JMBC Workshop

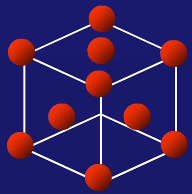
Jamming and glassy behavior in colloids

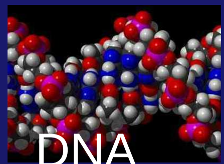
3. Insight from Colloidal Glasses

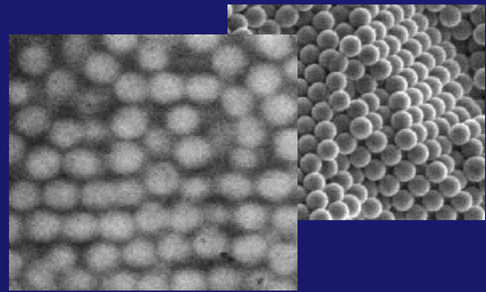
Peter Schall

University of Amsterdam

Colloidal suspensions


Atoms


DNA
Polymers


Colloids

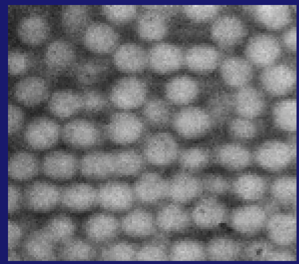

Granular

a

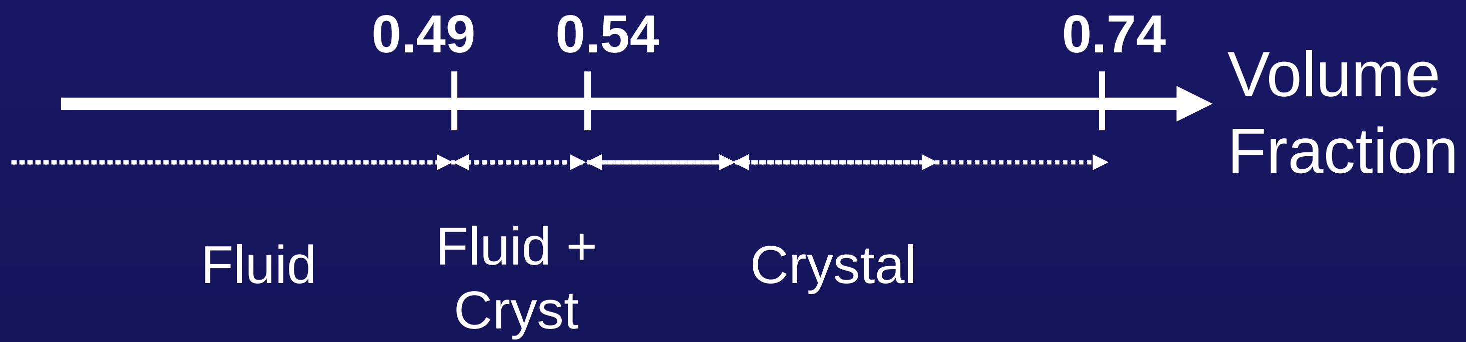
10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} m

Why important ?

Colloidal Hard Spheres

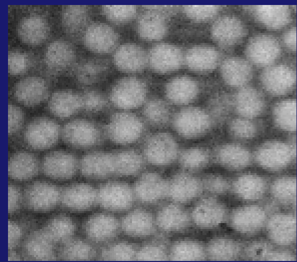


Hard-sphere Phase Diagram



(Alder, Wainwright 1957)

Colloidal Hard Spheres



Hard-sphere Phase Diagram

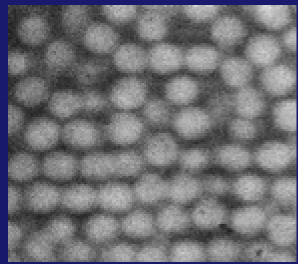
Quench **0.58** **0.64**

Volume Fraction

Glass

(Alder, Wainwright 1957)

