Experiments in two and three dimensions

A confocal microscopy study

Günter K. Auernhammer
MPI Polymer Research, Mainz

Twente, March 2016

Before I start

Physics at Interfaces
Max Planck Institute for
Polymer Research

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Director

Dr. Günter Auernhammer

Project Leader

Prof. Dr. Markus Mezger

Project Leader [more]

Dr. Rüdiger Berger

Project Leader [more]

PD Dr. Doris Vollmer

Project Leader [more]

Dr. Michael Kappl

Project Leader [more]

Dr. Stefan Weber

Project Leader [more]

Dr. Kaloian Koynov

Project Leader [more]

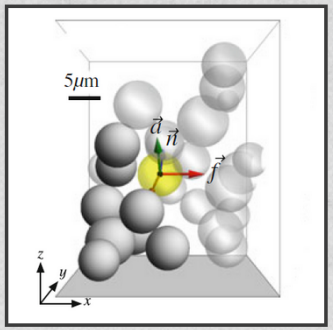
Dr. Si Wu

Project Leader

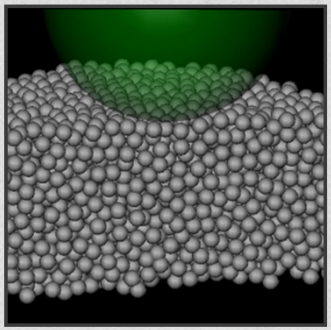
Auernhammer group

- **Colloids**

Dynamical processes in granular matter

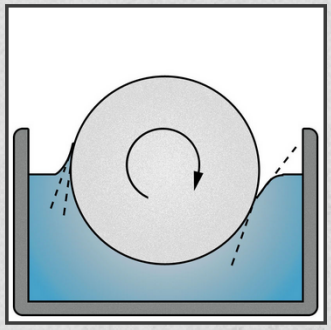


Mechanical properties of colloidal aggregates

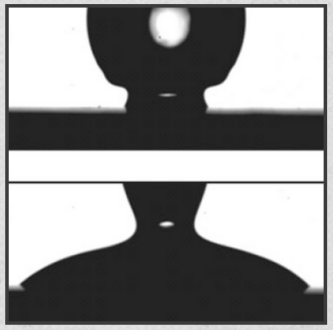


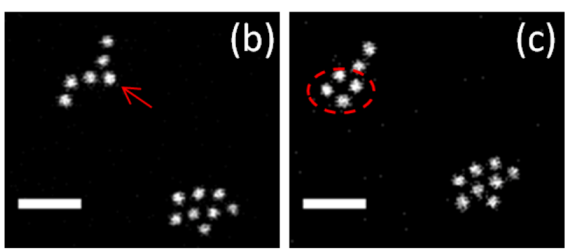
- **Dynamic Wetting**

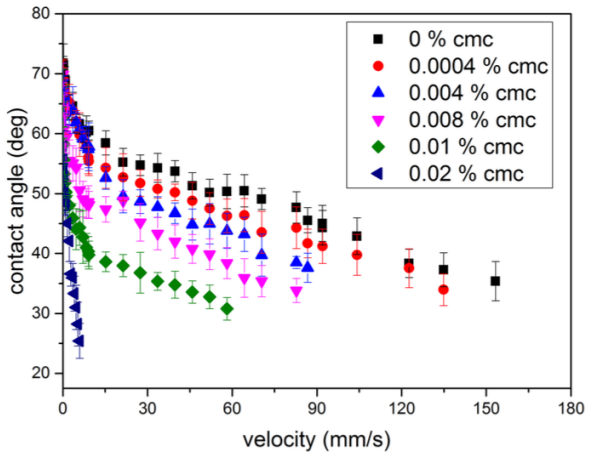
Wetting of surfactant solutions



Fast wetting by miscible and immiscible liquids







Thanks …

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- Heiko Briesen (TU München)
- Stefan Luding (U Twente)
- Andreas Menzel (U Düsseldorf)
- Christian Holm (U Stuttgart)

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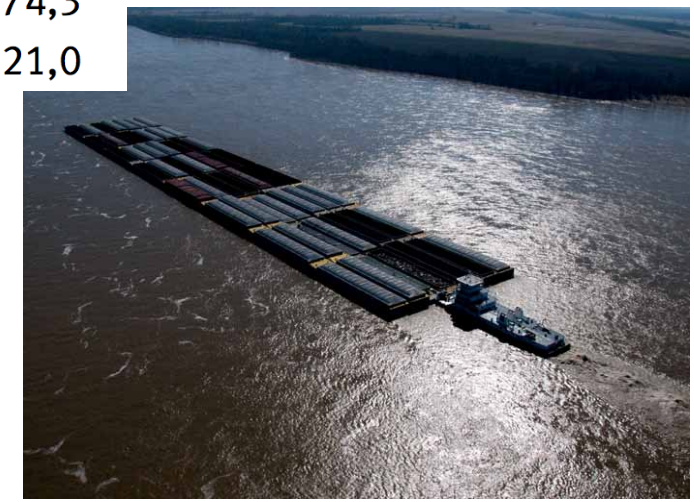
Why particles?

- Transported goods as bulk solids (granulates)
  - > 50% on inland water ways

July 2012	10^6 t km
Flüssiges Massengut	1 087,0
Schüttgut	2 939,6
Stückgut	574,3
20-Fuß-Container	221,0

