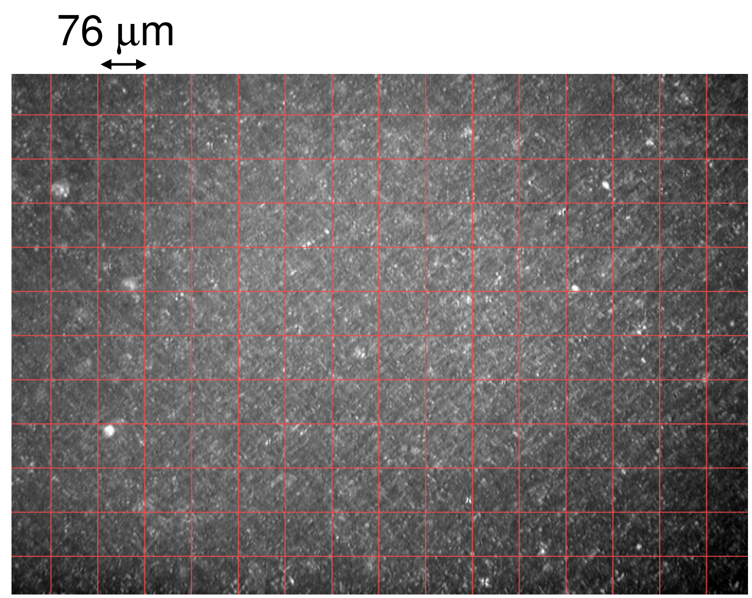
EXPERIMENTAL SYSTEM & METHOD



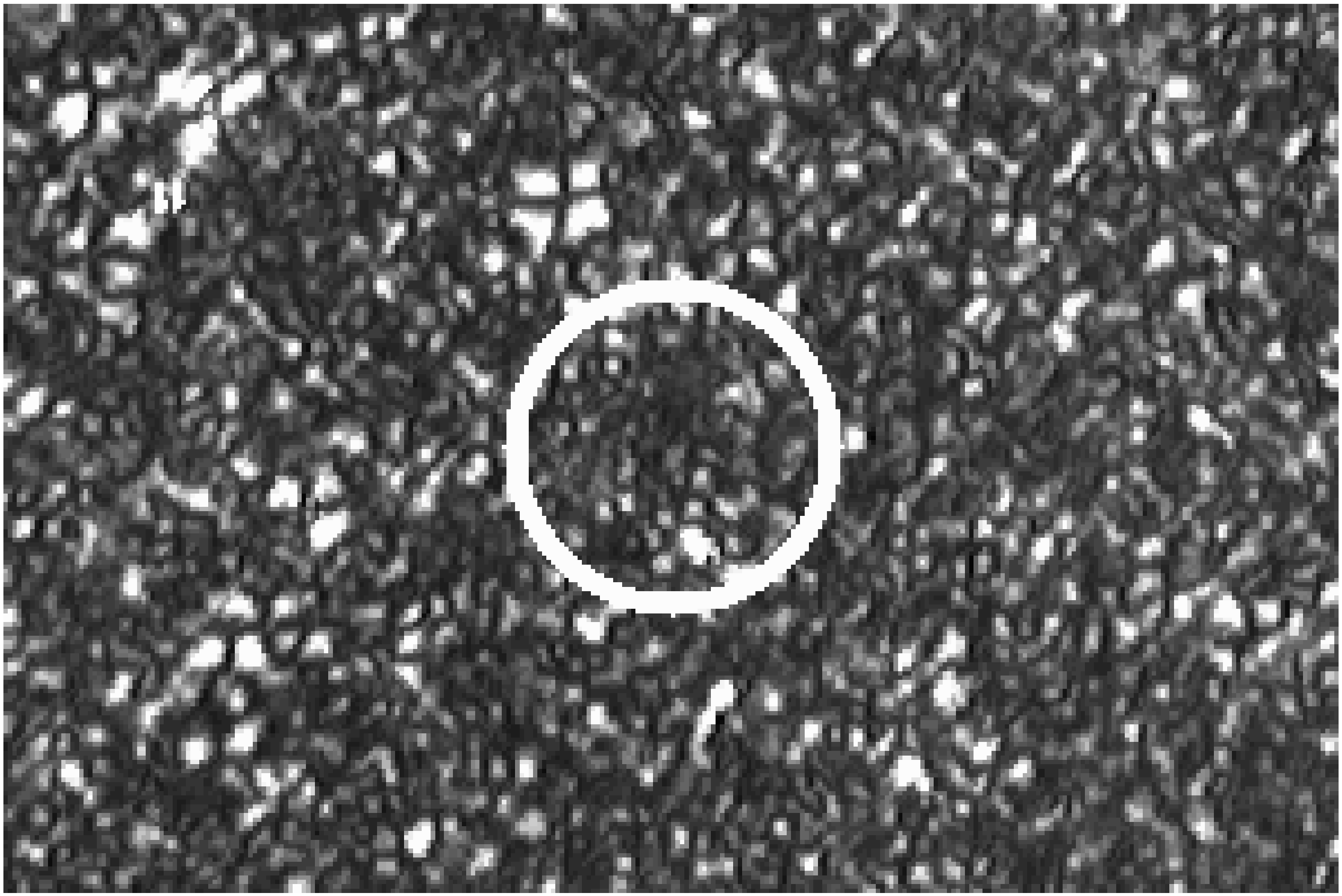
onion phase

- Slow dynamics after a temperature quench
- Time- and space-resolved measurements