Colloidal Hard Spheres



Scaling of the Moduli

Elastic Modulus ~ Energy / a^3

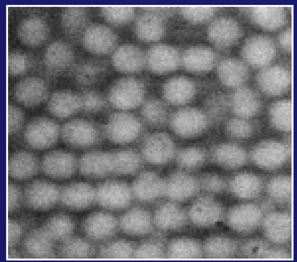
Atoms | Colloids

1eV / 1$Å^3$
=100 GPa

kT / 1μm^3
~1 Pa

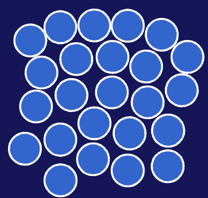
Colloidal suspensions

Colloidal Glasses

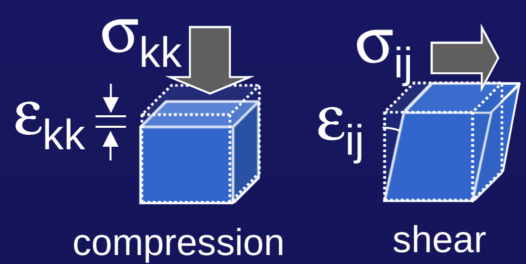


1. Thermal Energy
kT

2. Structure: Glass
no long-range order



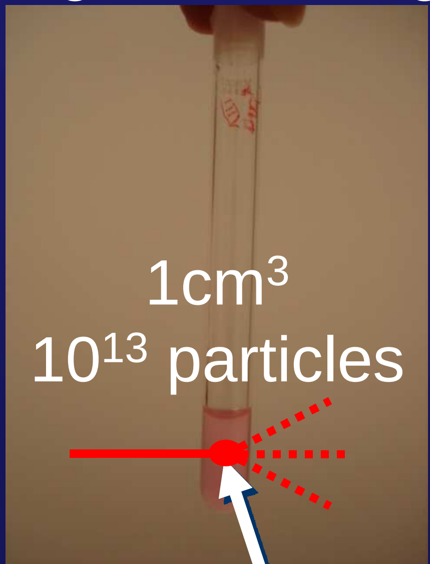
3. Dense system
Elastic modulus



Observation of Colloids

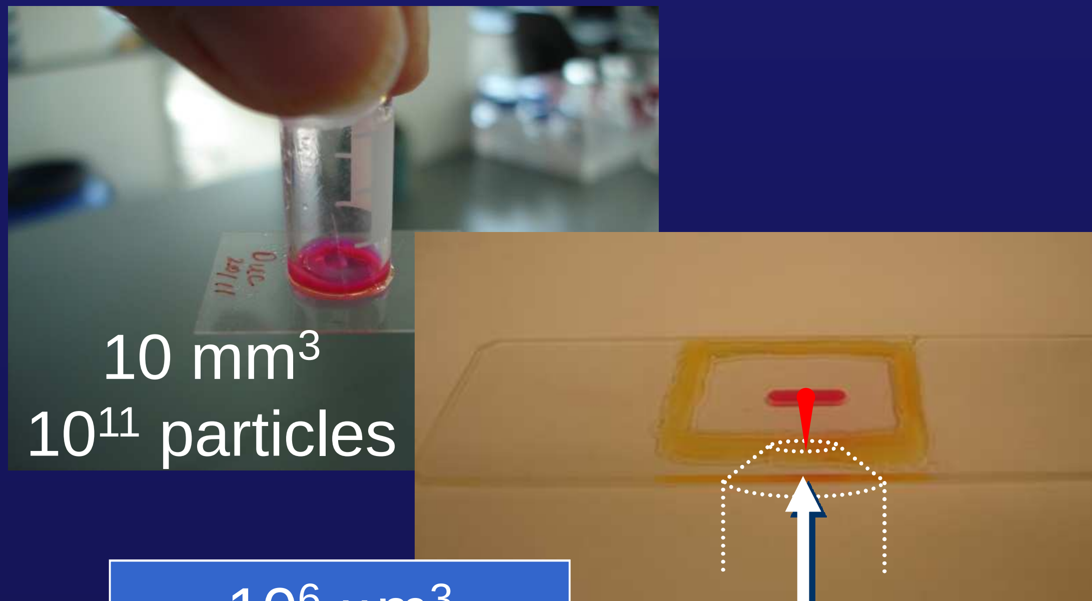
Colloidal Systems
Length Scale

Light scattering

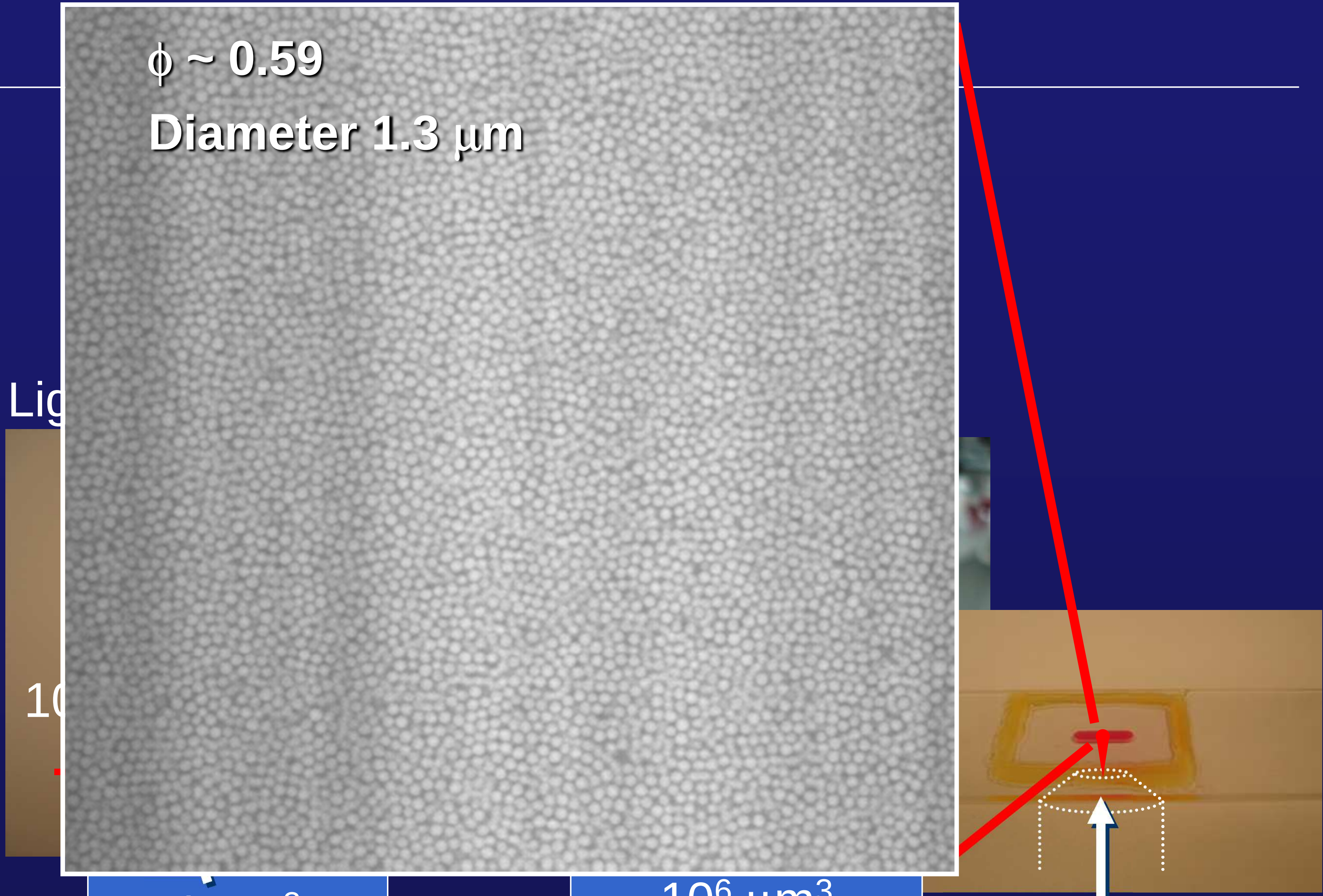


1mm³
10⁹ particles

Microscopy



10⁶ µm³
2x10⁵ particles

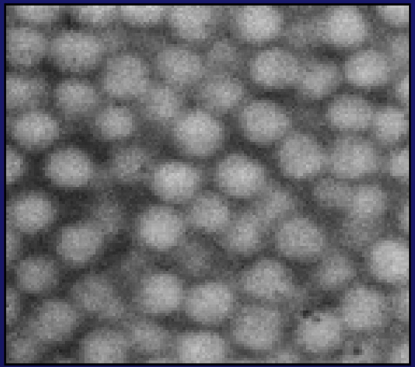


$1 mm^3$
10^9 particles

$10^6\ \mu m^3$
2×10^5 particles

Colloids: 3D Analogue Computers

Colloidal Systems
Time Scale

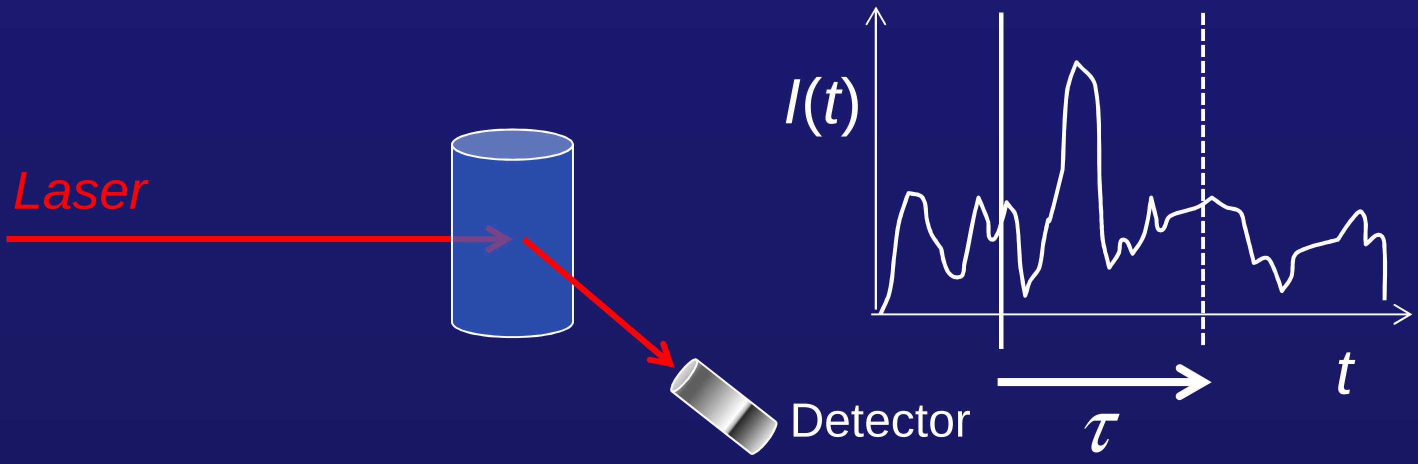


Collision time
τ = (1/100) s

Total “simulation“ time :   10 h ≈ 3million τ

Time increment :   1 min ≈ 6000 τ

Light Scattering

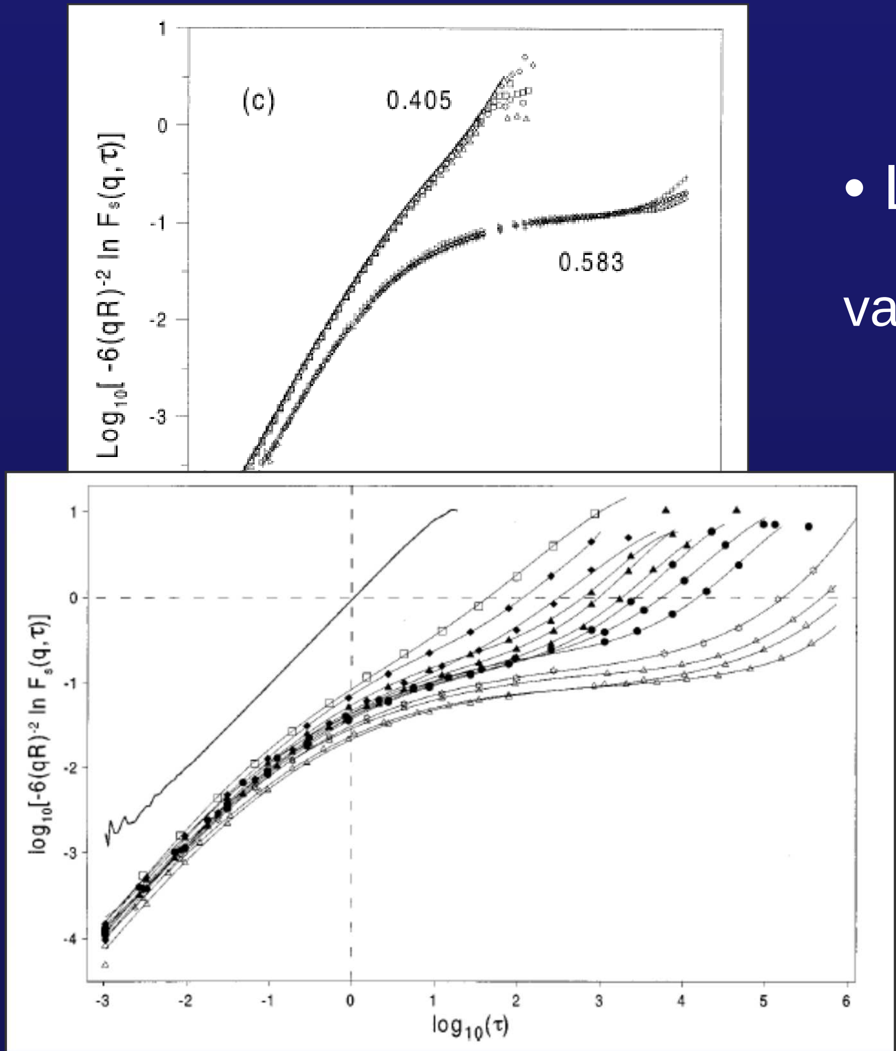


Time Auto Correlation Function

$$C(\tau) = \langle I(t) I(t+\tau) \rangle$$

$$C(\tau) \propto exp(-Dq^2\tau)$$

Light Scattering



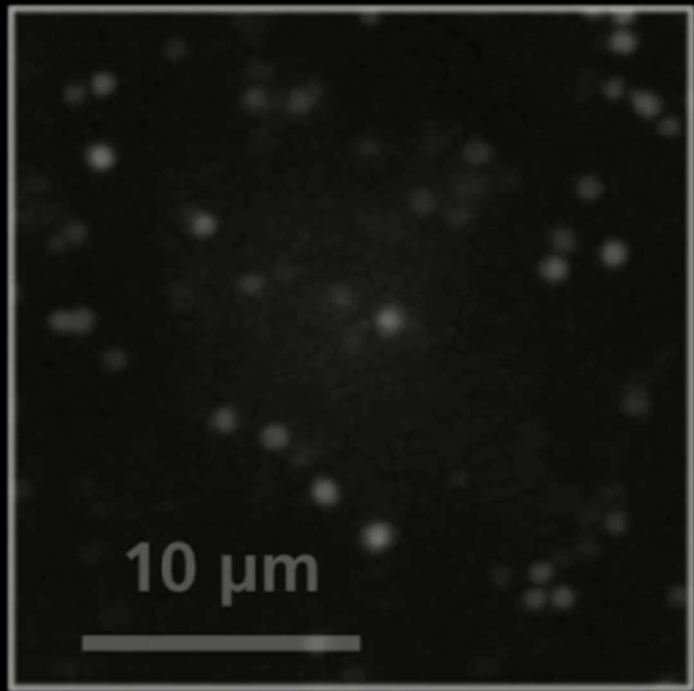
- Light scattering

van Megen *et al.* (PRE 1998)

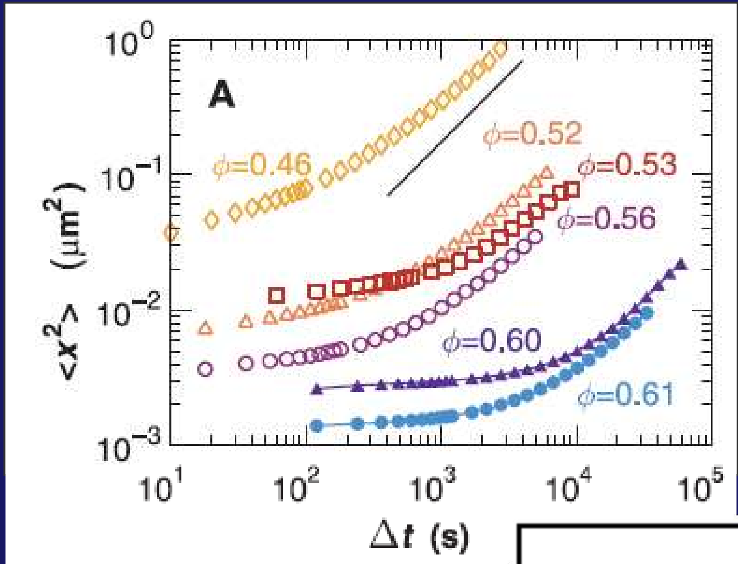
Colloidal glass transition

$\phi_g \sim 0.57$

Confocal Microscope Image

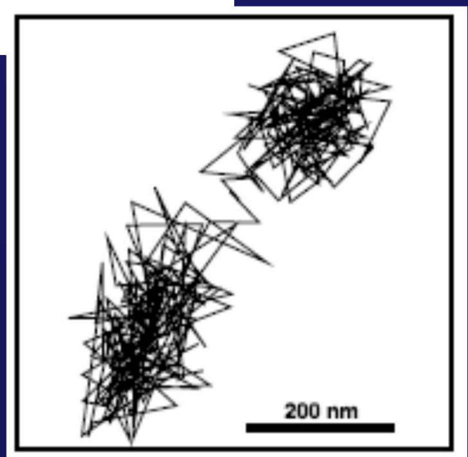


Colloidal Glasses

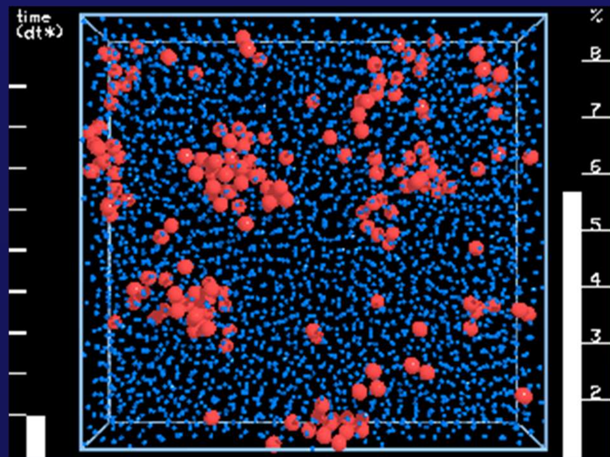


- Microscopy

Weeks, Weitz *et al.* (Science, 2000)

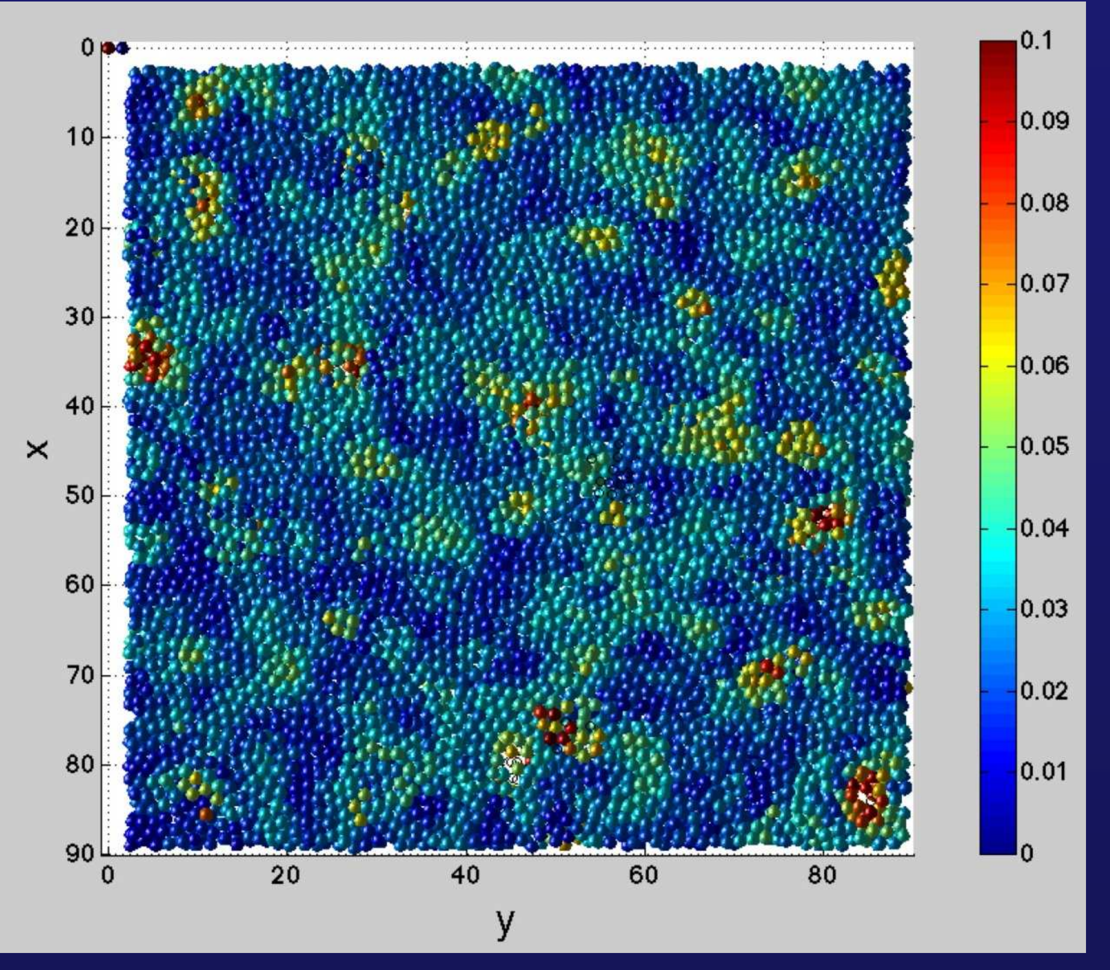


Caging



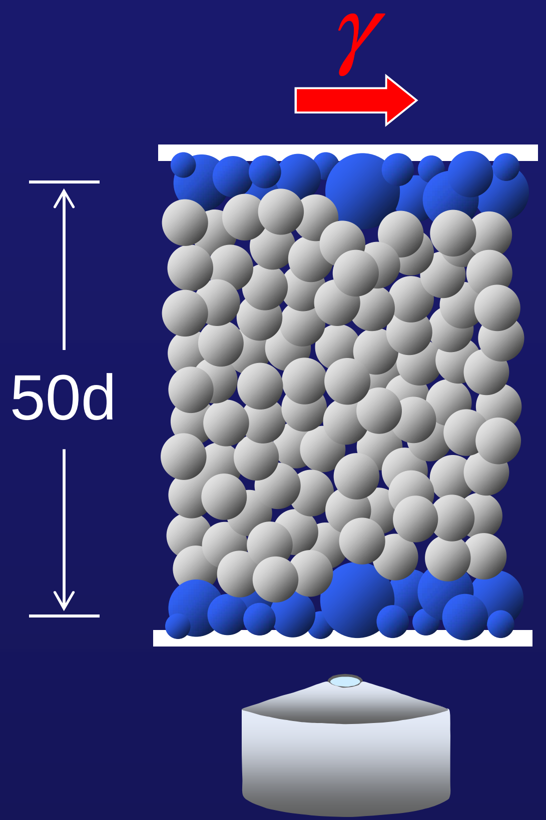
Dynamic heterogeneity

Free volume distribution



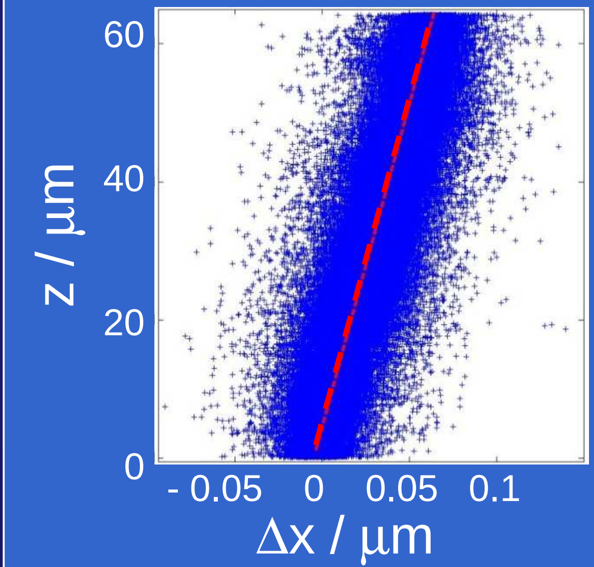
Heterogeneous!

Application of str

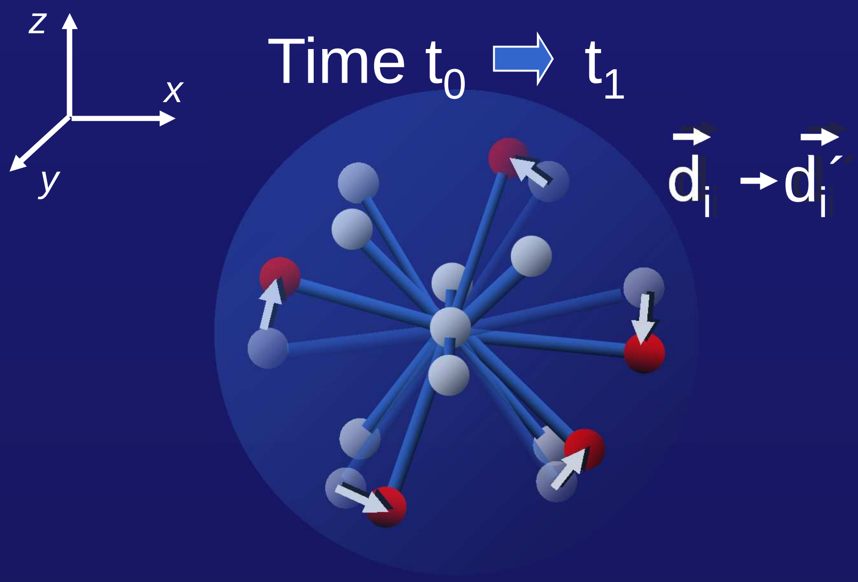


Confocal microscopy

Particle displacements



Strain and non-affine displacements



Affine transformation : γ

$$\boldsymbol{d_i}'^{aff} = \boldsymbol{d_i} + \gamma \boldsymbol{d_i}$$

$$D^2_{min} = \sum^{neighbors} (\underbrace{(\boldsymbol{d_i}' - \boldsymbol{d_i})}_{\text{actual change}} - \underbrace{\gamma \boldsymbol{d_i}}_{\text{affine change}})^2$$