Statistisches Bundesamt



http://www.drycargomag.com

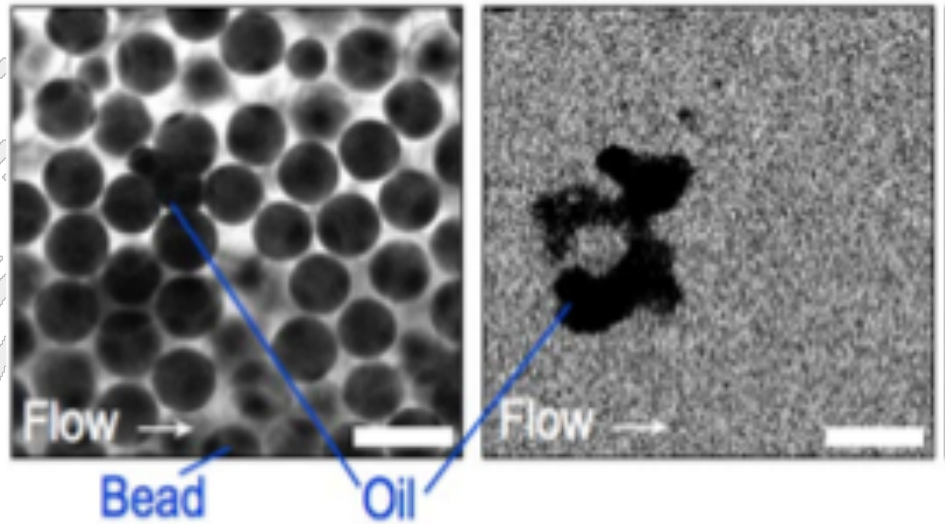
- Paints, coatings, etc.

Source: http://www.codinghorror.com/blog/archives/2006_04.html

Why wet particles?

Flow through porous media

Clogging

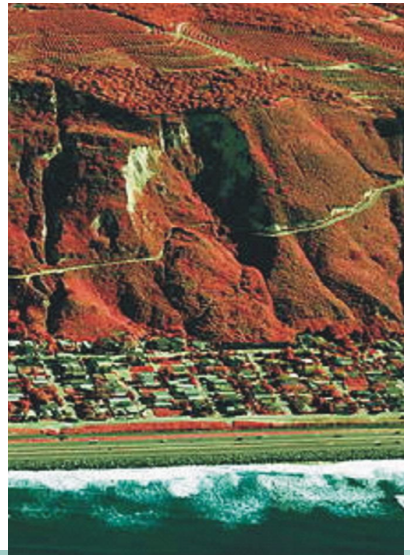


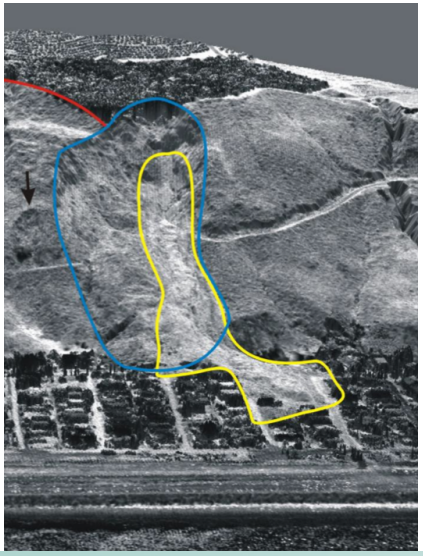
*A. T. Krummel, S. S. Datta, S. Münster, D. A. Weitz, AIChE Journal **59**, 1022 (2013).*