↪ $\Delta r_i(\tau, t_w)$

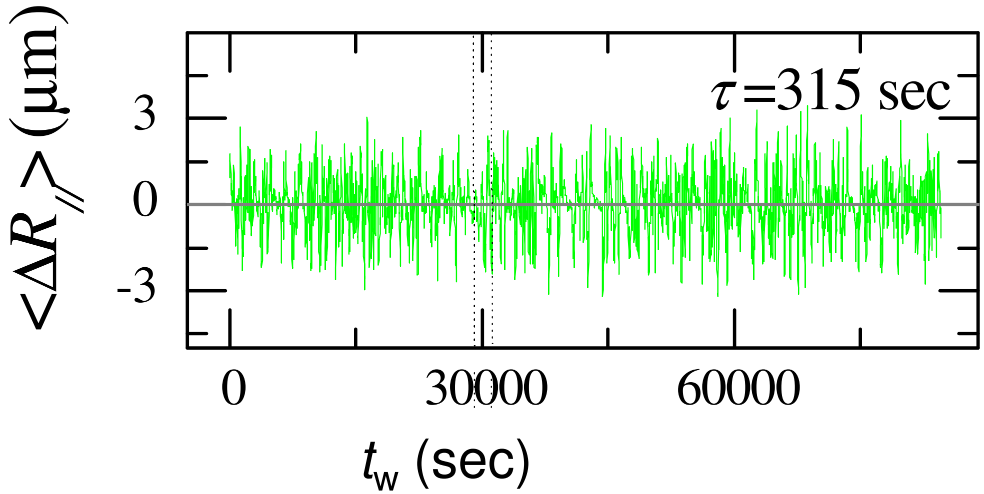


Time- and Space-Resolved Measurements



Role of Temperature ?

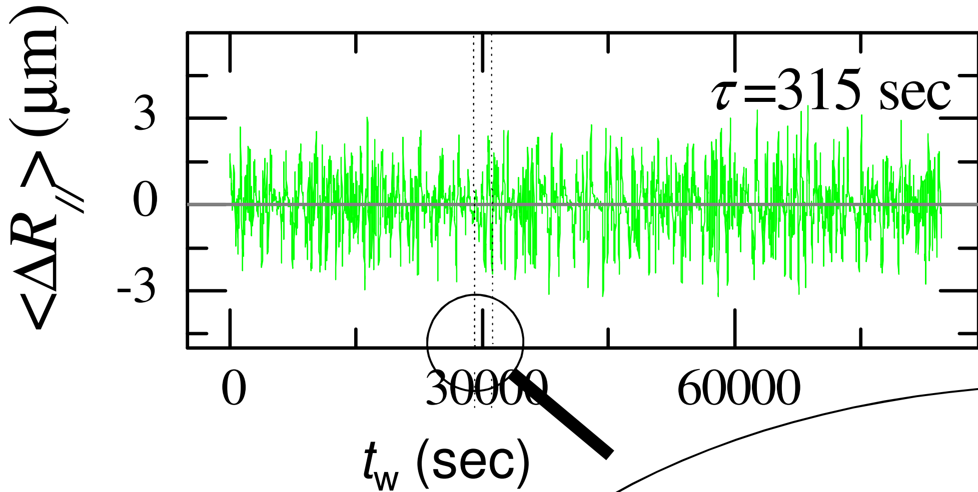
Global displacement



- Intermittent motion
- Fluctuations around an average position

Role of Temperature ?