Symmetric part of γ

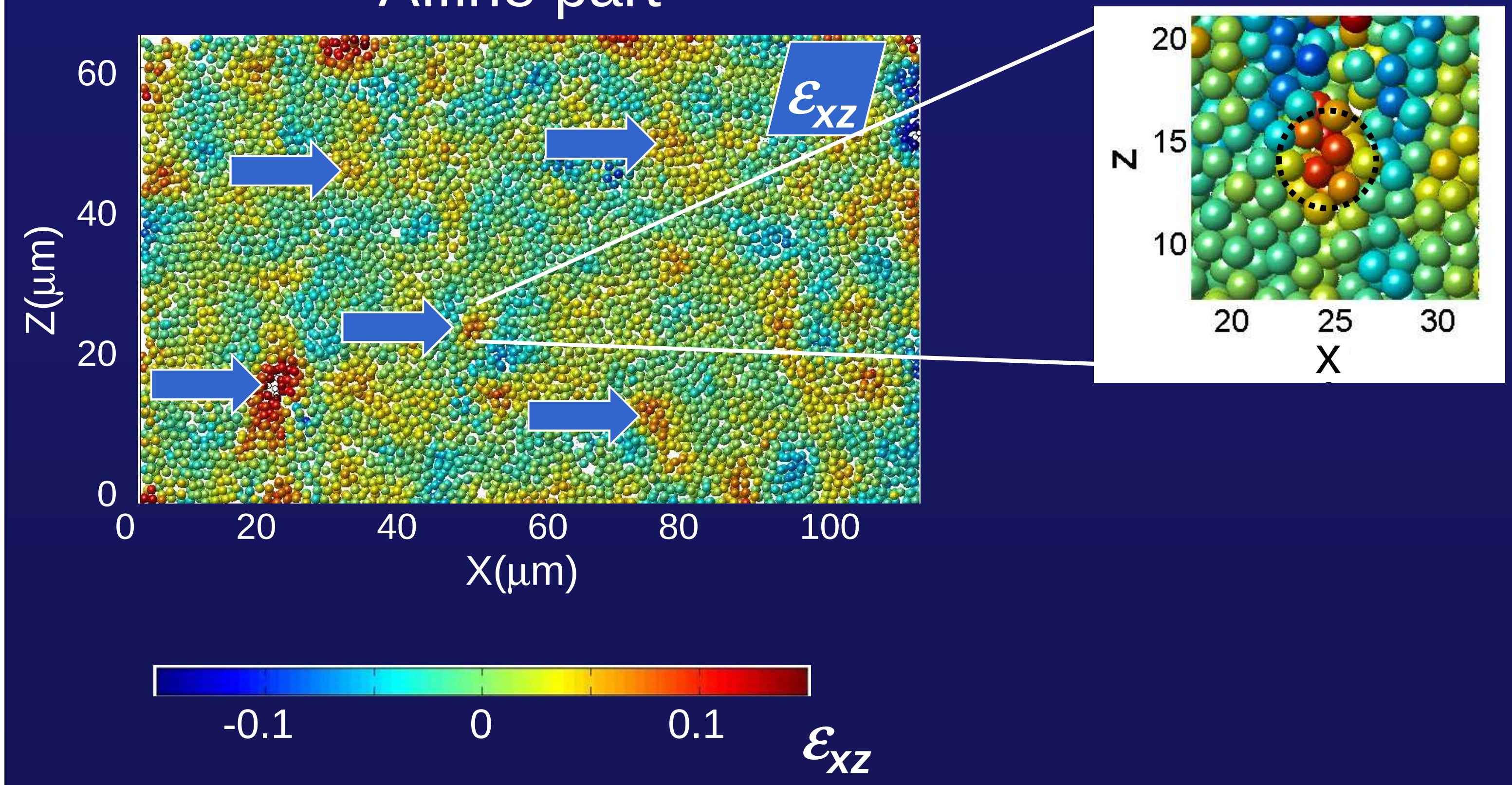
Strain tensor $\varepsilon_{ij} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix}$

STZ in colloidal glasses

$\dot{\gamma} \sim 1 \times 10^{-5}\ s^{-1}$

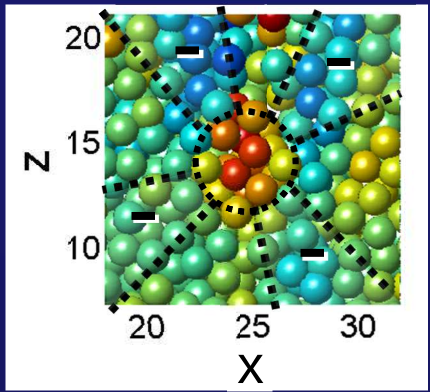
$\dot{\gamma}\tau \sim 0.1$

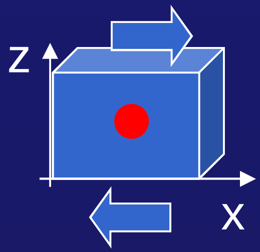
Affine part

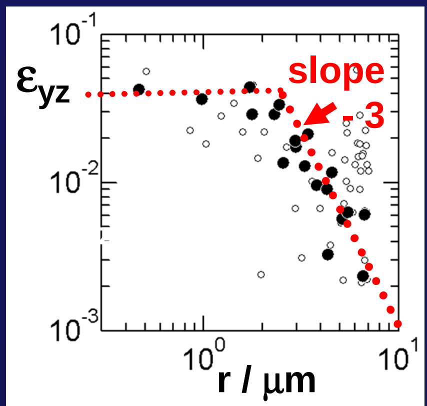


STZ in colloidal glasses

Incremental strain

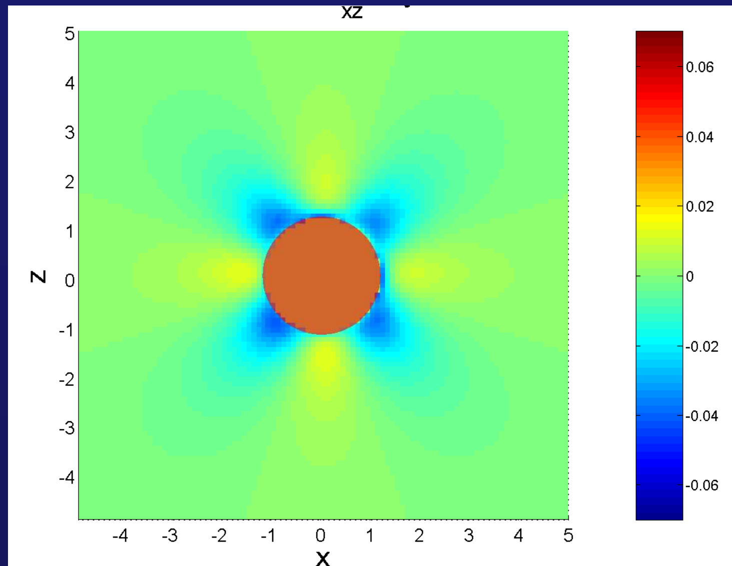






$$\varepsilon_{yz} \sim \frac{1}{r^3}$$

Continuum elasticity

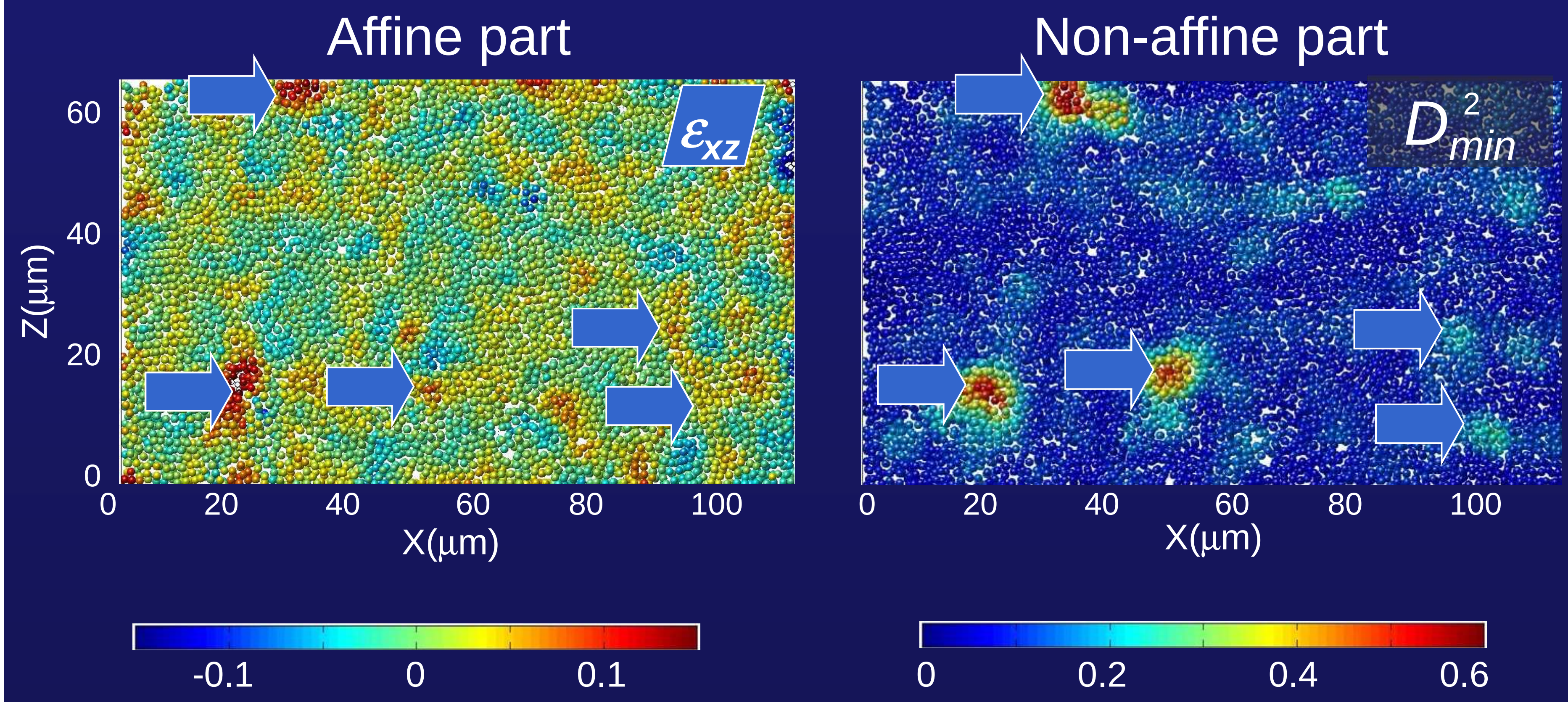


(PS, Weitz, Spaepen, Science 2007)

STZ in colloidal glasses

$\dot{\gamma} \sim 1 \times 10^{-5}\ s^{-1}$

$\dot{\gamma}\tau \sim 0.1$

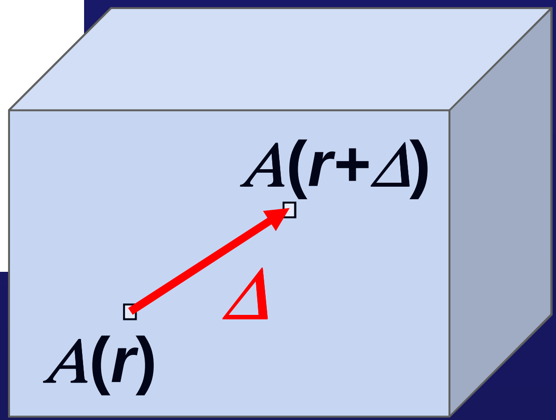


Spatial Correlations

$$C_A(\Delta) = \frac{\langle A(\bar{r})A(\bar{r}+\Delta)\rangle - \left(\langle A\rangle\right)^2}{\left\langle (A)^2 \right\rangle - \left(\langle A\rangle\right)^2}$$

Δ : *difference vector*

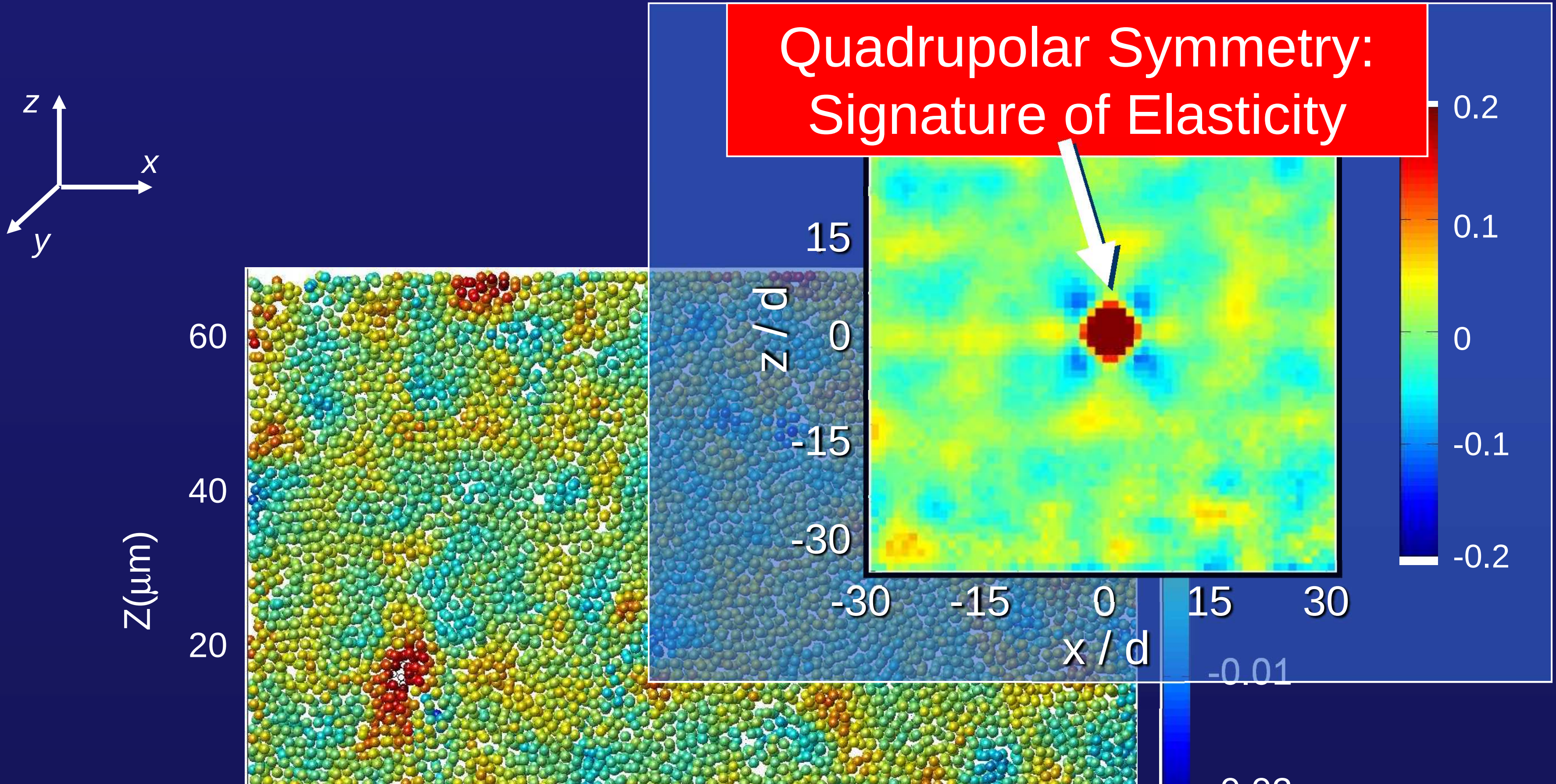
$\langle\ \rangle$: *spatial average*



Strain correlation : $A = \varepsilon_{xz}$

Non-affine correlation : $A = D^2_{min}$

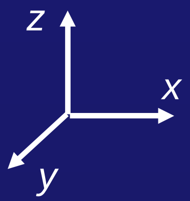
Affine part: Shear Strain ε_{xz}

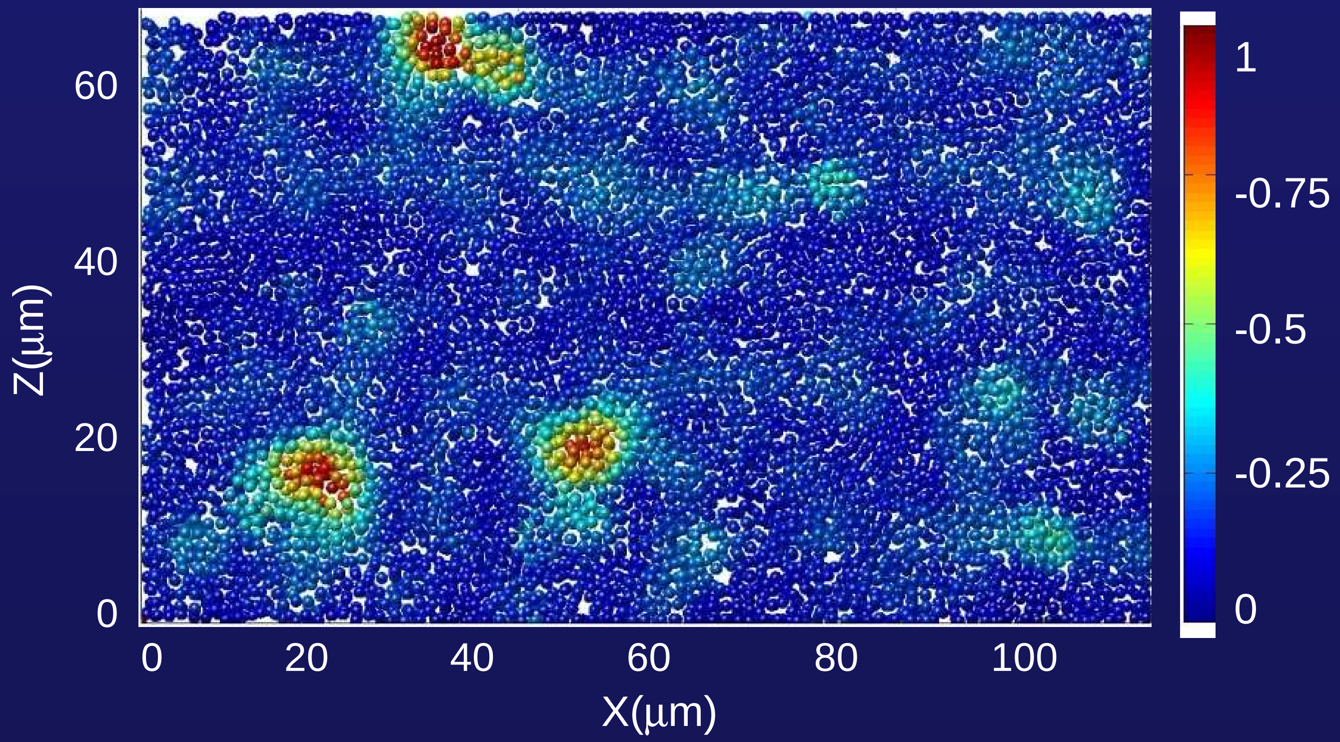


Quadrupolar Symmetry:
Signature of Elasticity

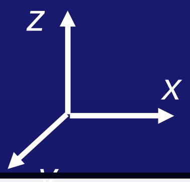
Elastic interactions
→ Self organization of STZ