oil sand

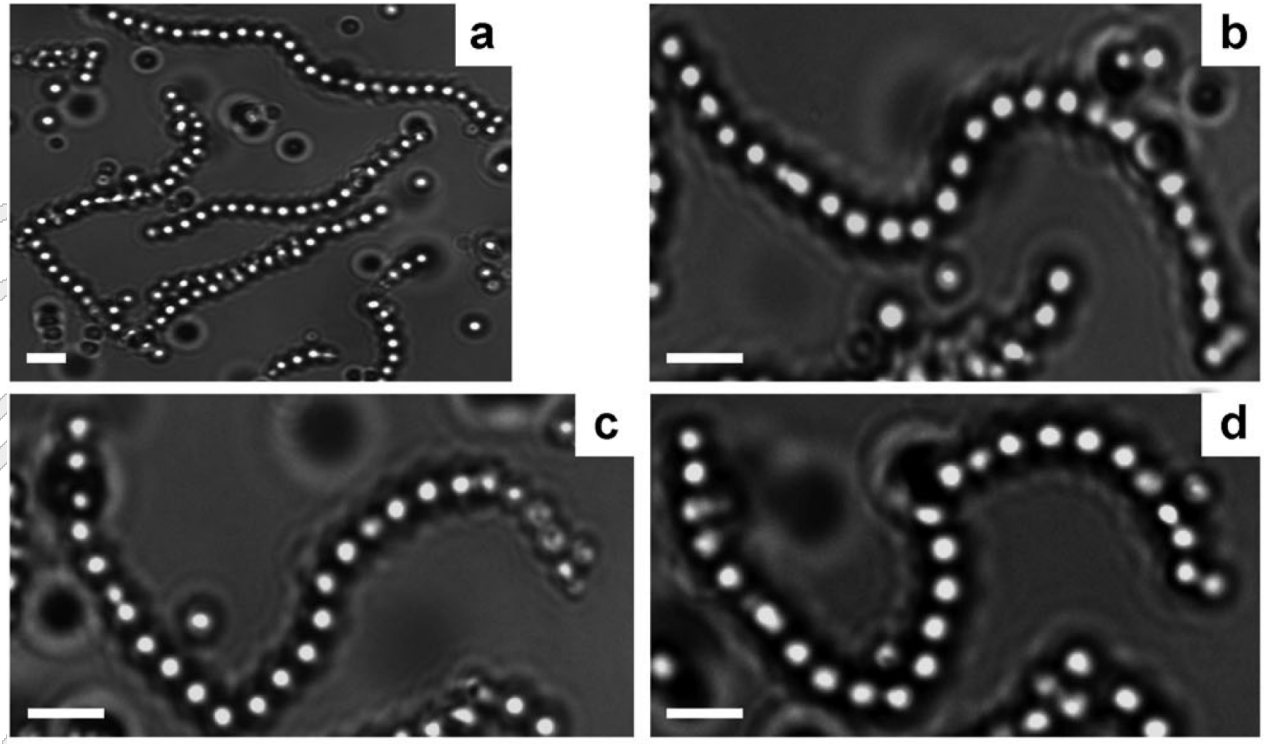
www.wirtschaftsblatt.at

Landslides



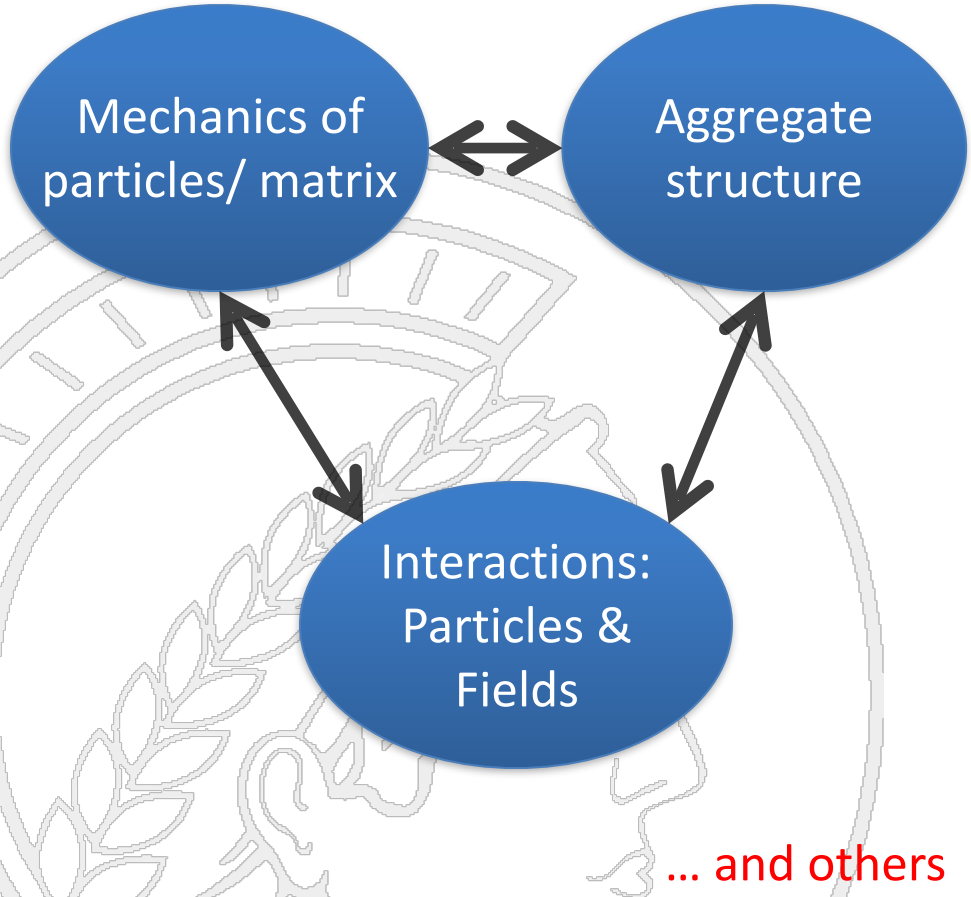


Particles as model atoms



Vutukuri, H. R., A. F. Demirörs, B. Peng, P. D. J. van Oostrum, A. Imhof and A. van Blaaderen (2012). "Colloidal Analogues of Charged and Uncharged Polymer Chains with Tunable Stiffness." Angewandte Chemie International Edition **51**(45): 11249-11253.

Bottom up approach to mechanics of particulate systems



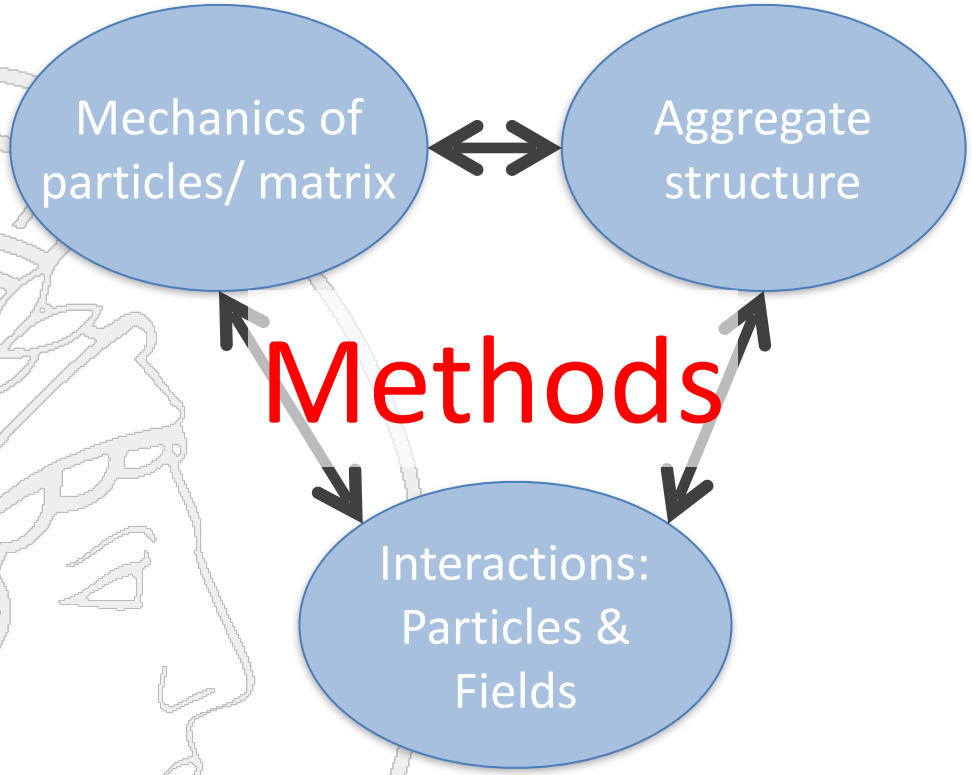
Particles ⟷ Colloids

1 µm

?