Global displacement



- Intermittent motion
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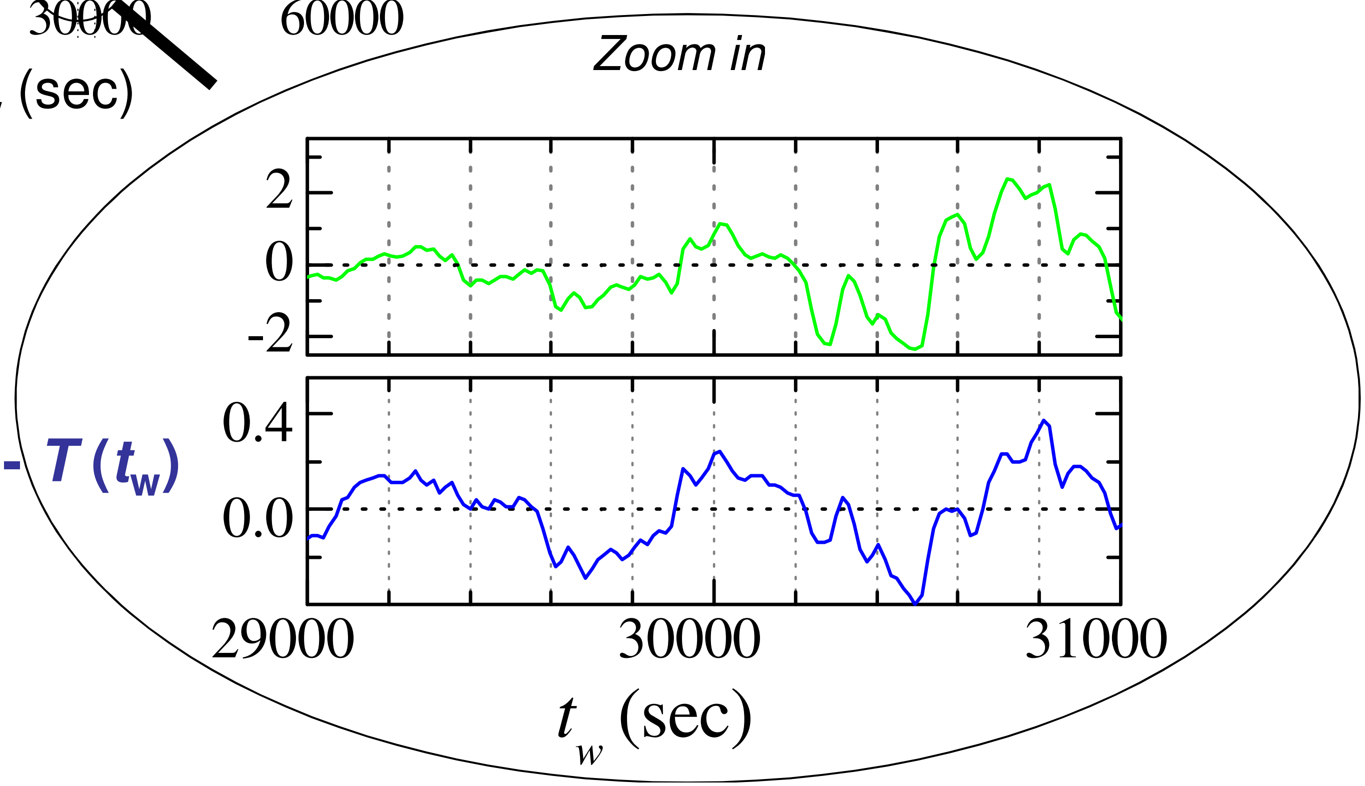
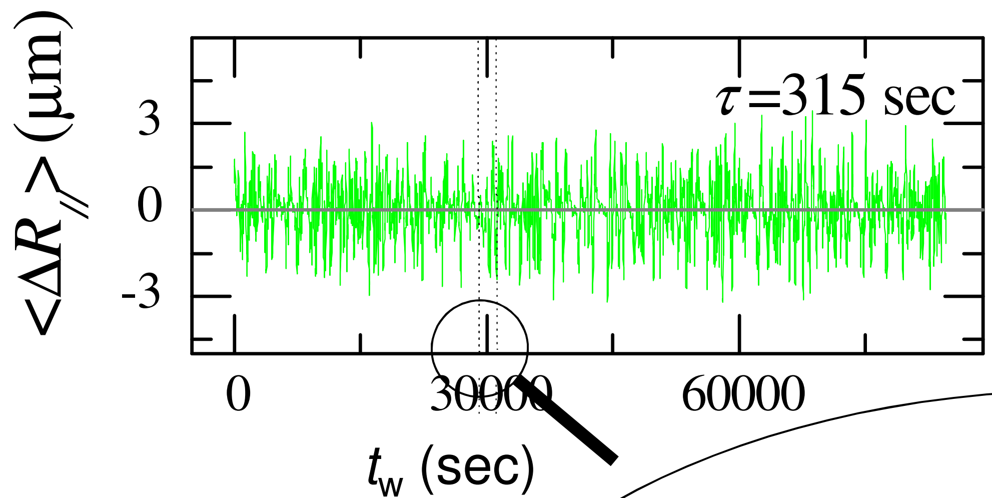


ΔT (℃) = $T(t_w+\tau) - T(t_w)$

Role of Temperature ?