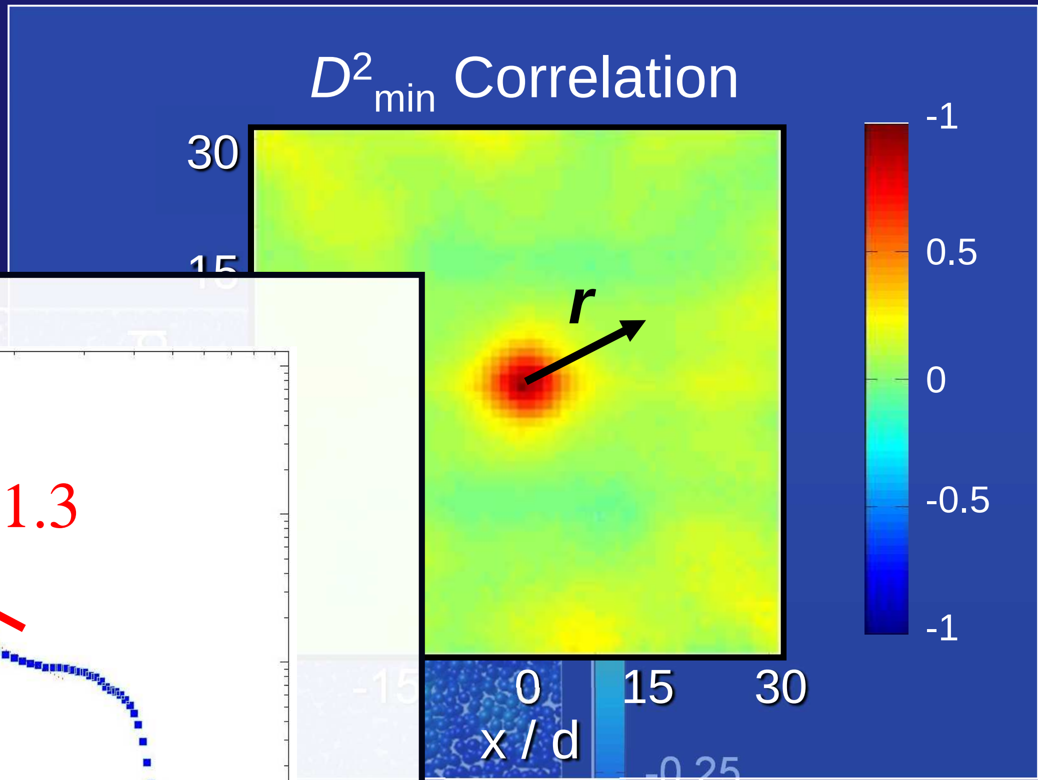
Non-affine part

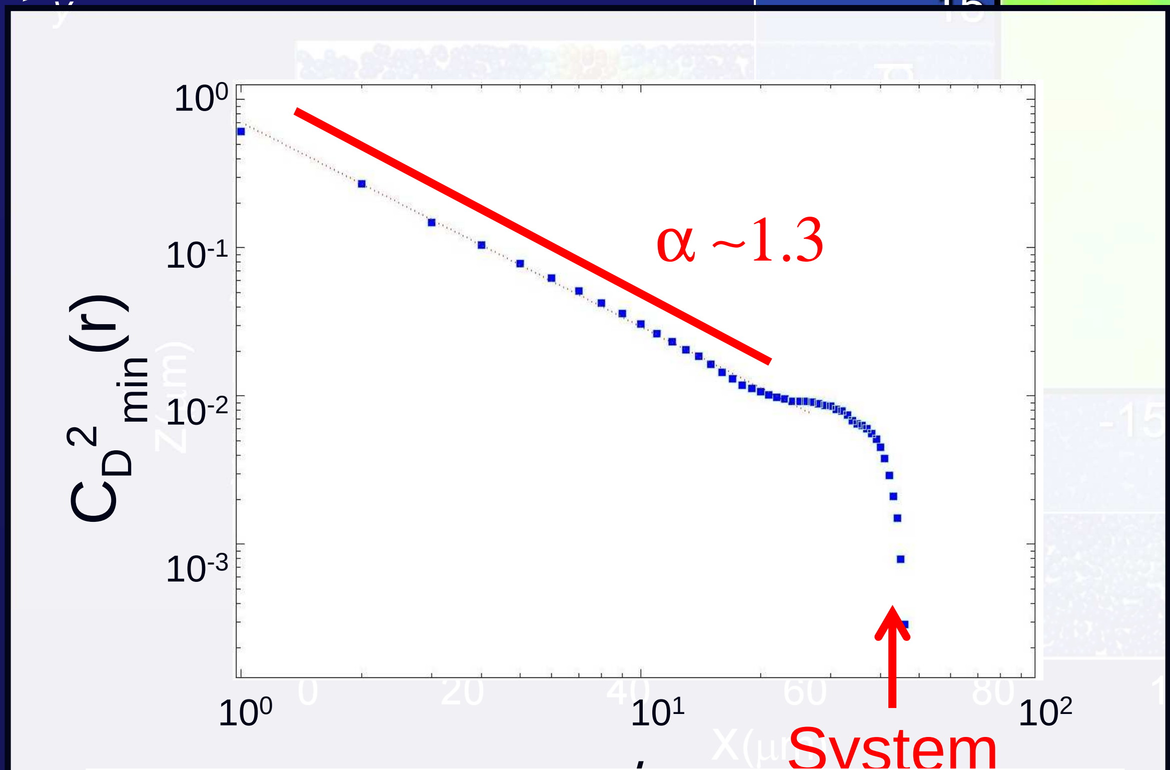




Non-affine part



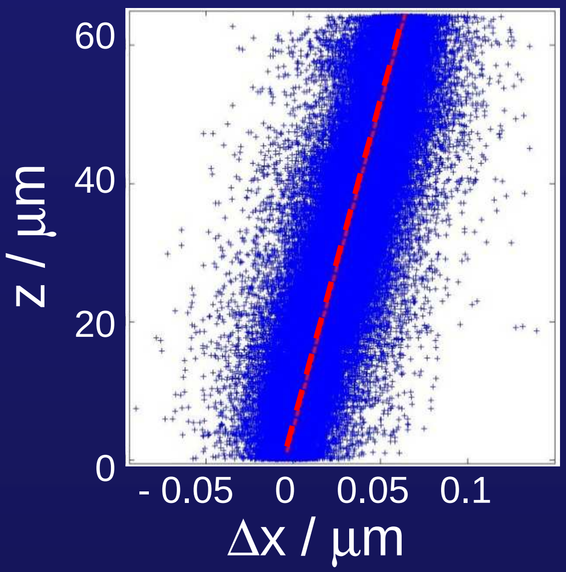




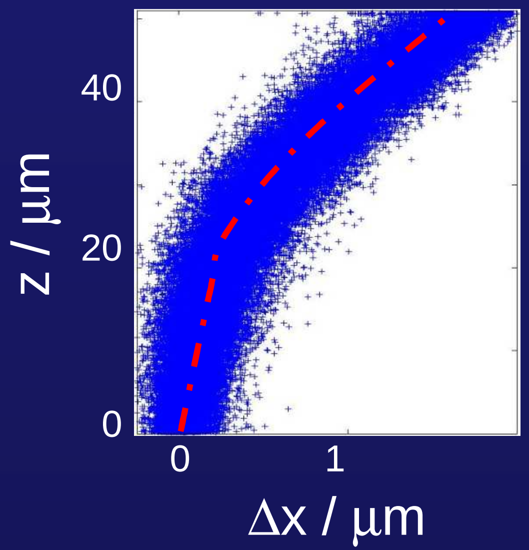
Power-law scaling
up to system size

Solid-Liquid transition: Shear banding

Homogeneous



Inhomogeneous

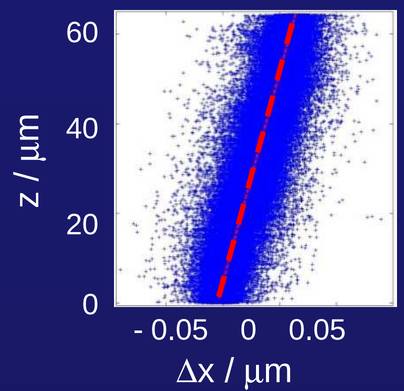


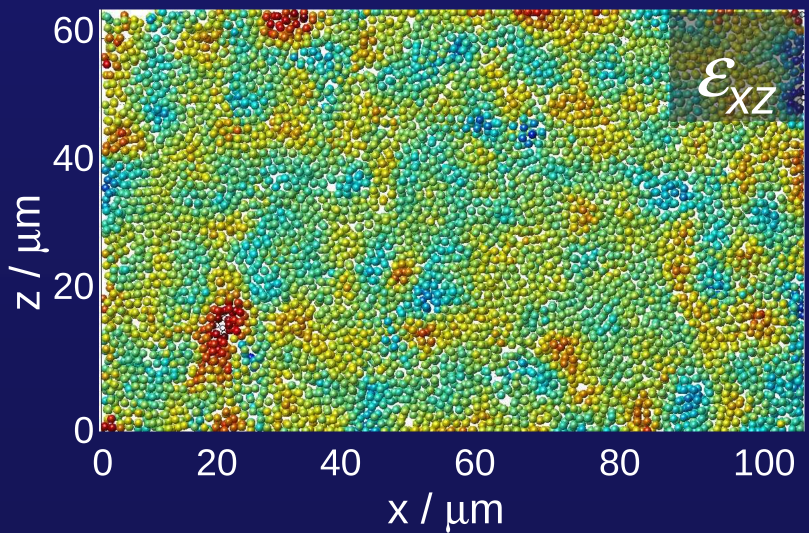
$\dot{\gamma}_c$

$\dot{\gamma}$ (s^{-1})