en.wikipedia.org

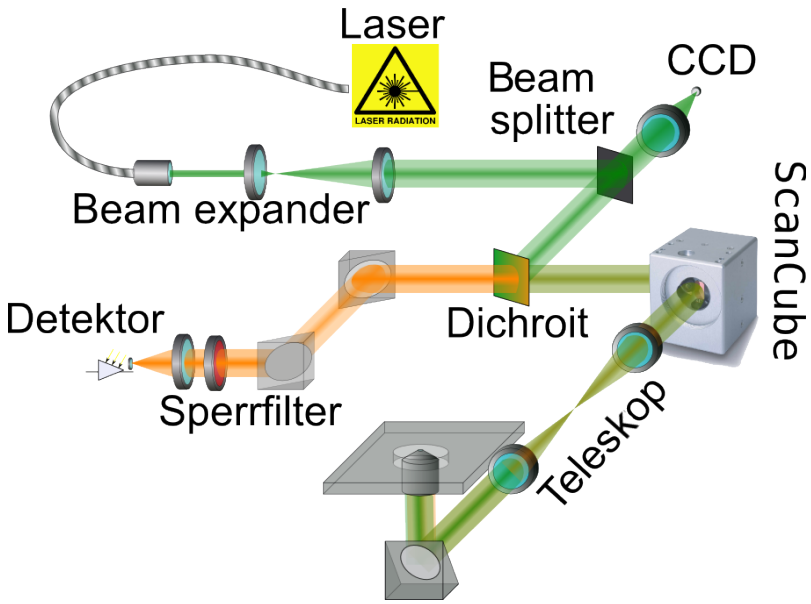
www.i-c-m.at


Mechanics of particles/ matrix
Aggregate structure
Methods
Interactions: Particles & Fields

Methods I

Requirements:

- Fluorescent particles
- Looking deep: index-matching



Home-made:

-> Very flexible

-> **slow mode**: 1 2D frames/s; **fast mode**: ~ 1000 2D frames/s

-> compatible with **nano indenter** and **piezo rheometer**

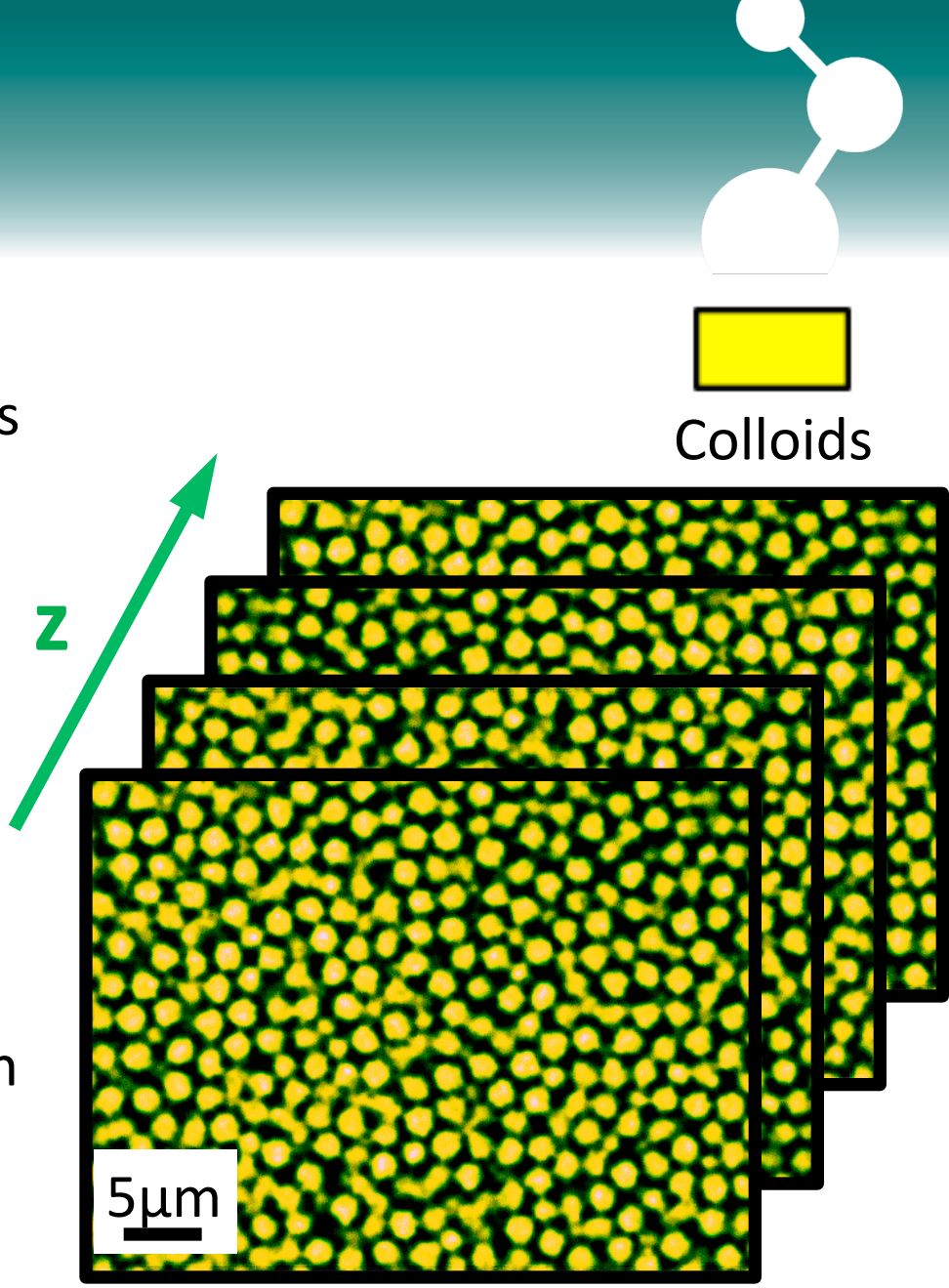
Methods II

Sample

- Fluorescently labeled colloids
- Index-matching liquid
- Imaging layer by layer