Global displacement



- Intermittent motion
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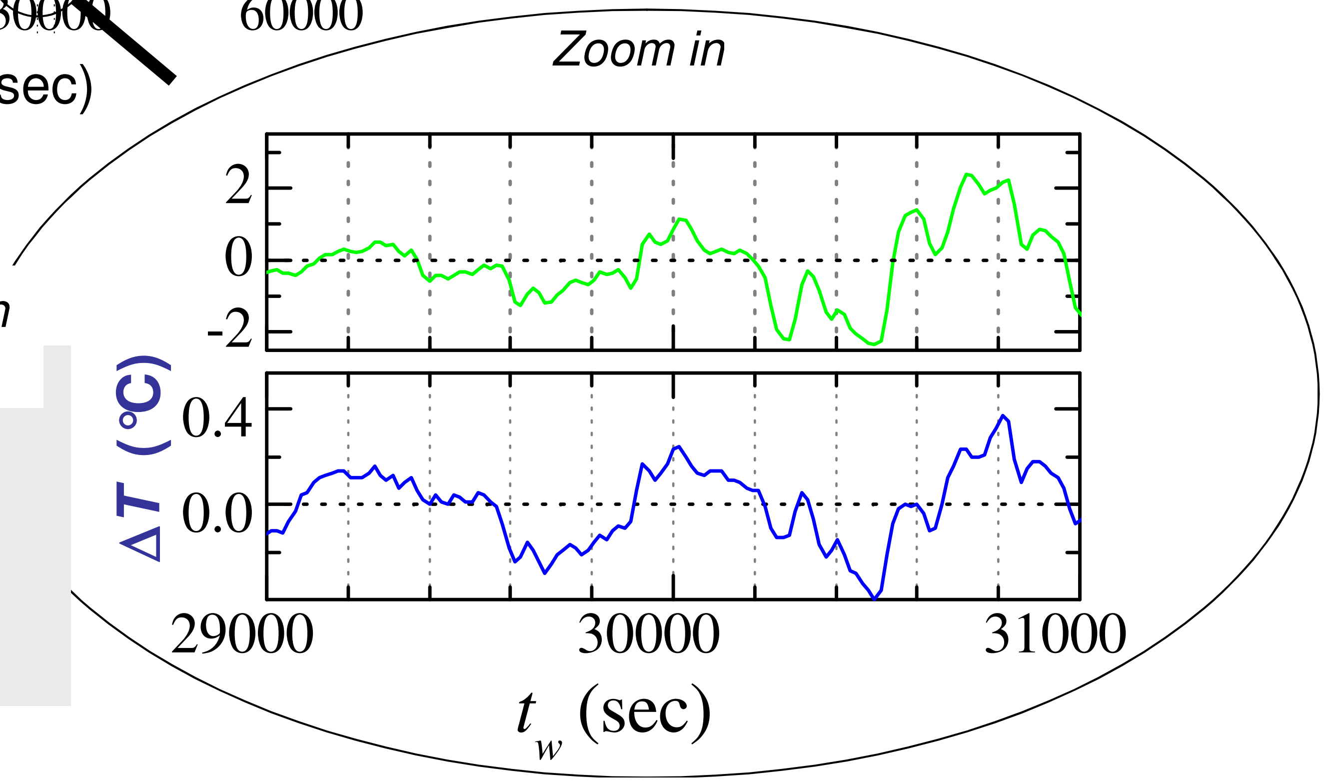
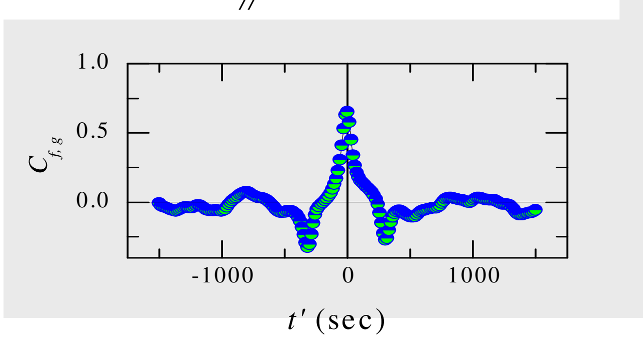
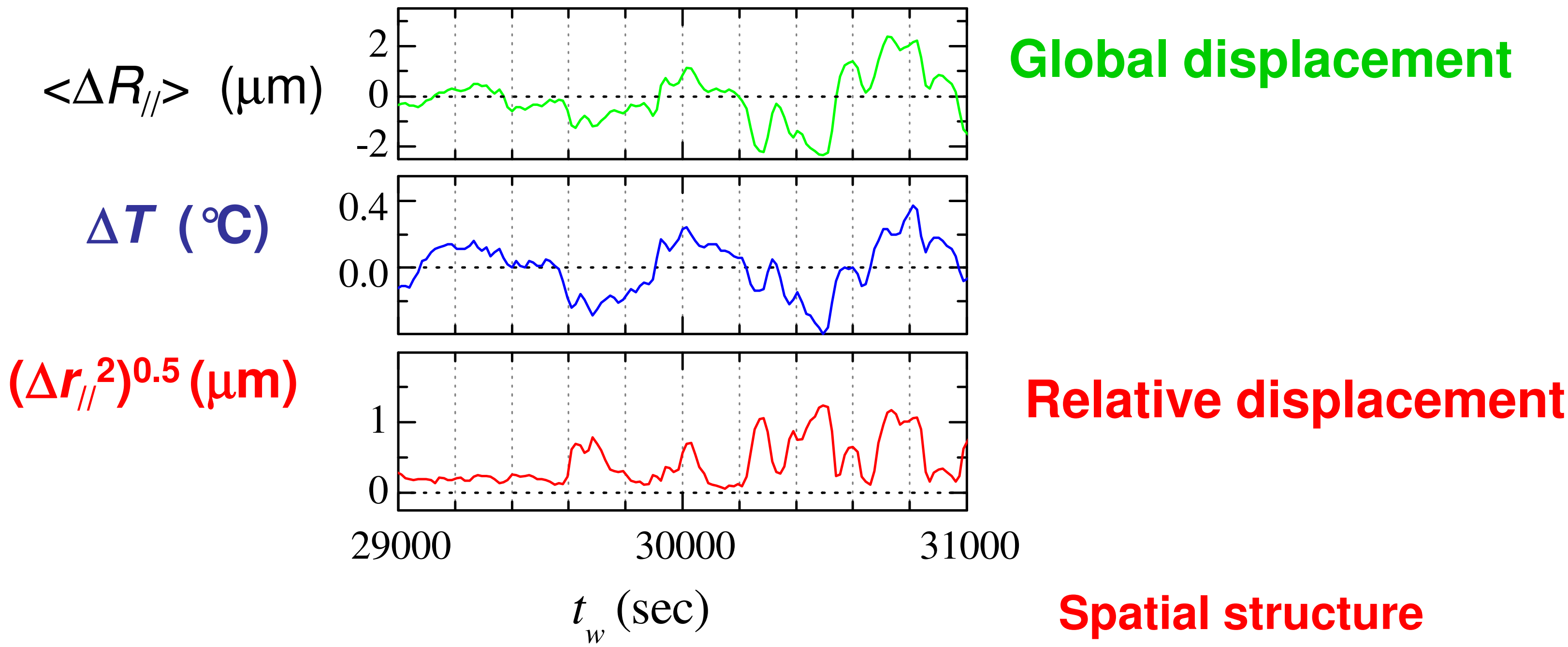