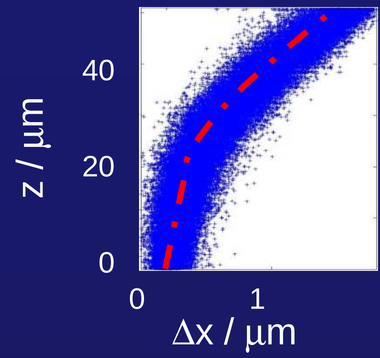
Shear banding transition

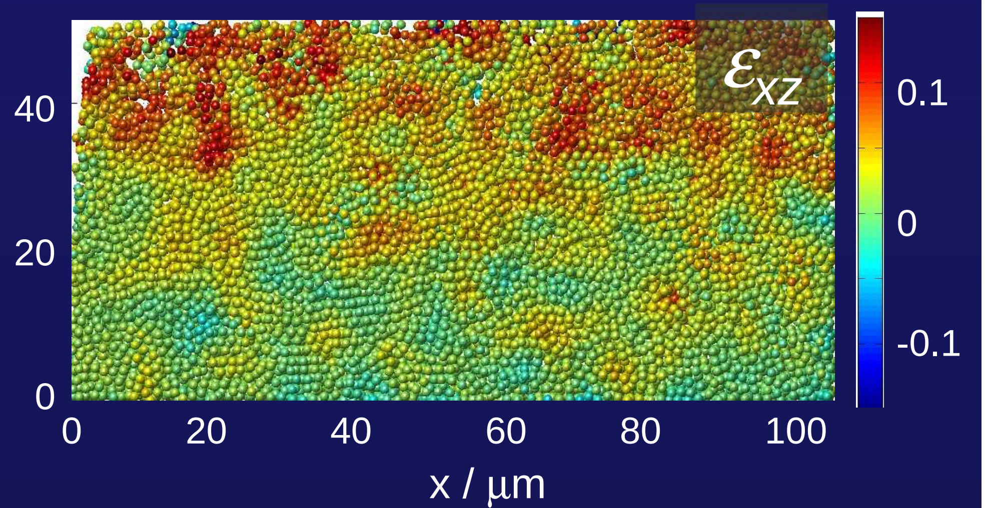
Homogeneous





Inhomogeneous

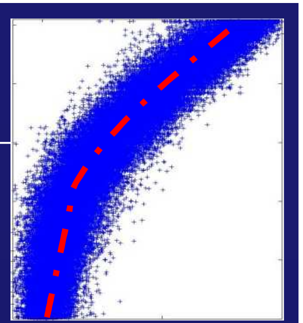




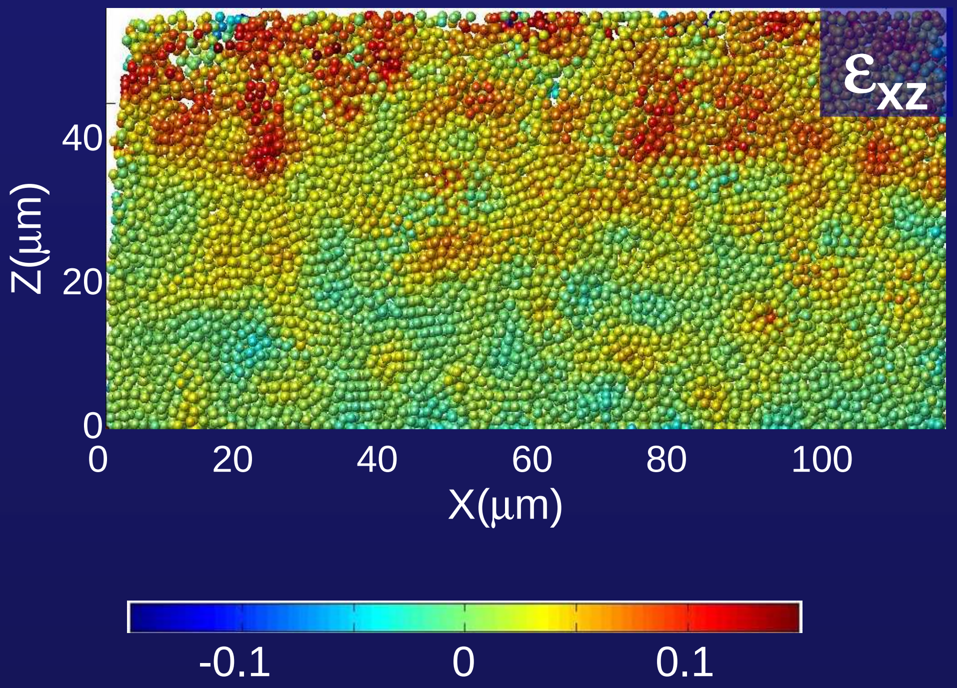
$\dot{\gamma}_c$

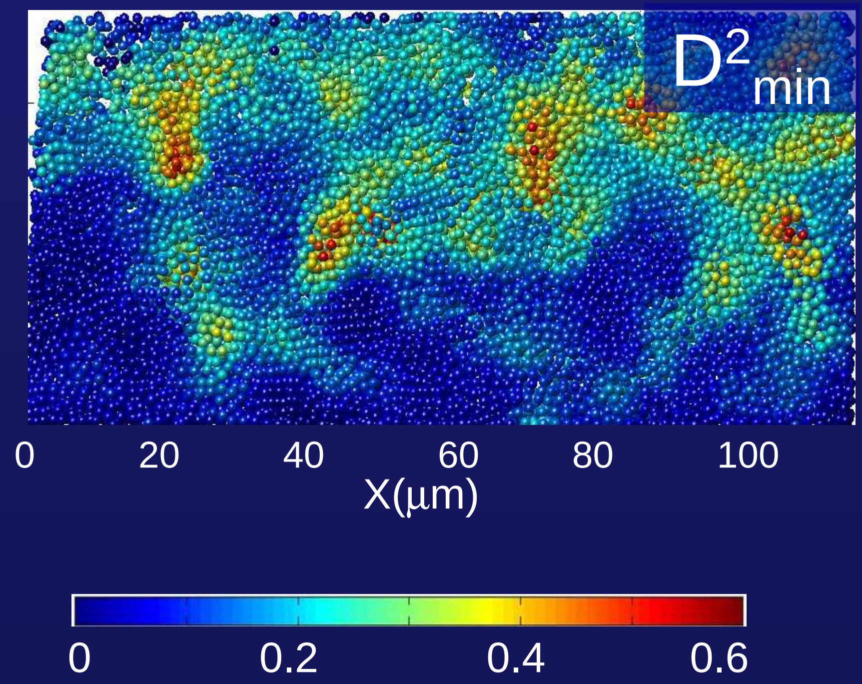
$\dot{\gamma}$ (s^{-1})

Shear banding

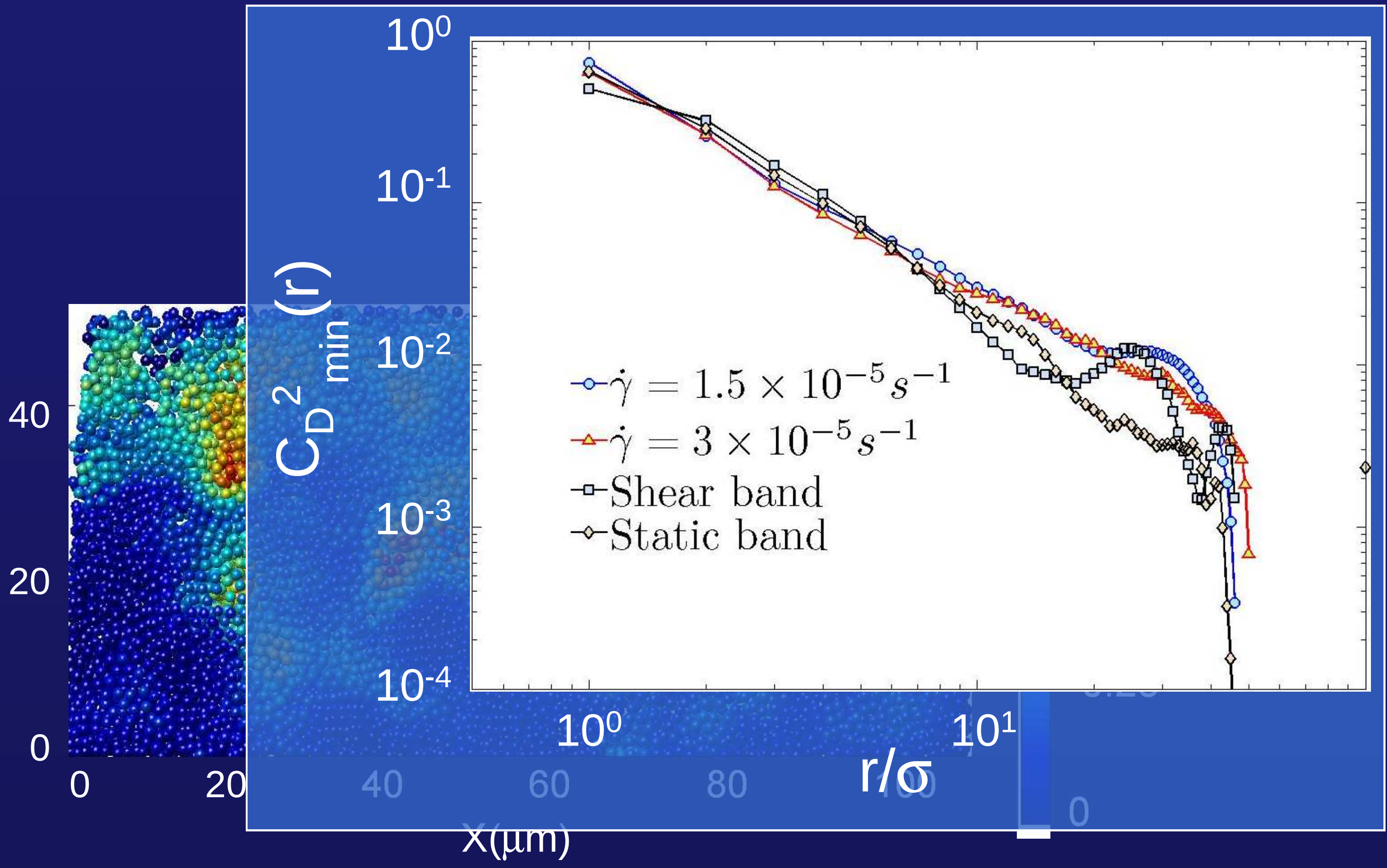


$\dot{\gamma} \sim 1 \times 10^{-4}\ s^{-1}$



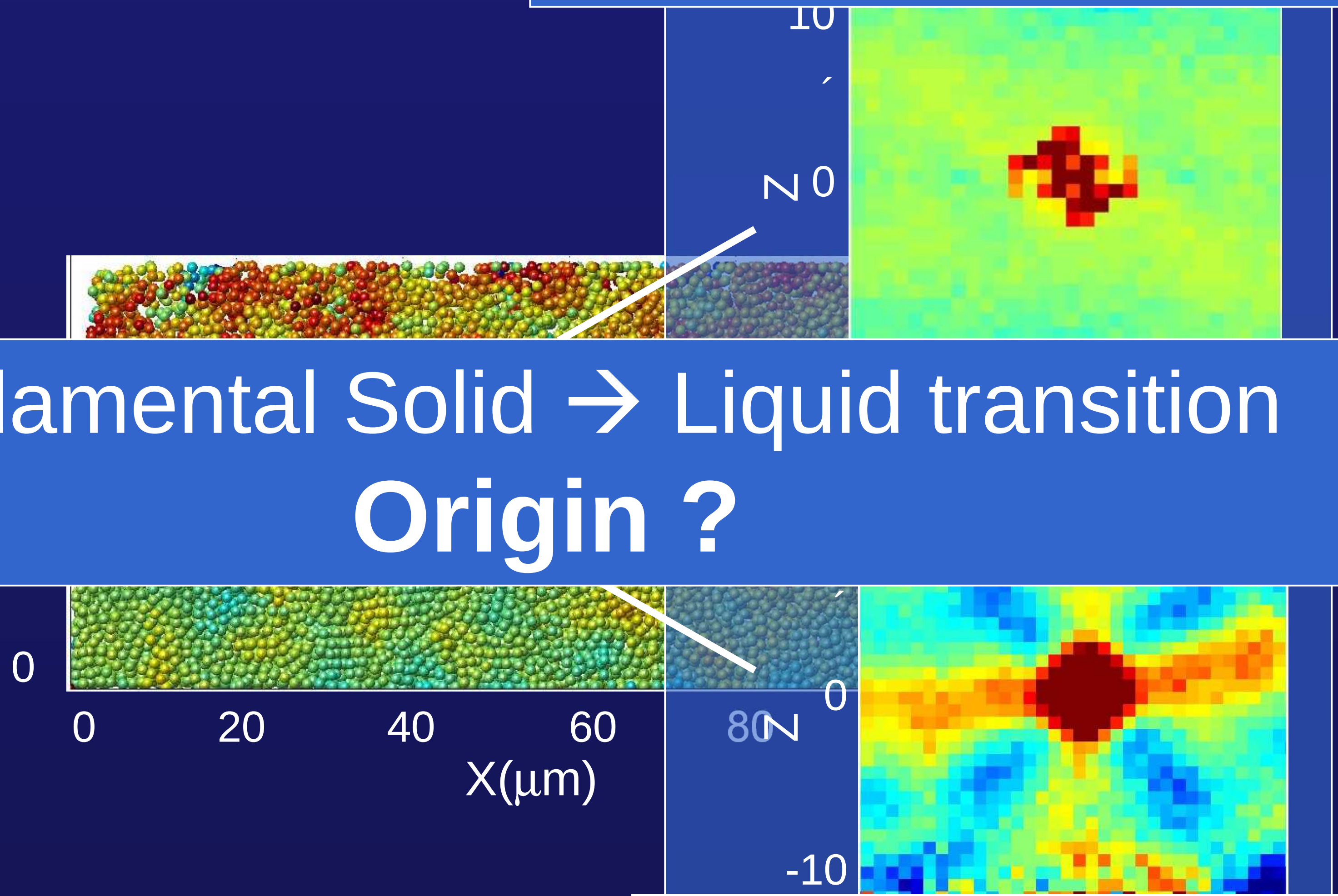


Spatial distribution of Flow ?



Strain Correlation functio…

No quadrupolar symmetry
liquid like

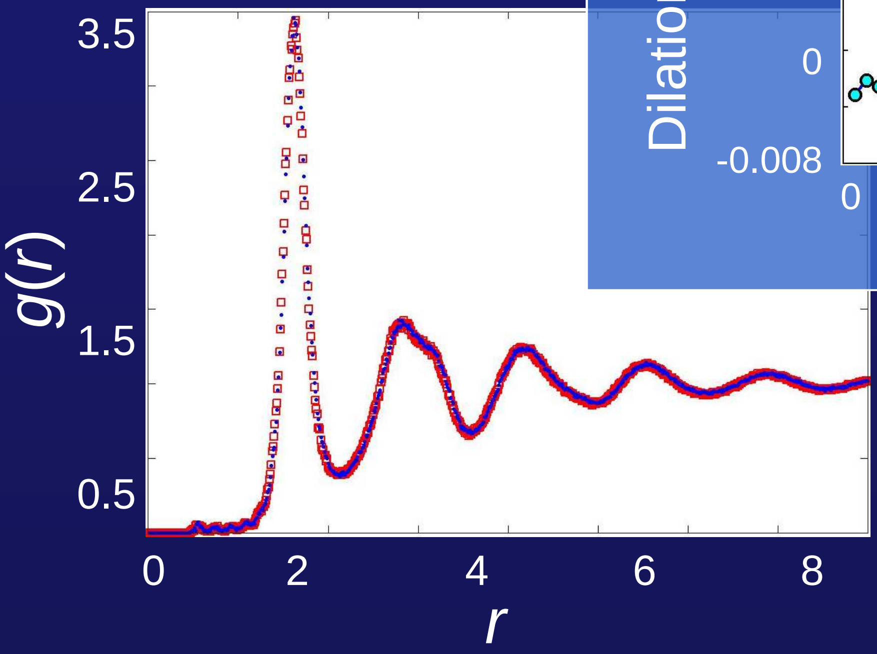


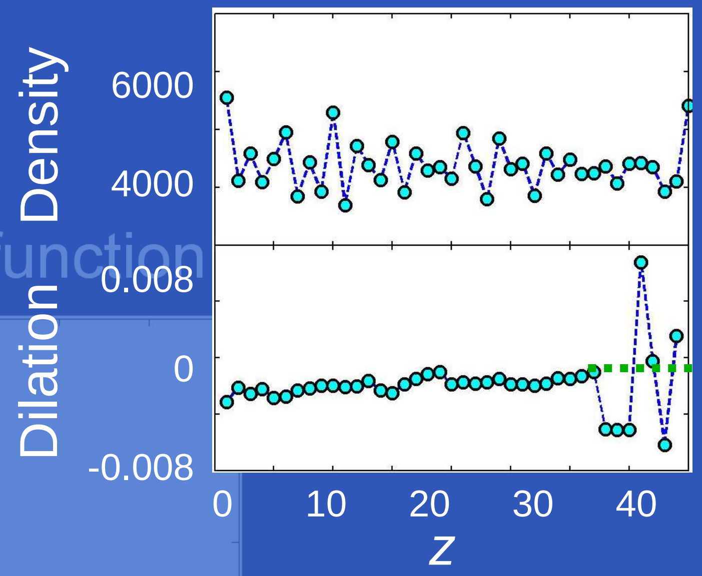
Fundamental Solid → Liquid transition
Origin ?

Quadrupolar symmetry
solid like

Structural transition ?