Determining the structure

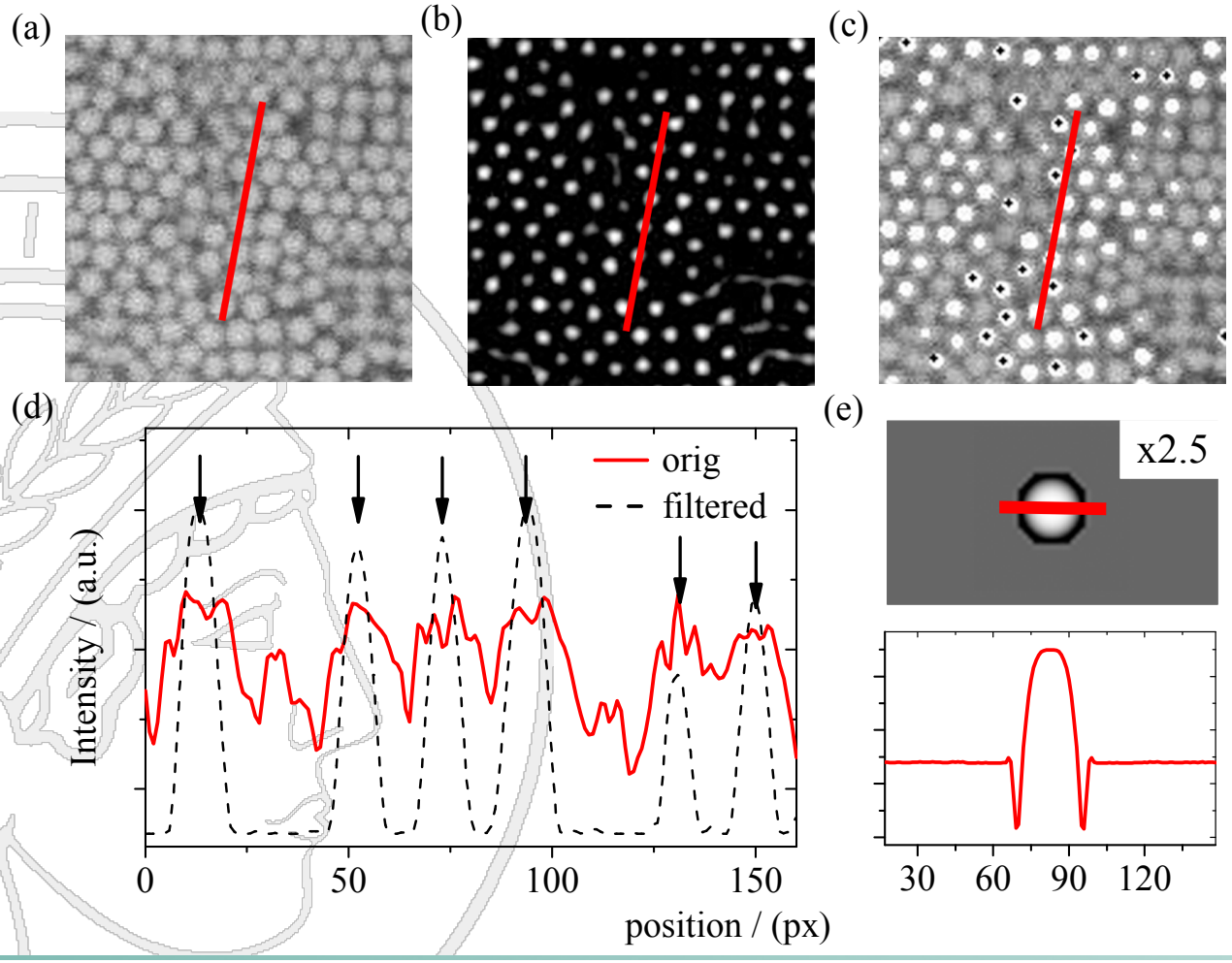
- Colloids = local maxima
- Finding the colloids
  Better than optical resolution



Crocker, Grier, J. Coll. Interf. Sci. **(1996)** 179, 298
Wenzl, et al., Granul Matt 15 **(2013):** 391-400.