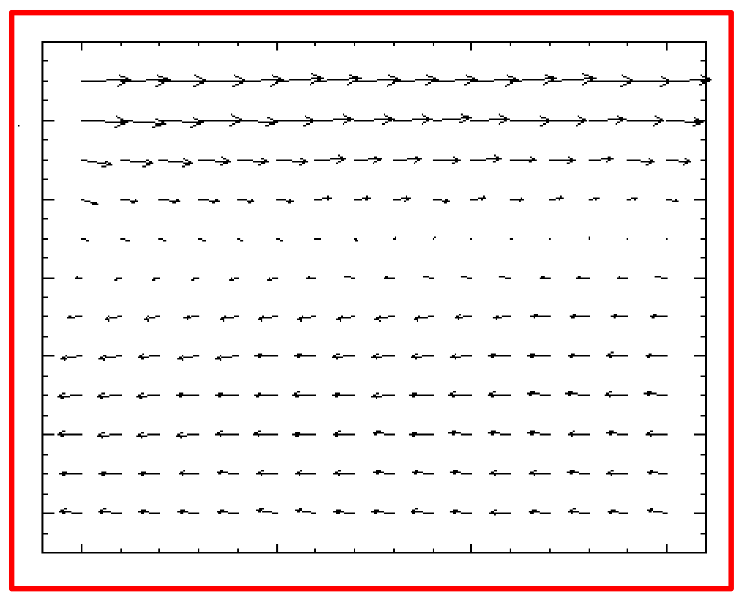
Cross-correlation between
<ΔR//> and ΔT



Temperature-driven Intermittent SHEAR Deformations

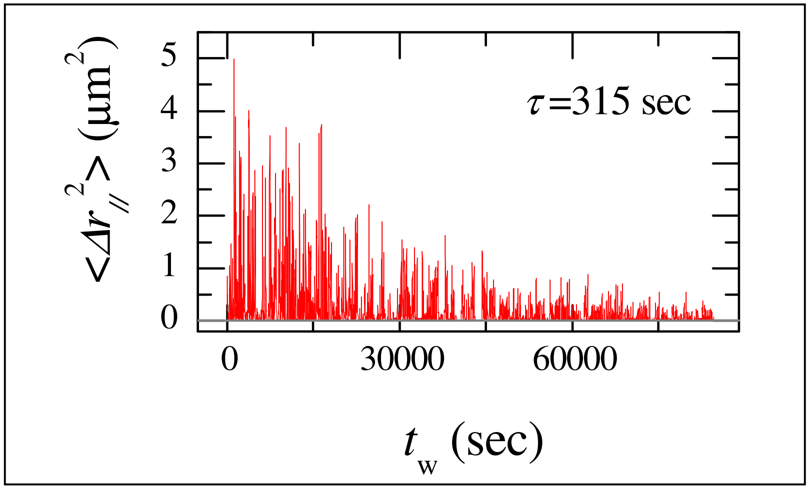


Spatial structure

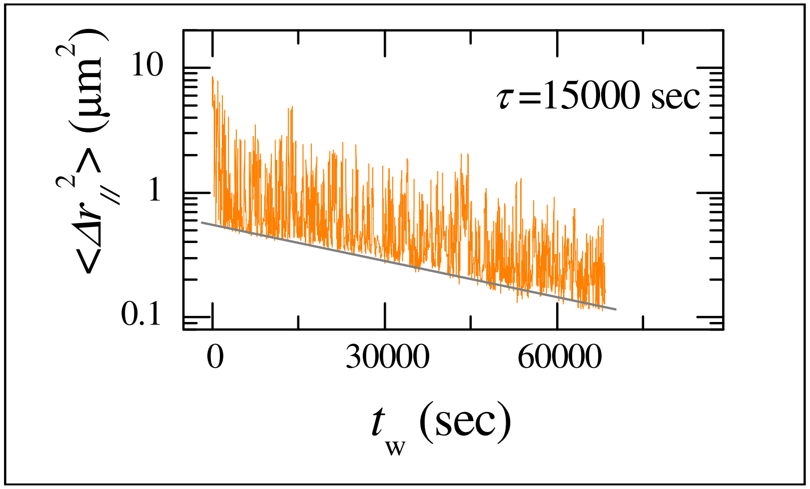