Pair correlation function

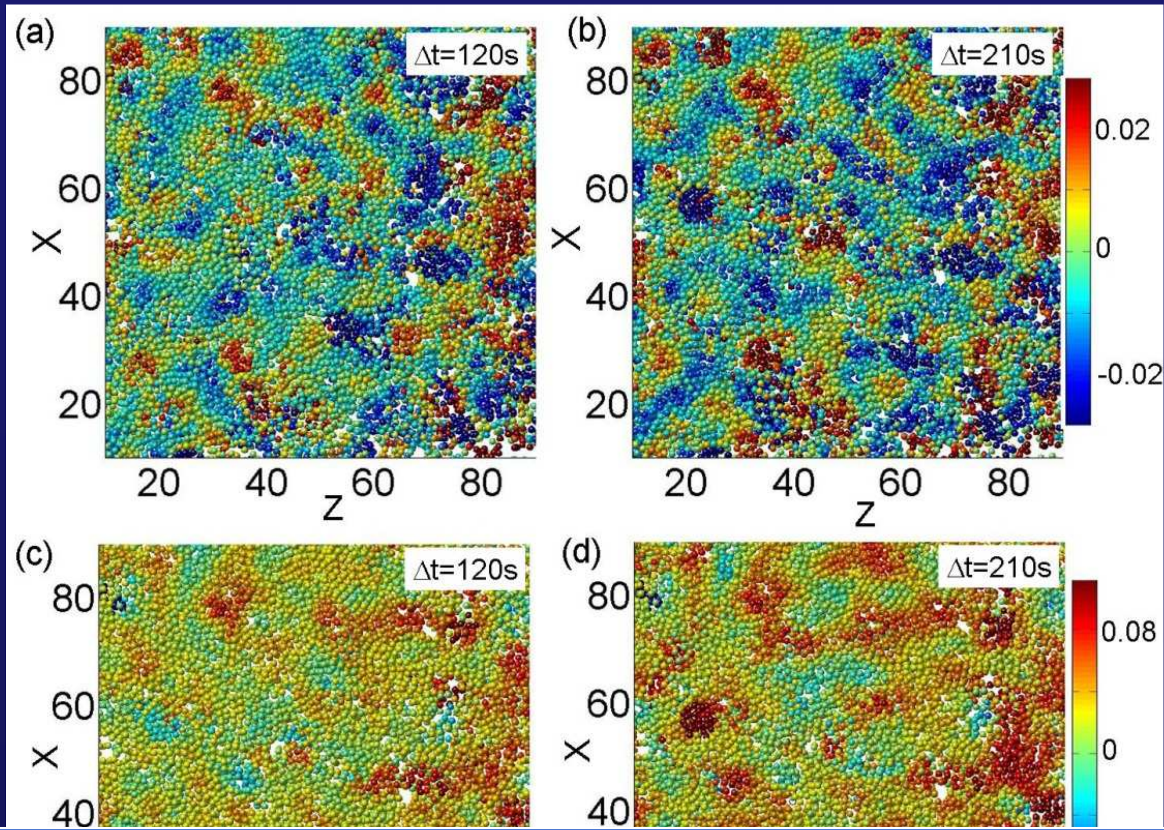




Shear banding

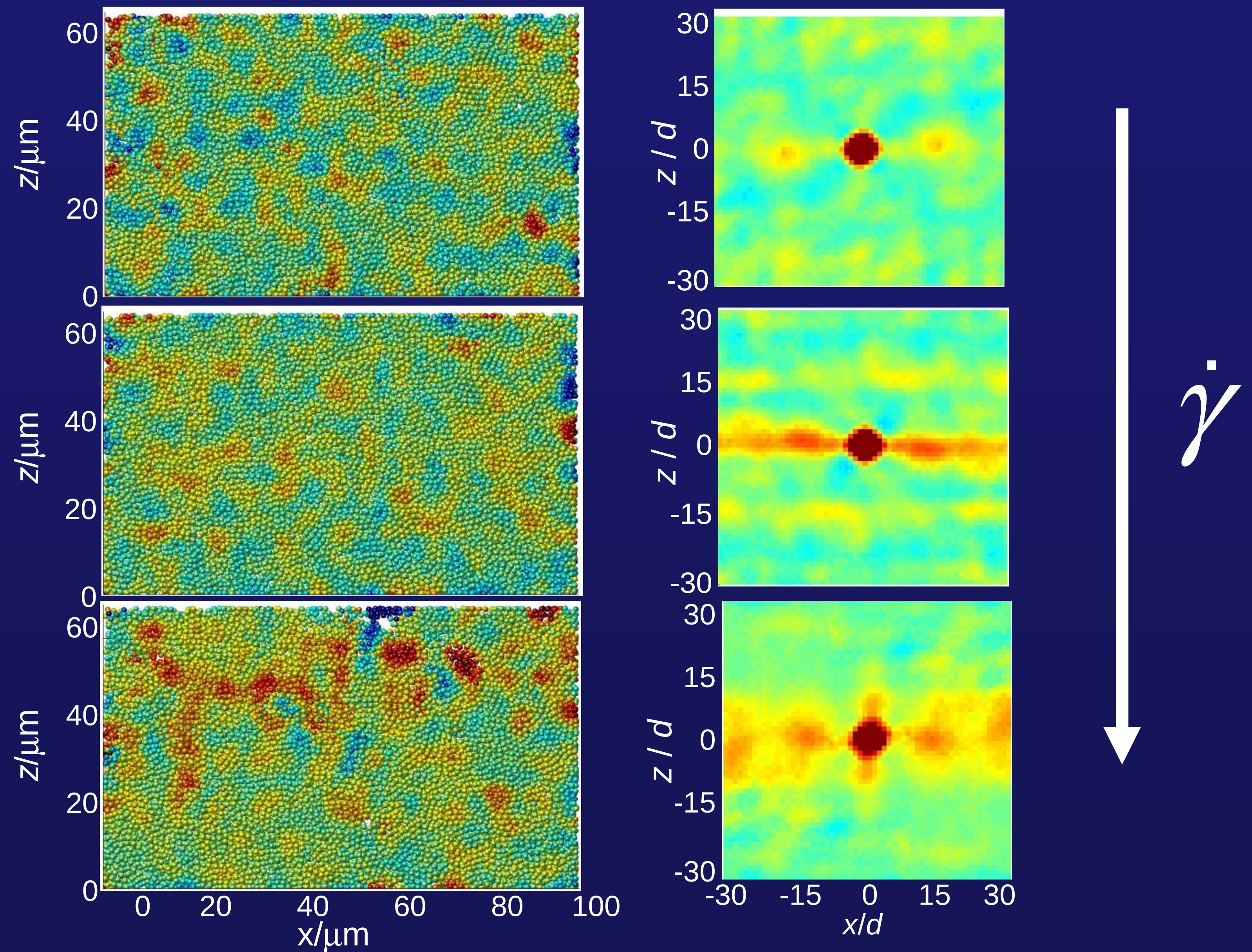
Dilation

Shear



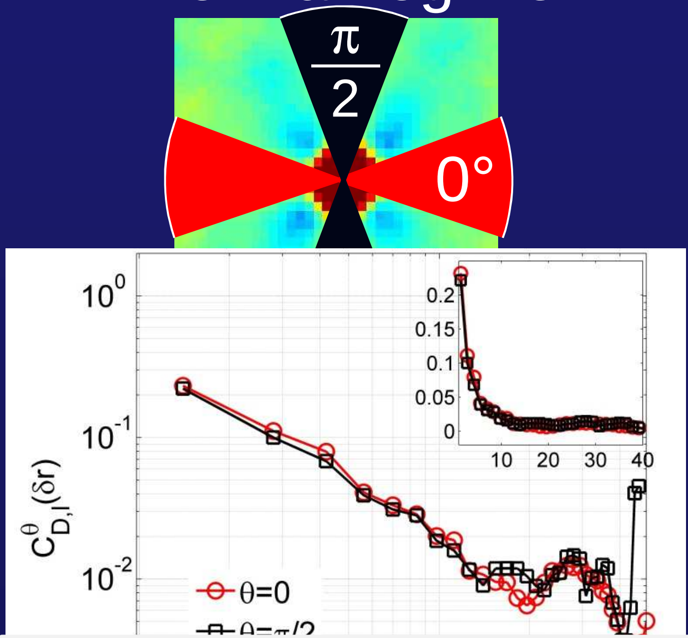
Very weak correlation between dilation and shear, $C_r \sim 0.01$!

Increasing Strain rate

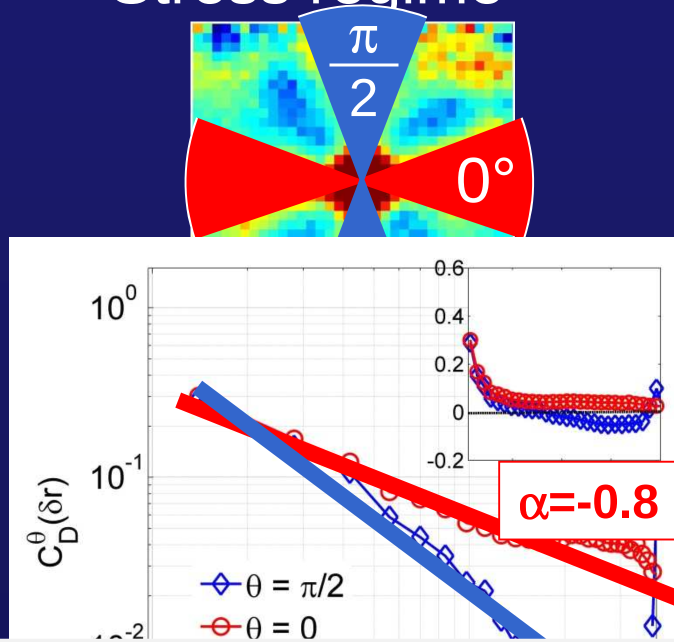


Anisotropy of Strain correlations

weakly driven:
Thermal regime

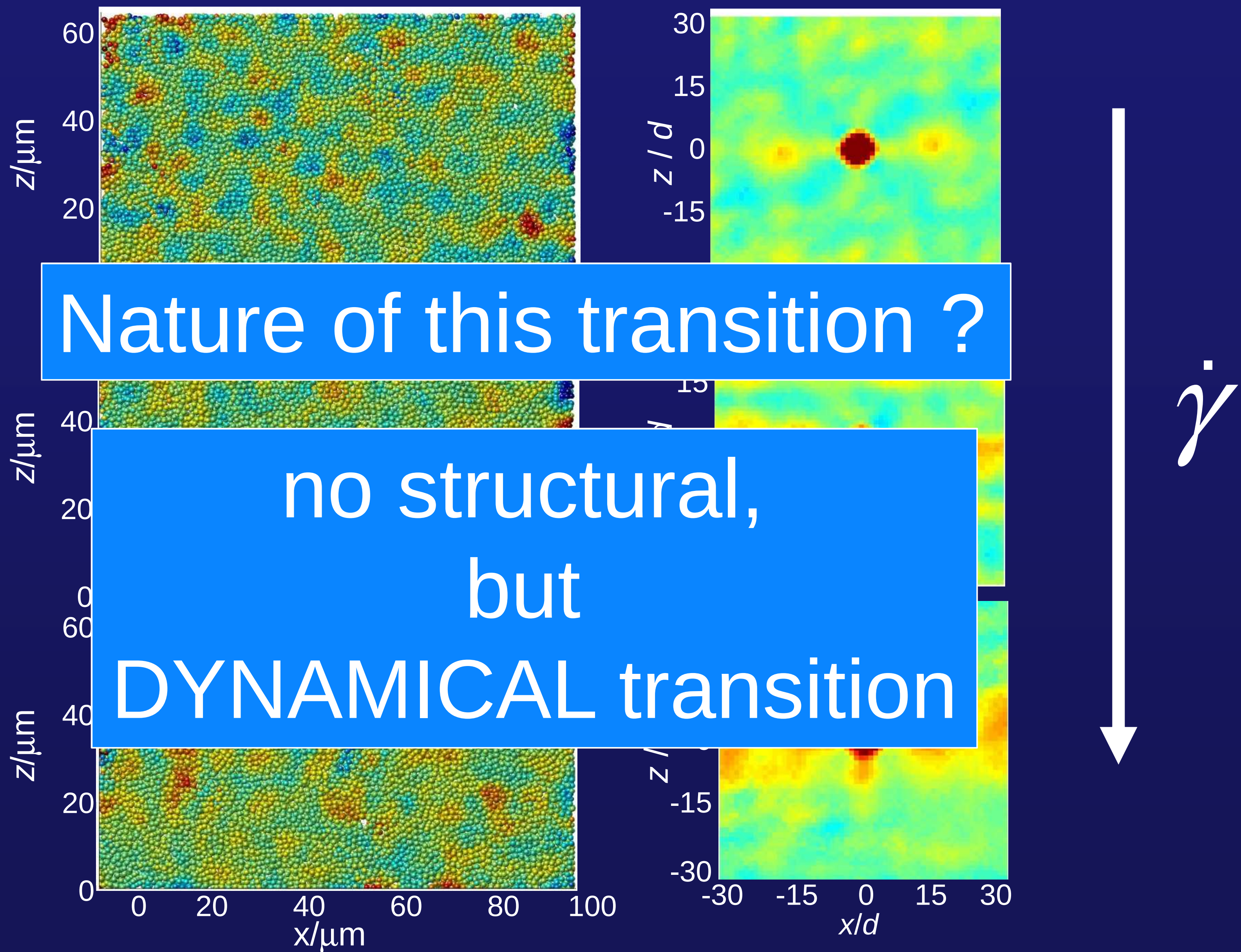


strongly driven:
Stress regime



New correlations with anisotropic, stress-dependent scaling

Shear banding transition



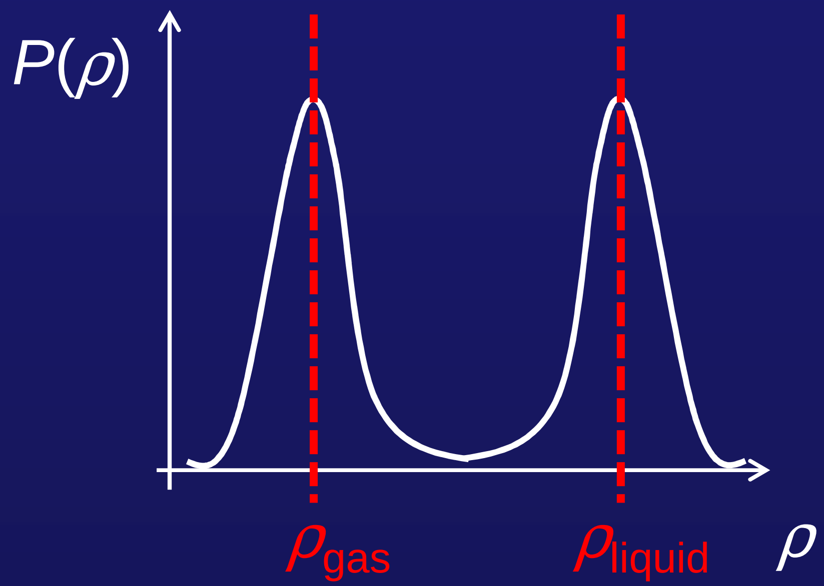
Nature of this transition ?

no structural,
but
DYNAMICAL transition

First order transition ?

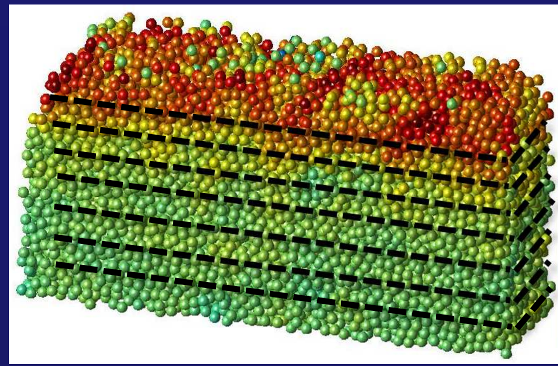
Gas – Liquid transition:

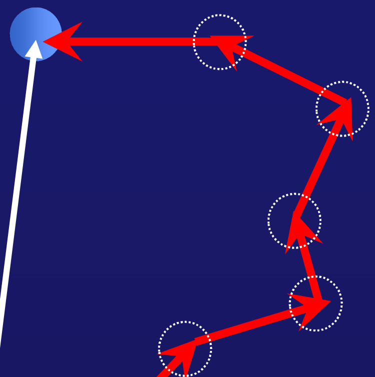
$\zeta \rightarrow$ Density ρ

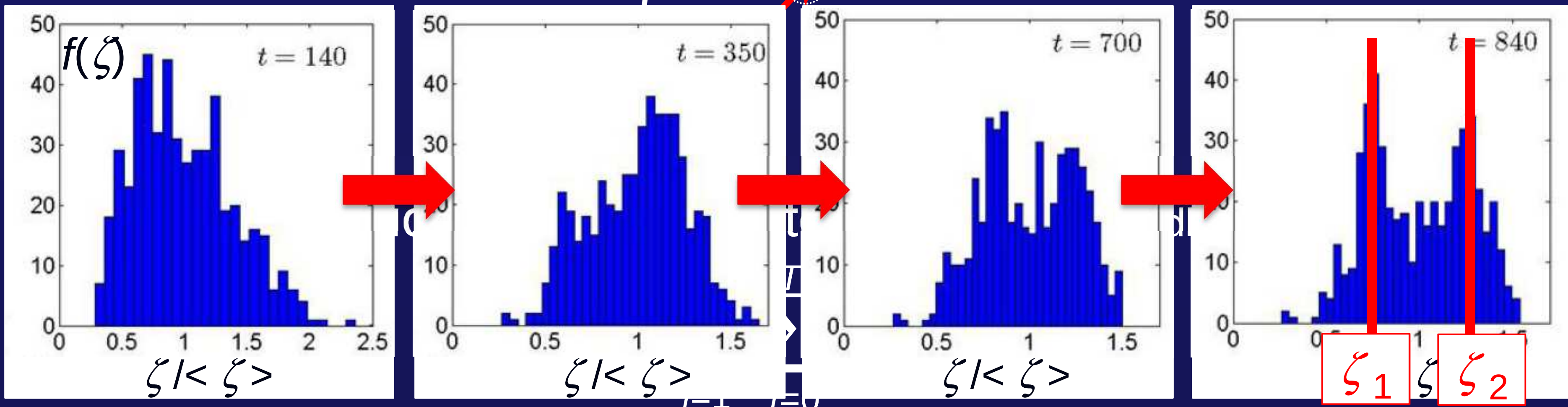


What is the right order parameter ?