Reconstructing the structure

Original => Convolution => Detect max

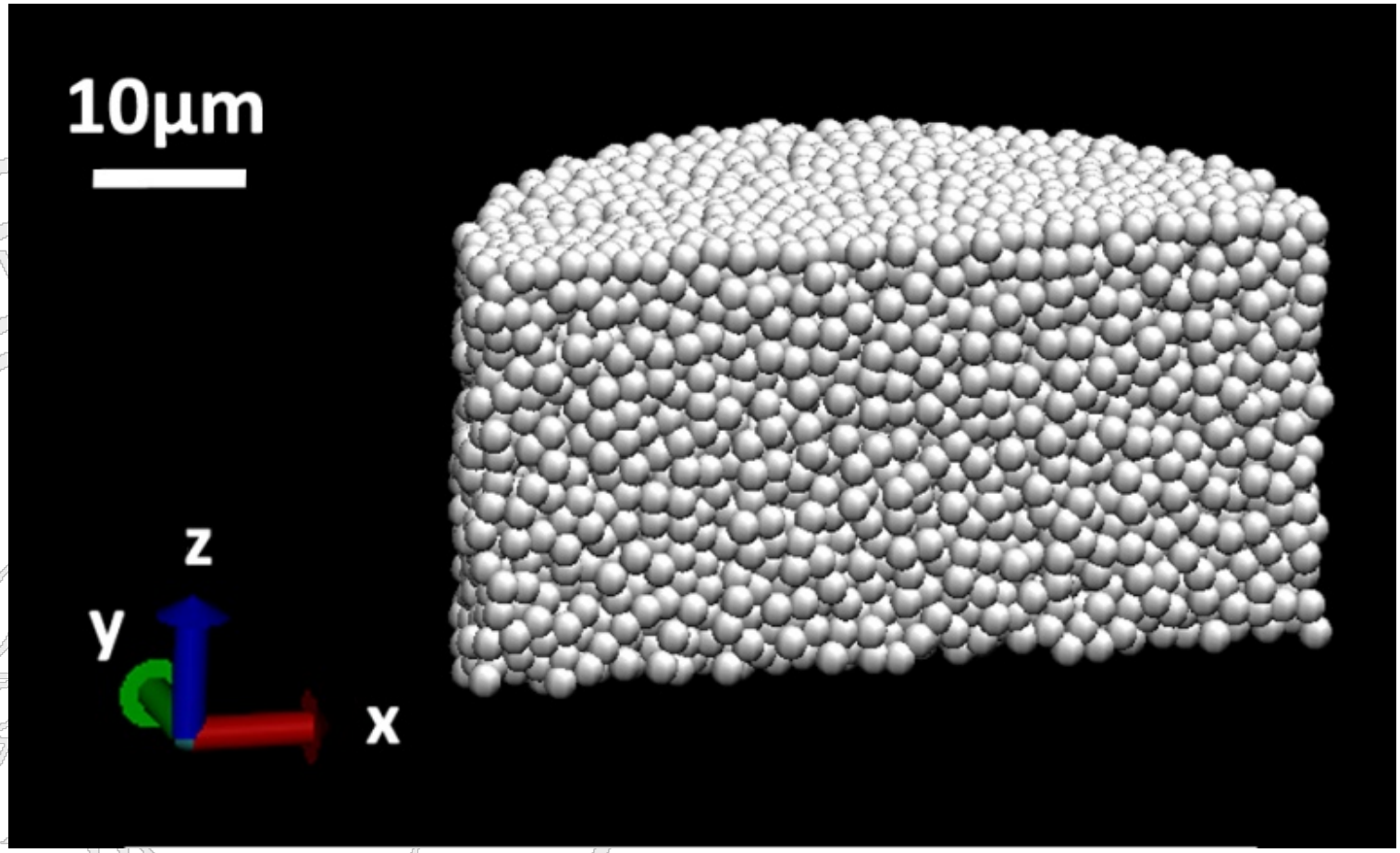


Profiles

Kernel

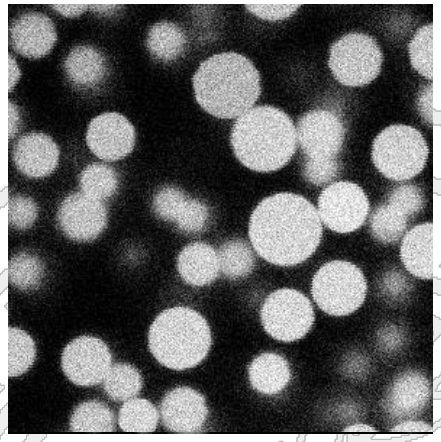
M. Roth, M. Franzmann, M. D'Acunzi, M. Kreiter, G. K. Auernhammer; arXiv:1106.3623v2 [cond-mat.soft] (2011).