SHEAR

Temperature-driven Intermittent SHEAR Deformations

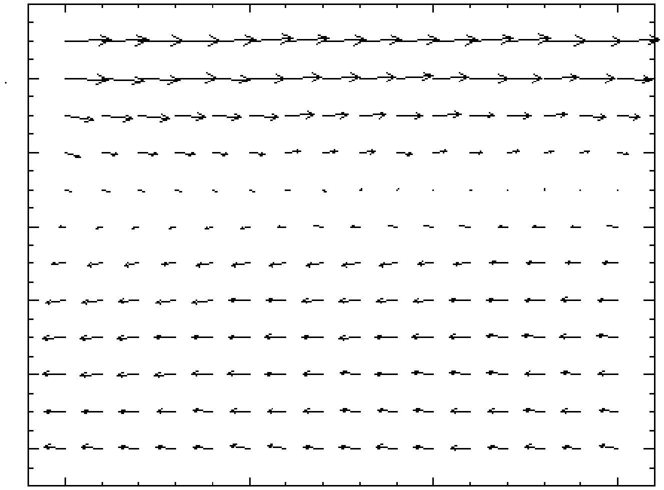


REVERSIBLE rearrangements



REVERSIBLE and IRREVERSIBLE rearrangements

SHEAR

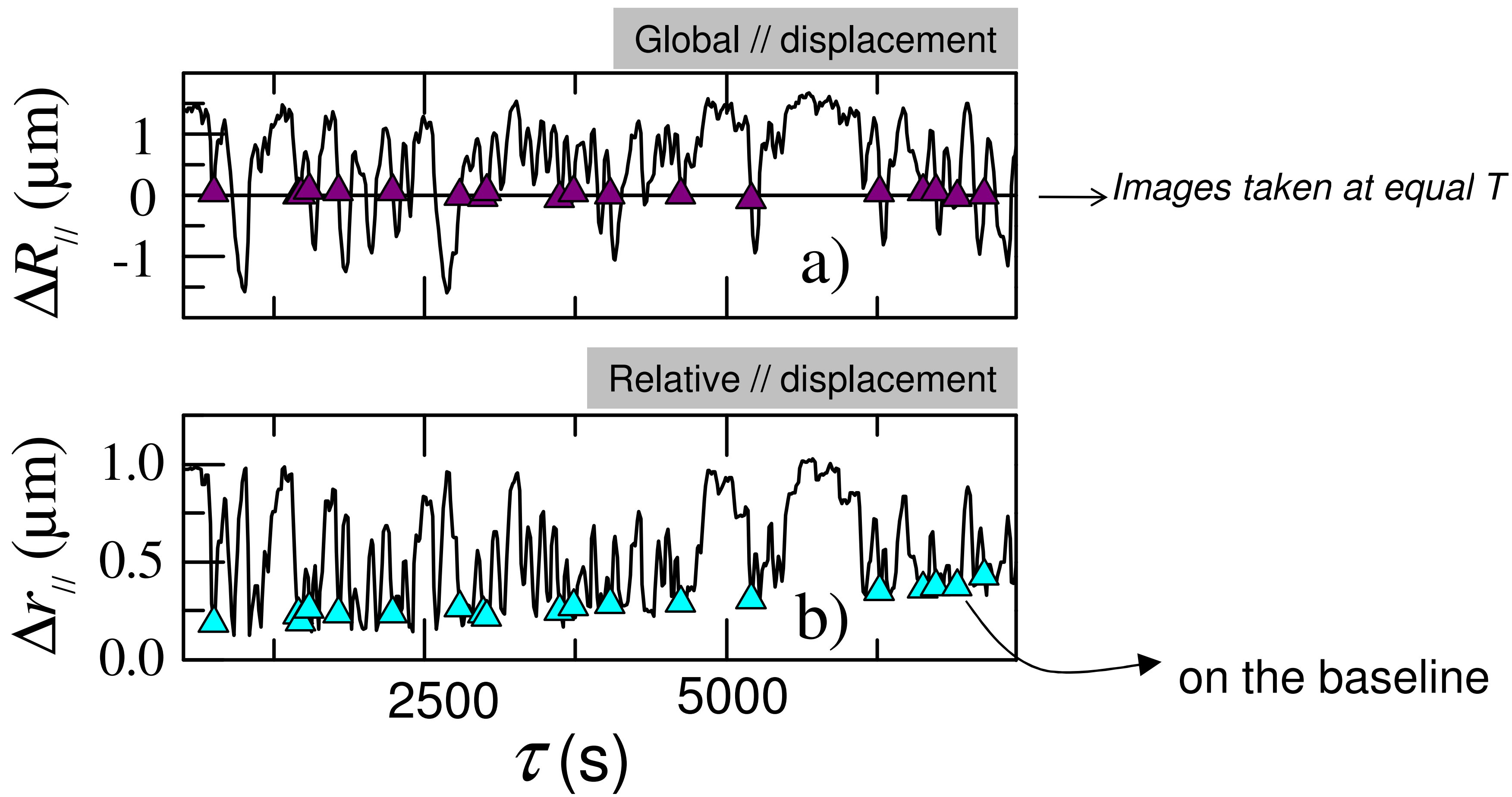


PLASTICITY