First order transition ?

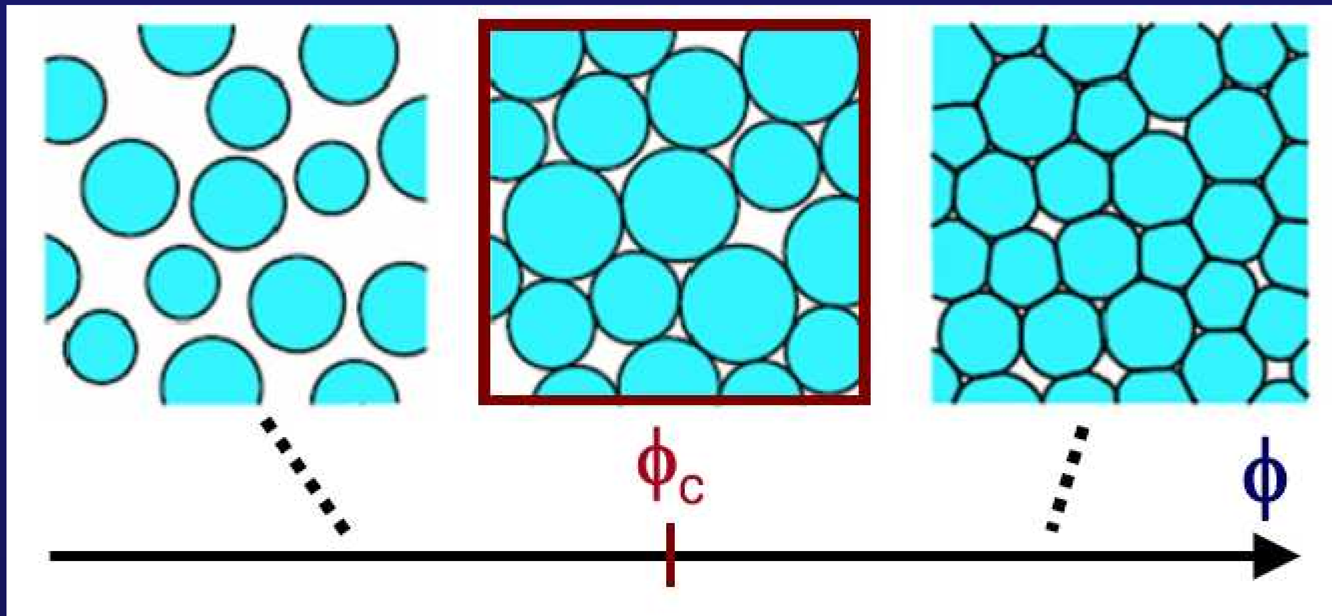






First order transition in 4D space-time

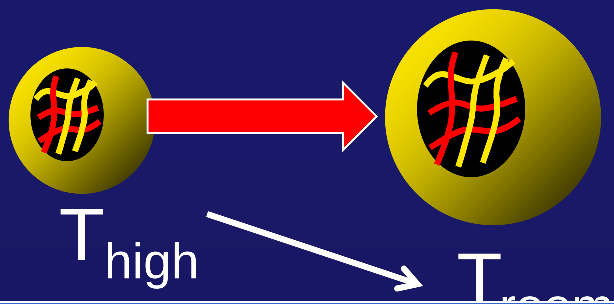
Soft Spheres:
beyond the glass transition



... compress beyond close packing

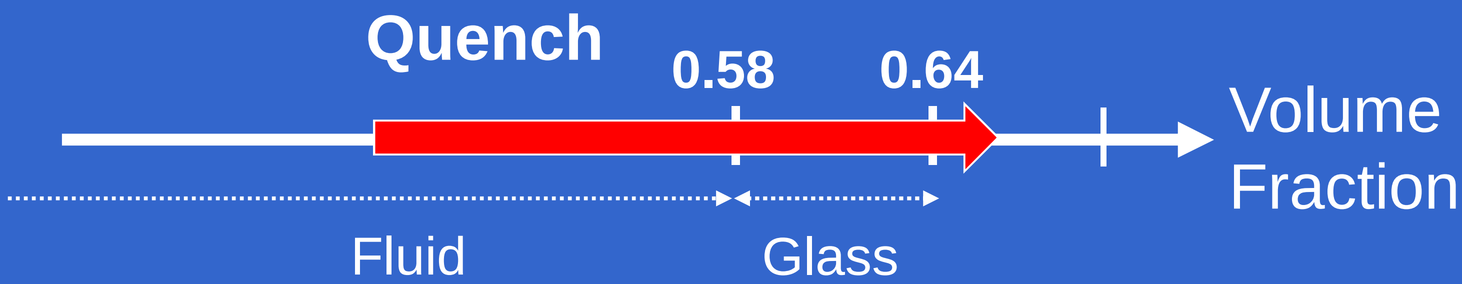
Soft Sphere Glasses

Temperature-sensitive colloids

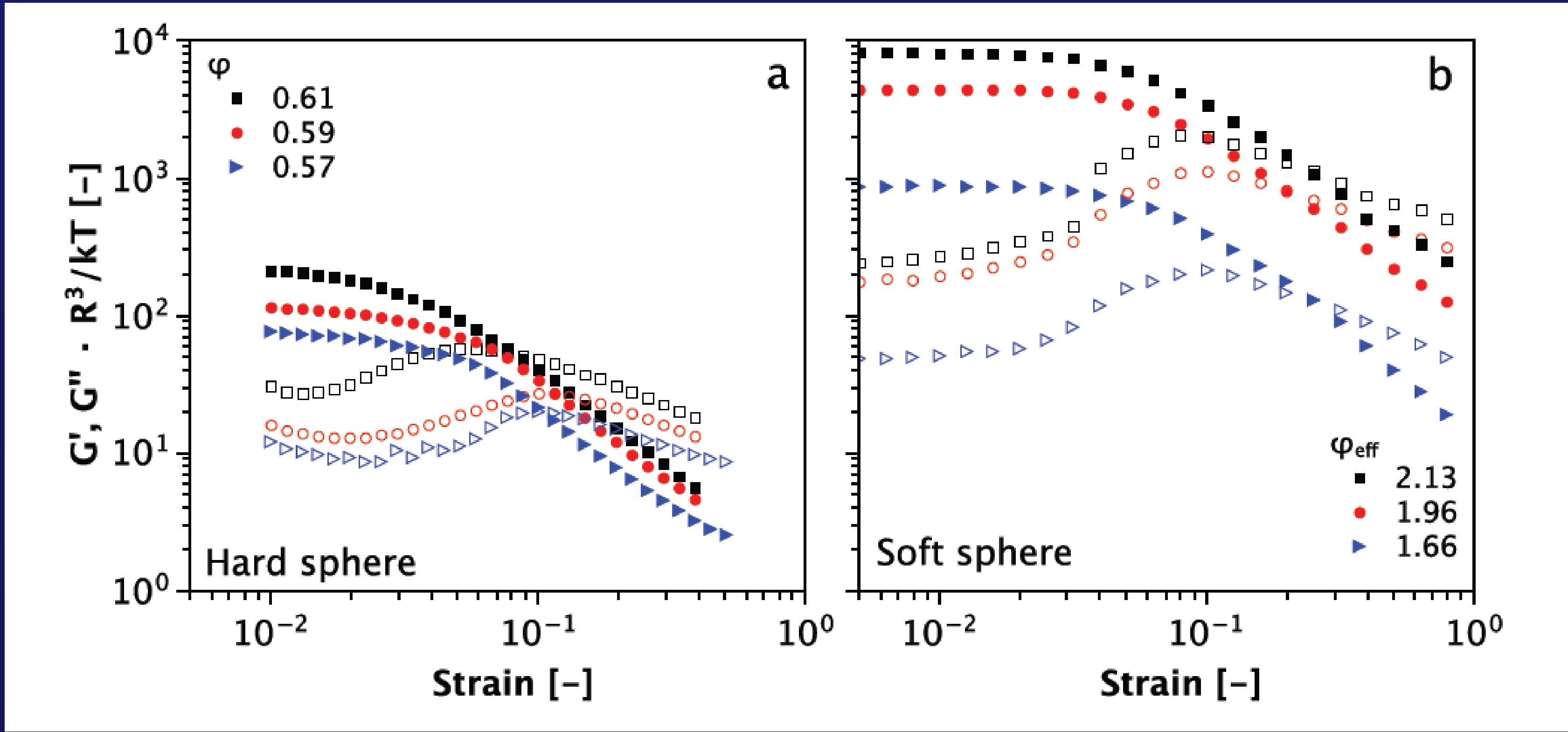


pNIPAm
(Poly-N-isopropoylacrylamide)

Quench beyond glass transition

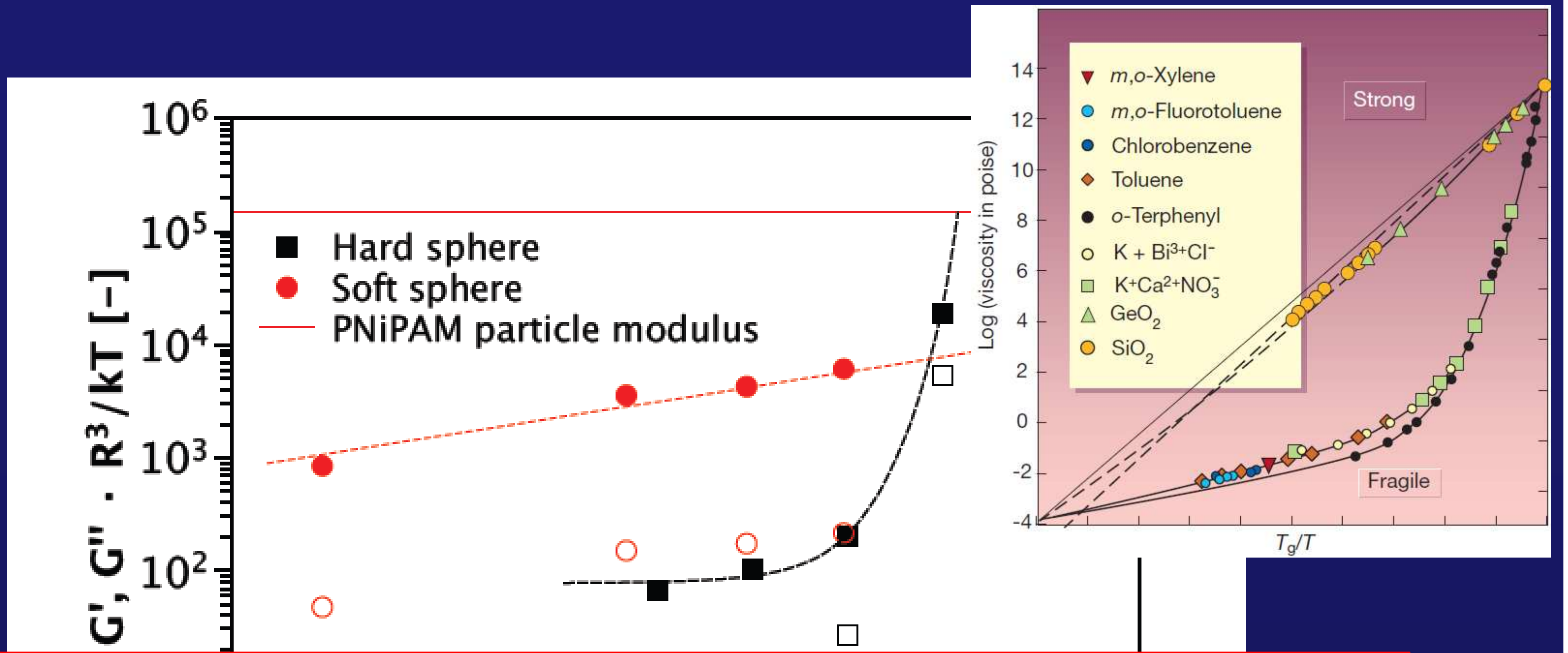


Rhology: Hard and Soft Sphere Glasses



Soft Spheres: High elastic component!

Rhology: Hard and Soft Sphere Glasses



Soft spheres → Strong Glasses

Hard Spheres → Fragile Glasses

Mattsson, Weitz (*Nature* 2010)

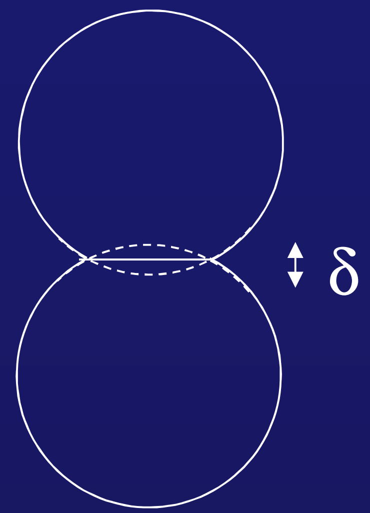
Soft Spheres

Weaker volume fraction dependence

Soft Spheres : Hertzian Interaction

Hertzian Interaction

$$u = \frac{8}{15}\sqrt{\frac{R}{2}}\; E_p\; \delta^{2.5},$$



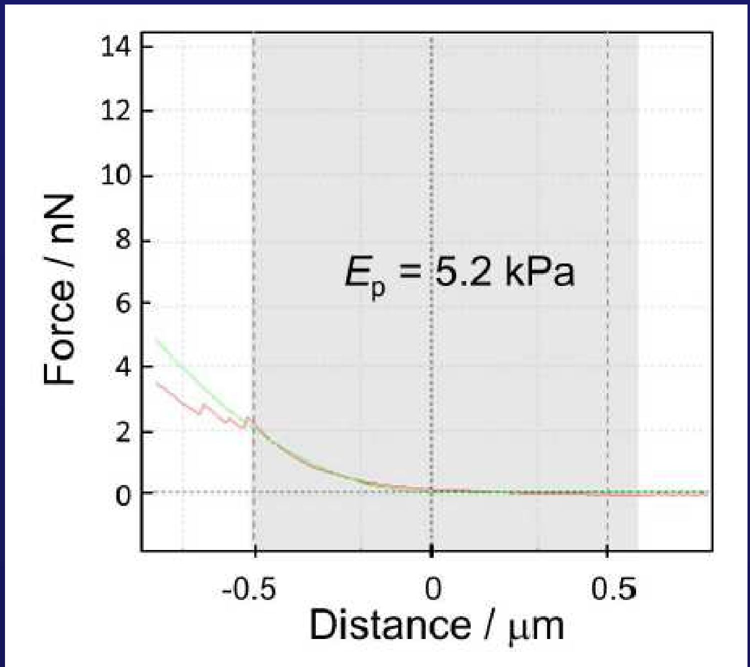
Suspension Modulus

$$G_\infty = \frac{2\pi}{15}\; n^2 \int_0^{2R} g(r)\frac{d}{dr}[r^4\frac{du(r)}{dr}]\, dr,$$

Cloitre, Bonnecaze (*J. Rheol.* 2006)