Reconstructing the structure

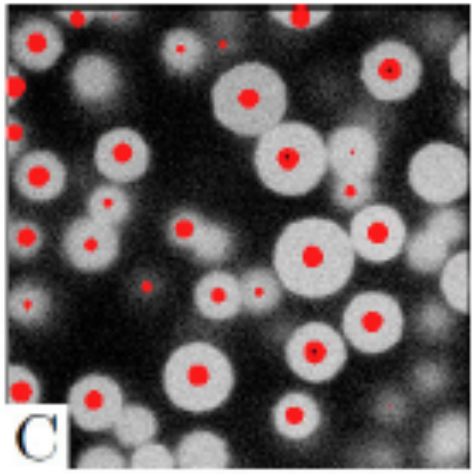


Data analysis: polydispersity

How to find polydisperse particles

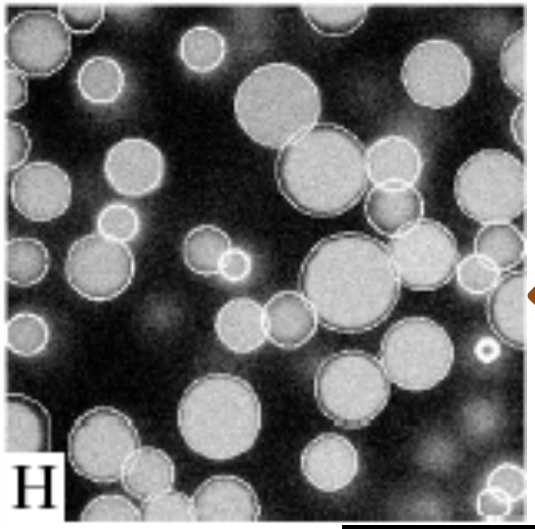


Image

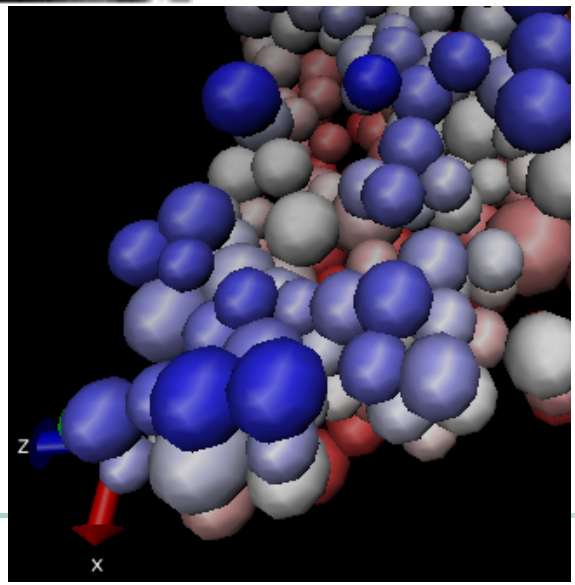


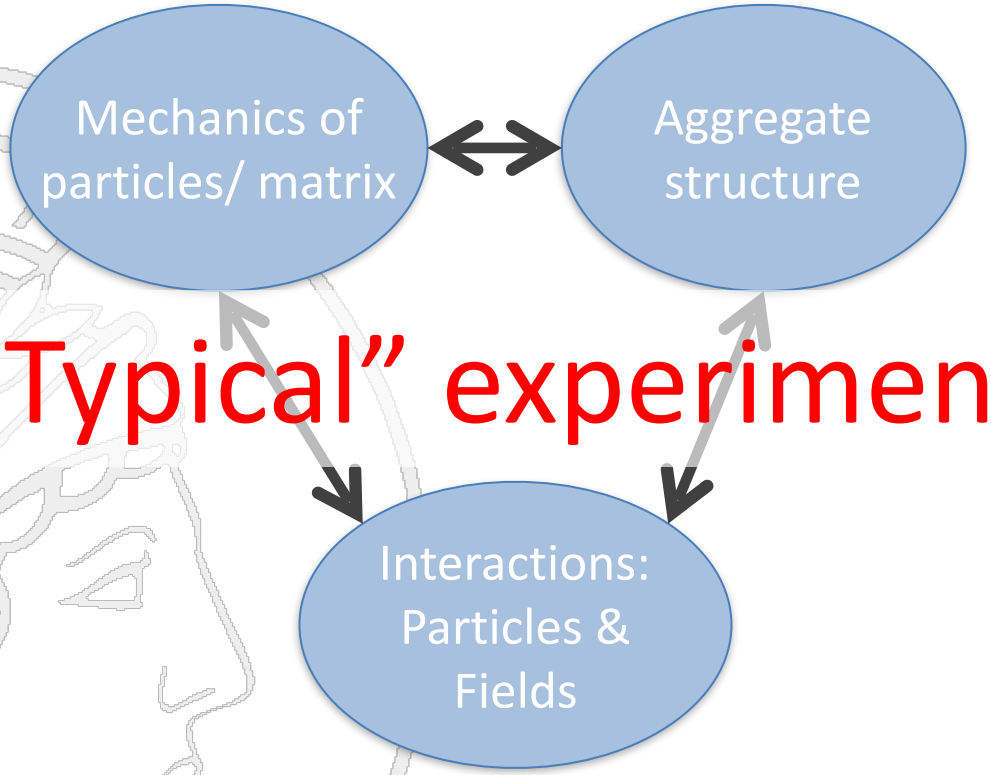
Localization in 3D

Diameter
of particles



Visualization



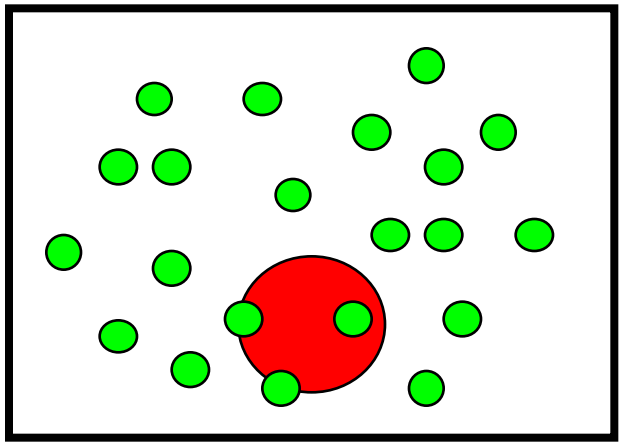


”Typical” experiment

“Hard” polymer spheres: electrostatics

PMMA colloids:
Diameter: 1.6µm
Fluorescently labeled

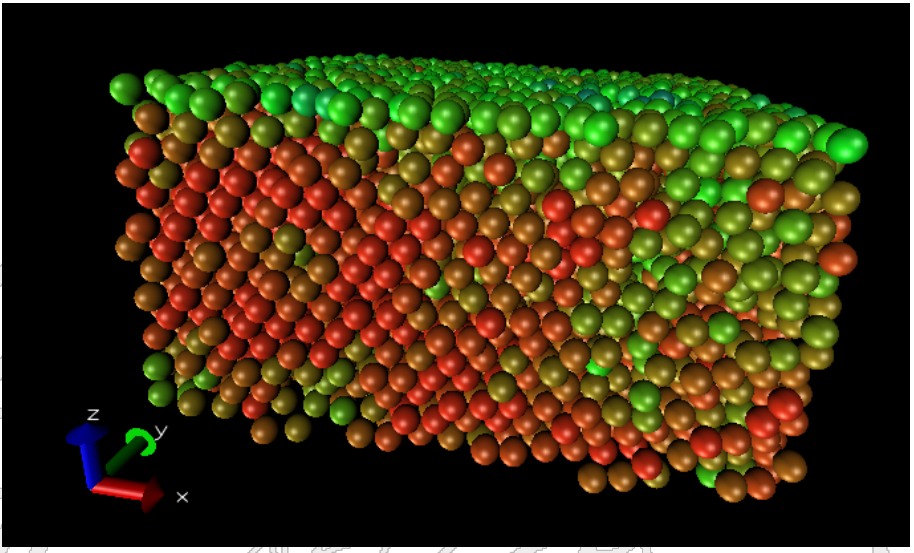
Magnetic colloids:
Diameter 4.4µm
Concentration Magn./PMMA ~10^{-5}