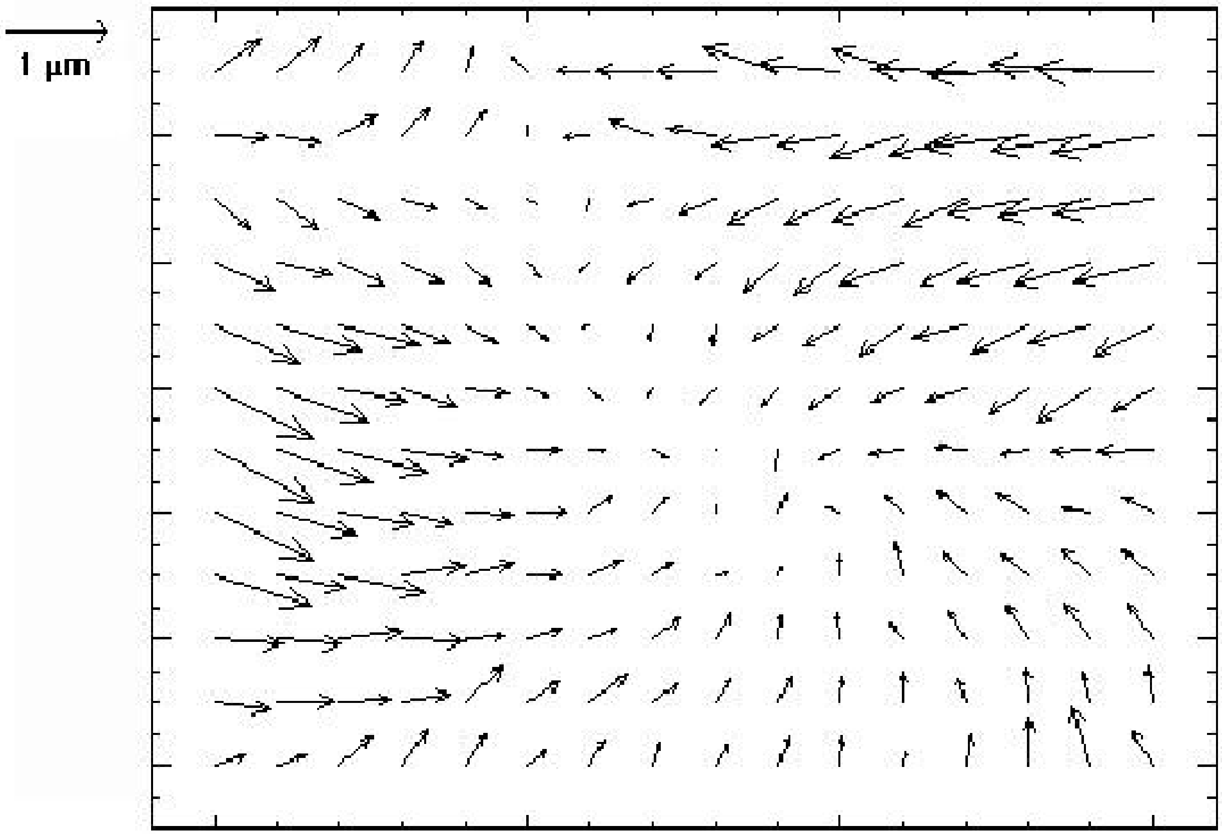
Identification of the Plastic events

Decoupling the purely plastic events fom the reversible shear deformations

Find plastic events ▲ ↷ delay τ between images such that $\Delta R_{//}(\tau) = 0$