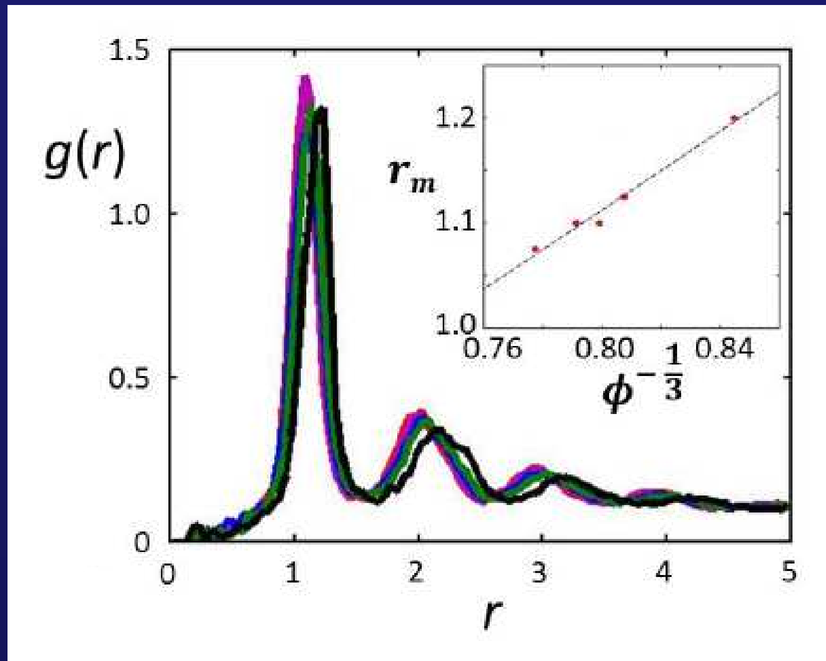
Soft Spheres : Hertzian Interaction

1. Particle Modulus



(Atomic Force Microscopy)

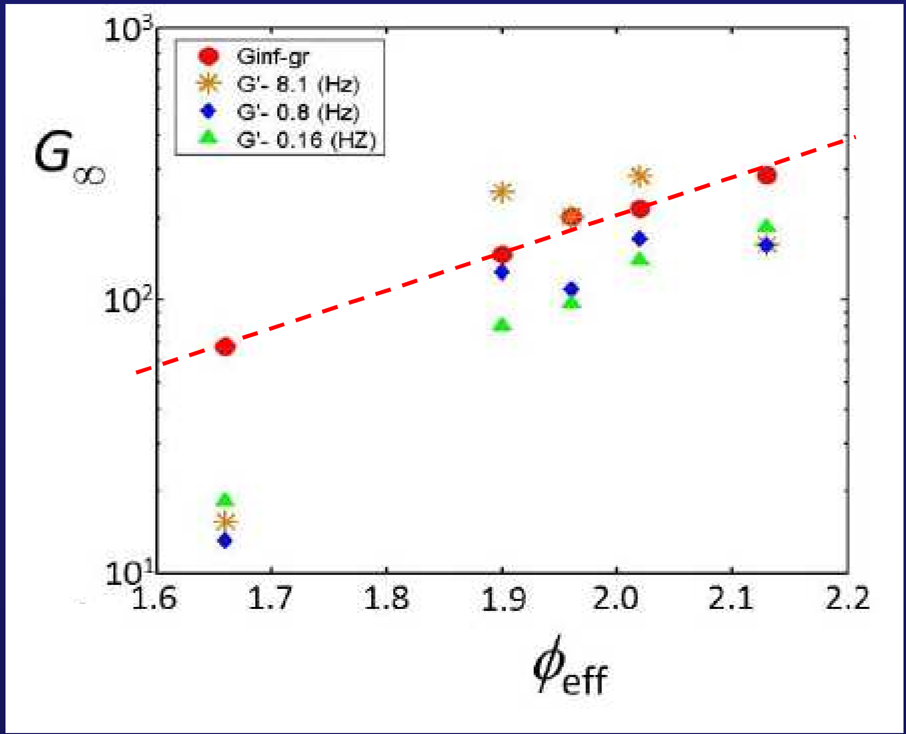
2. Pair Distribution Function



(Confocal Microscopy)

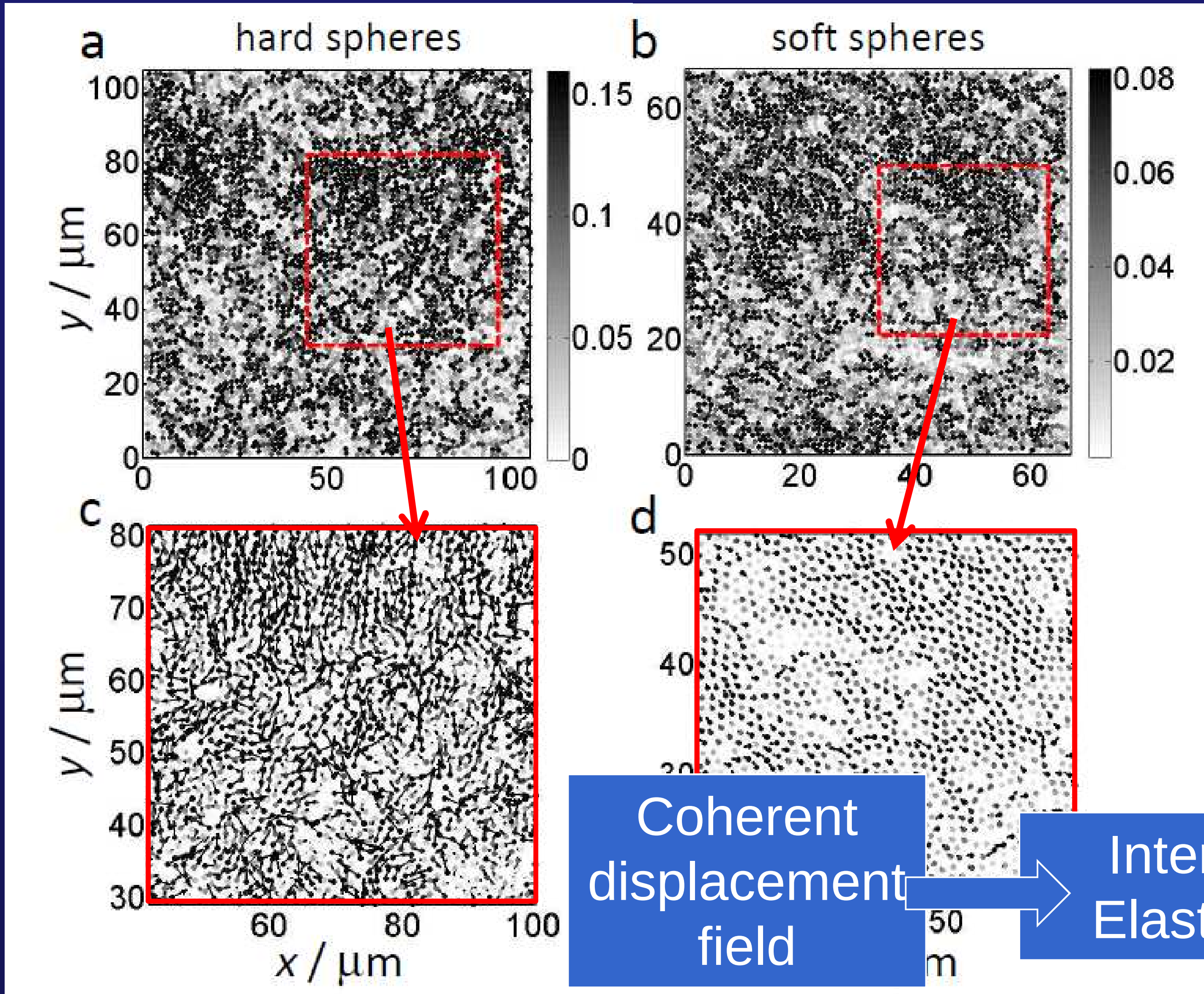
Soft Spheres : Hertzian Interaction

Shear Modulus: Model & Measurement



How does elasticity affect microscopic relaxation?

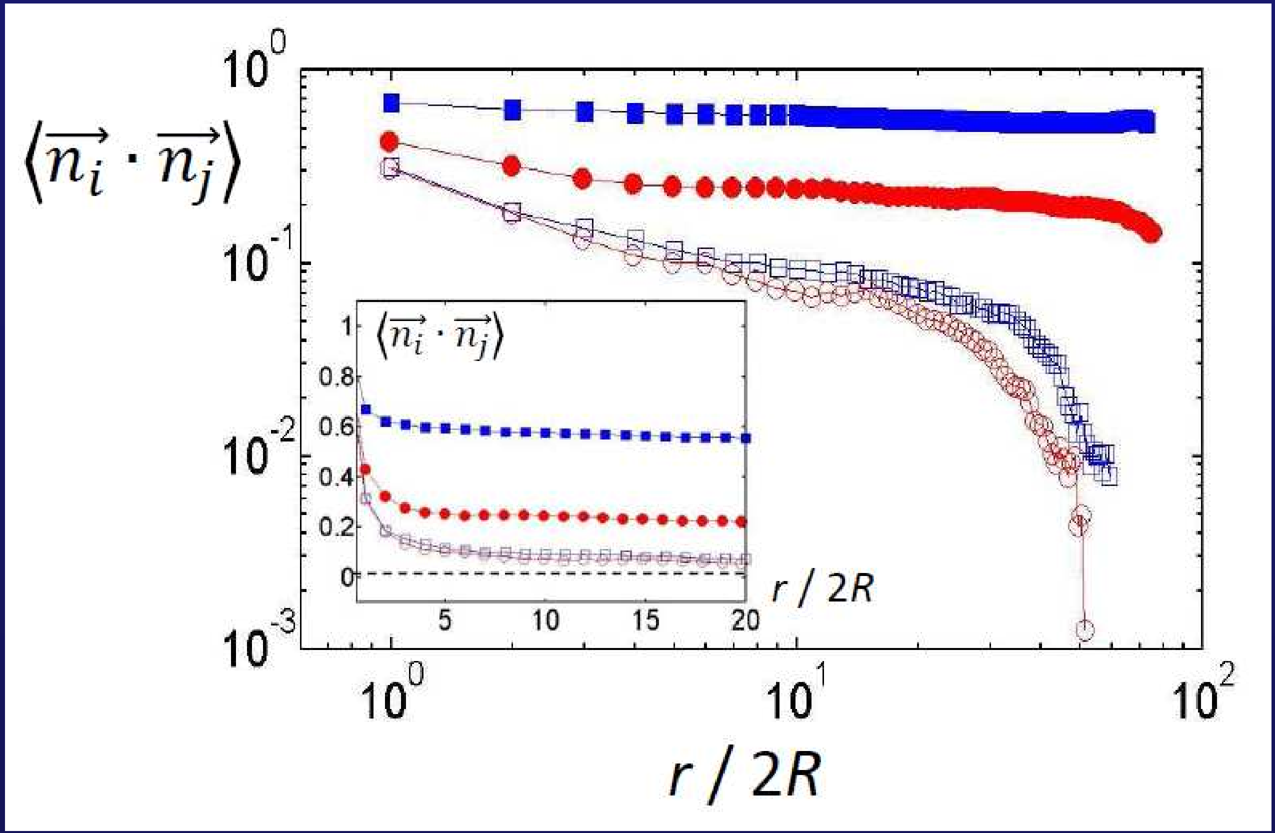
Soft Sphere Glasses



Coherent displacement field → Internal Elasticity

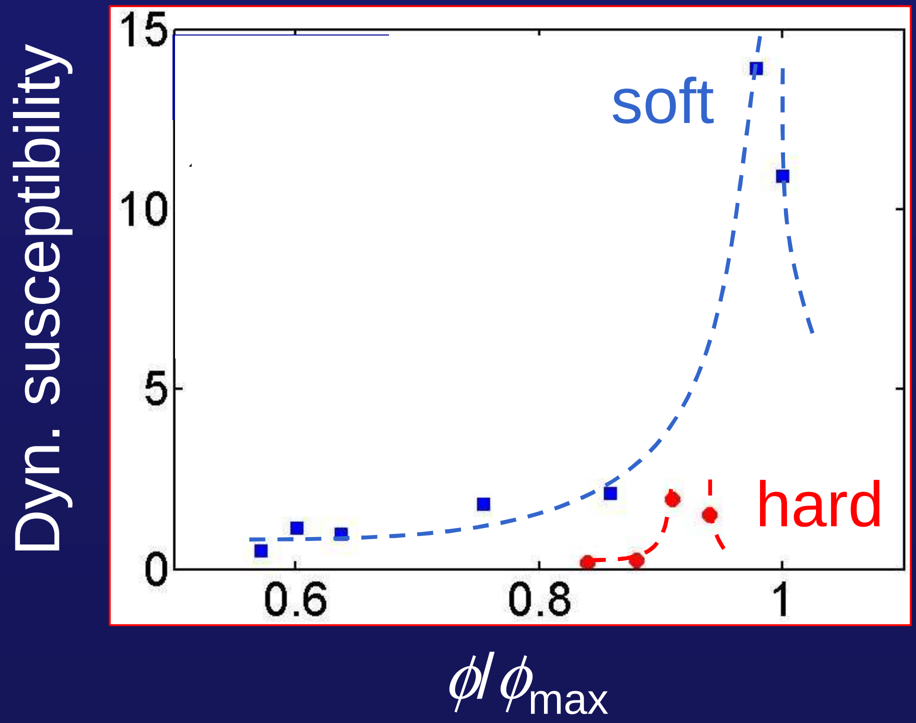
Soft Sphere Glasses

Correlations of Displacements



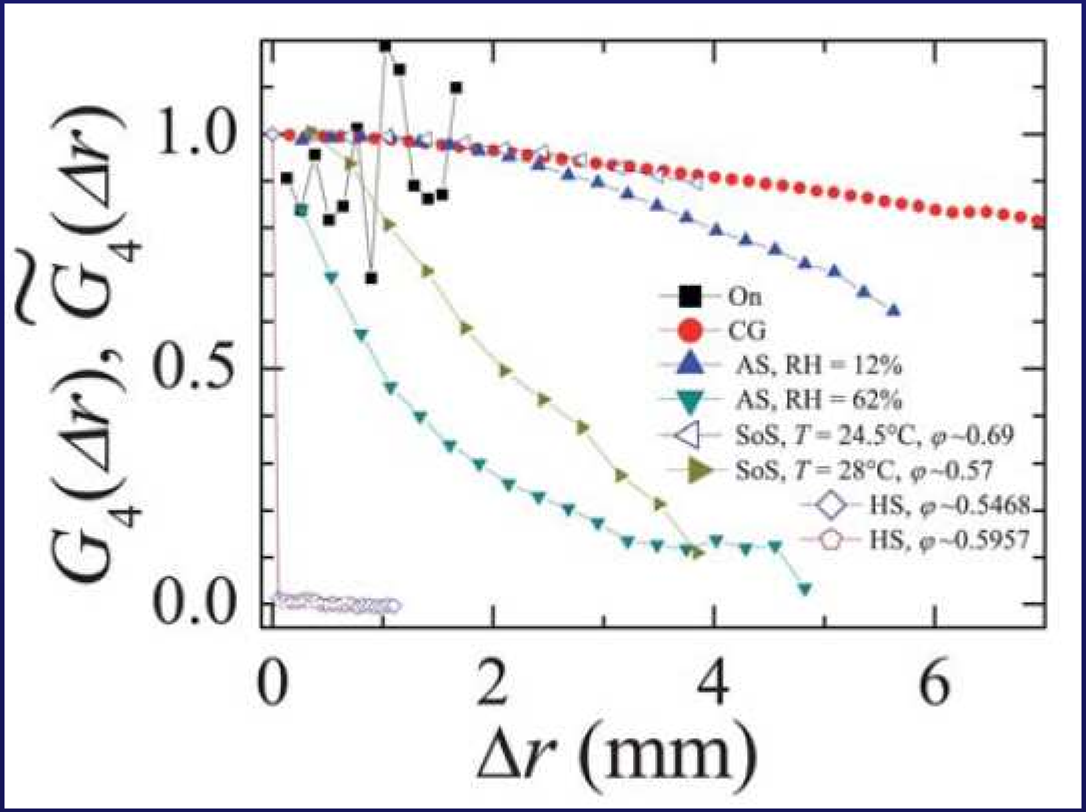
Soft Sphere Glasses

➡ Large Dynamic susceptibility!



Soft Sphere Glasses

Long-range correlations ...



... ubiquitous in Soft Matter!

Conclusions

- Colloidal Glasses
  Insight into flow of amorphous materials

- Strain correlations :
  central to material arrest, flow and failure

- **New anisotropic** correlations:
  Stress-dependent anisotropic scaling → Strain localization

- → Dynamic first order transition in 4D space-time