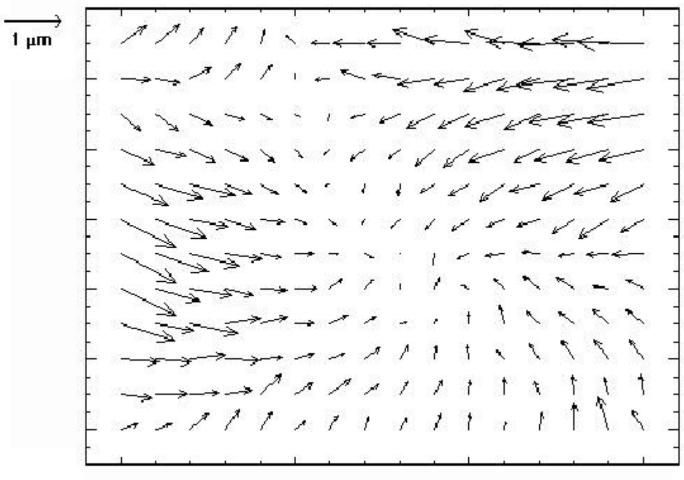


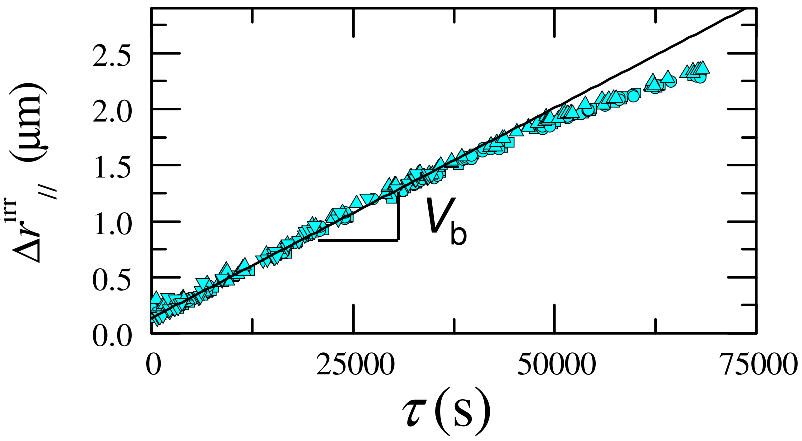
Structure of the Plastic Events



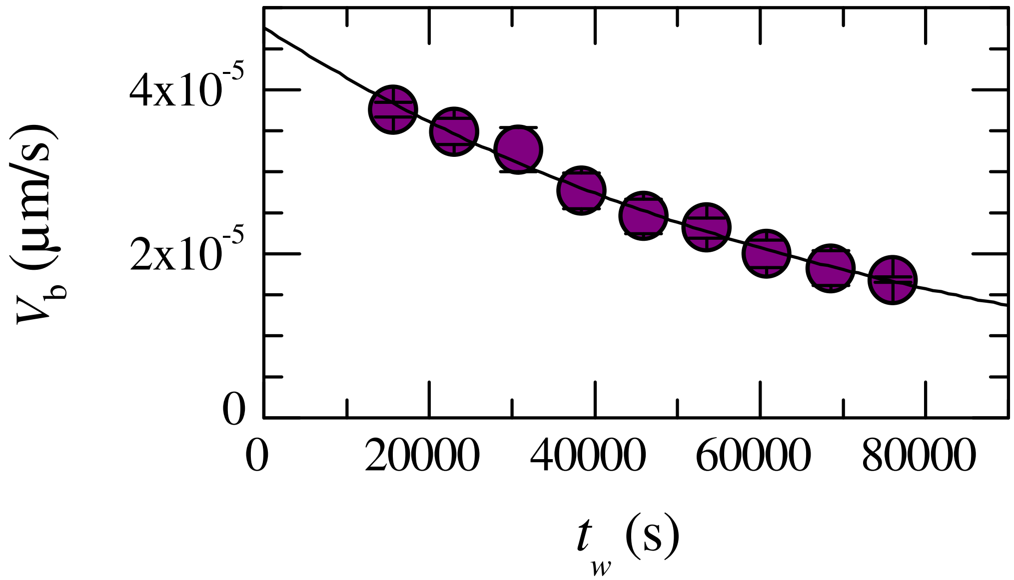
- Correlated on large length scale (~ 1 mm >> onions)
- Vortex-like
- Analogy with simulation of 2D hard spheres deep in the glass phase
  (Brito and Wyart, J. Stat. Mech. 07)

Aging Dynamics of the Plastic Events



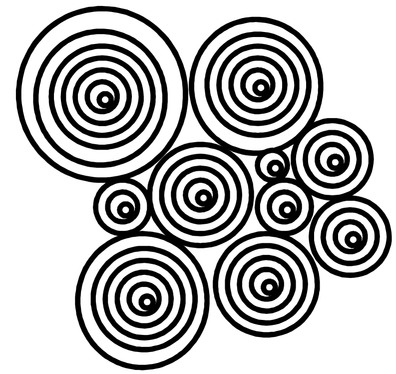


Same spatial structure but decrease of the amplitude with sample age



exponential decay
characteristic time: 72 000 s

Summary



Aging dynamics of a deeply jammed system (ϕ=1)

Origin:

ΔT ➡ mechanical shear deformations ➚ reversible rearrangements
➘ PLASTIC rearrangements

Ballistic motion
Vortex-like
Aging

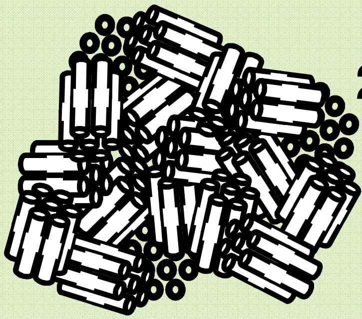
Mazoyer, Cipelletti & LR, PRL (2006) ; PRE (2009)

- **General behavior?**
  Elastic systems (concentrated pastes, copolymer phase, emulsions, fractal colloidal gels, …)

- **Analogy with**
  sheared athermal suspensions? (Pine and coll.)
  granular materials under thermal cycling? (Géminard and coll.)

CONCLUSIONS

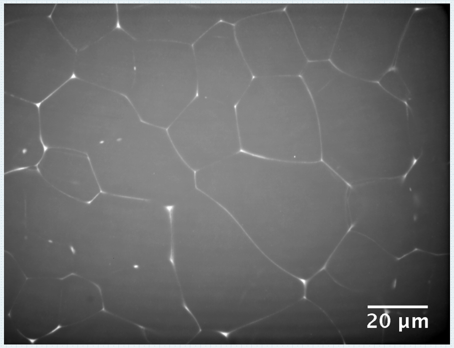
Probing the structure of soft materials under shear



2D crystal, 1D liquid

Fourrier space

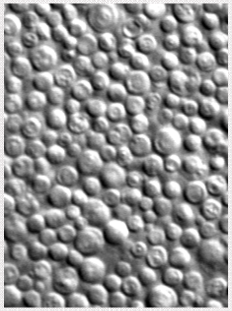
Shear-induced transition interpretated using model for crystalline solids
Plasticity / a physical mechanism for the solid-to-fluid transition



3D crystal

direct space

Plasticity ?



3D amorphous solid

direct space

Plasticity and spontaneous dynamics / a physical mechanism at the origin of the slow aging dynamics

Many thanks to

2D soft columnar crystals

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3D soft polycrystals

Neda Ghofraniha, *Elisa Tamborini & Luca Cipelletti (Montpellier)*

AND YOU