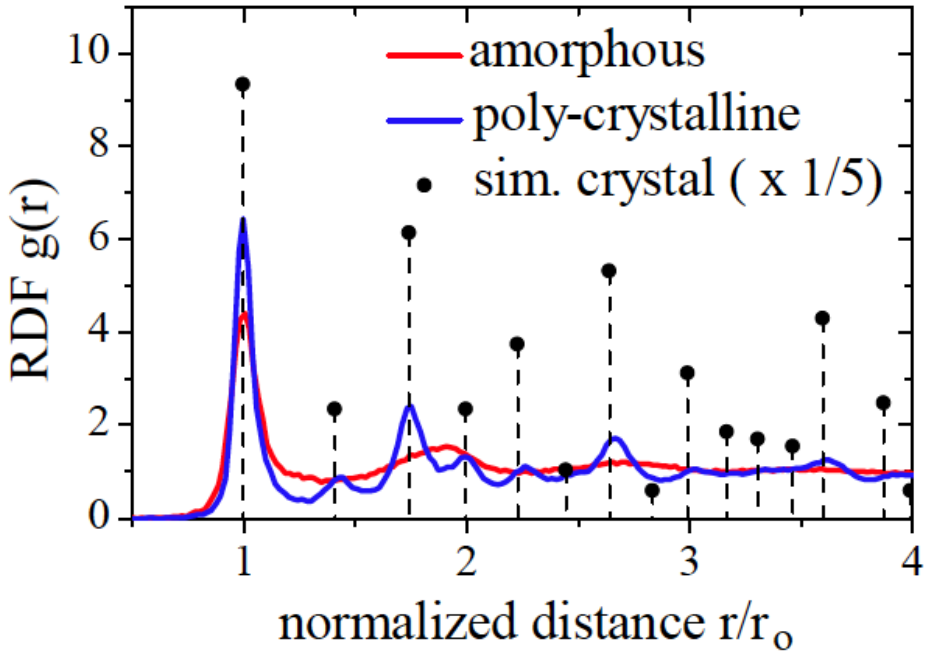
Colloidal crystals with defects

Confocal microscopy => Dynamics of defects

Reconstruction

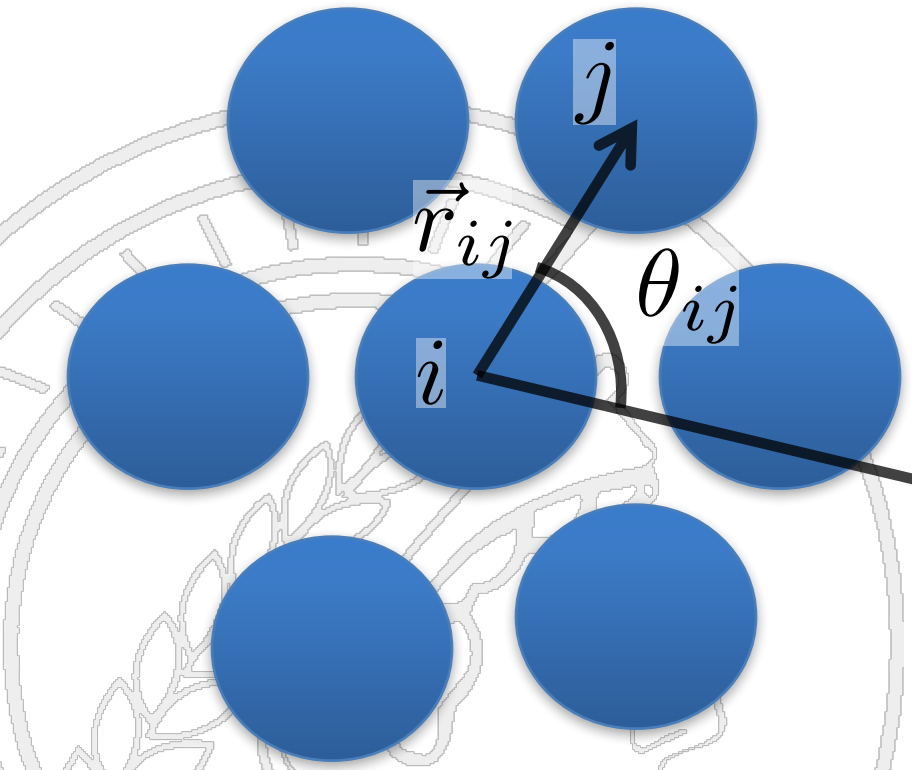


Radial distribution function



Number of nearest neighbors:
closer than $1.2\ r_0$

Degree of order in 2D



$$\Psi_6 = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{6}\sum_{j}\exp(i6\theta_{ij})$$

Projecting bond vectors to nearest neighbors

Averaging over small volume

J. Chakrabarti and H. Löwen, Phys. Rev. E **58**, 3400 - 3404 (1998).

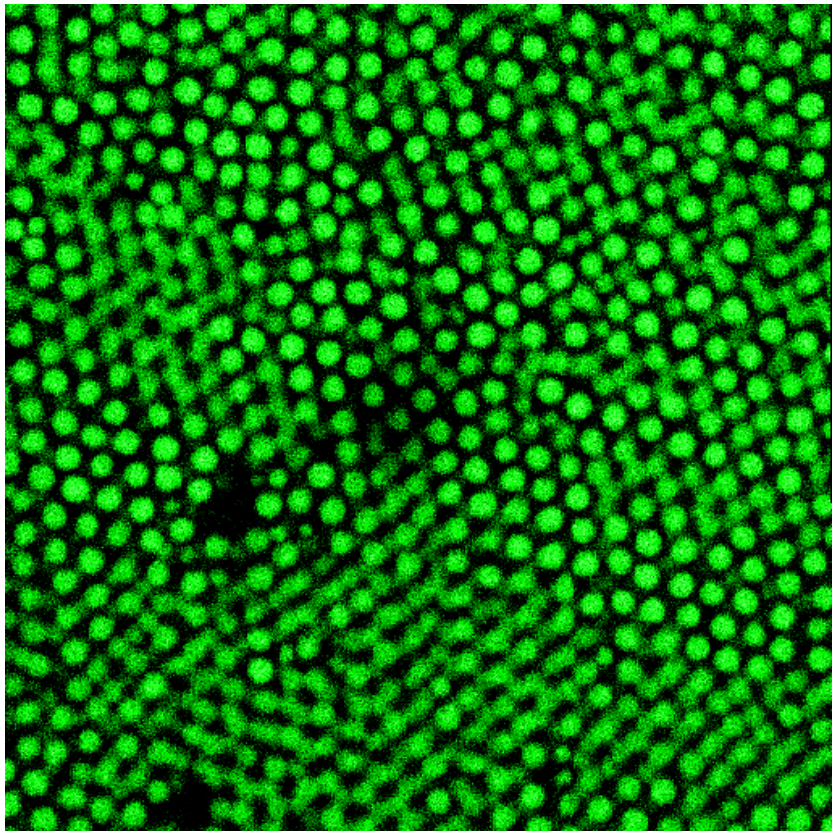
Degree of order in 3D

Bond order parameter in 3D

$$Q_{lm}(\vec{r}) \equiv Y_{lm}(\theta(\vec{r}), \phi(\vec{r}))$$

$$Q_l \equiv \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} | \bar{Q}_{lm} |^2 \right]^{1/2}$$

Steinhardt, et al., *Phys Rev B* **28**, 784 (1983).



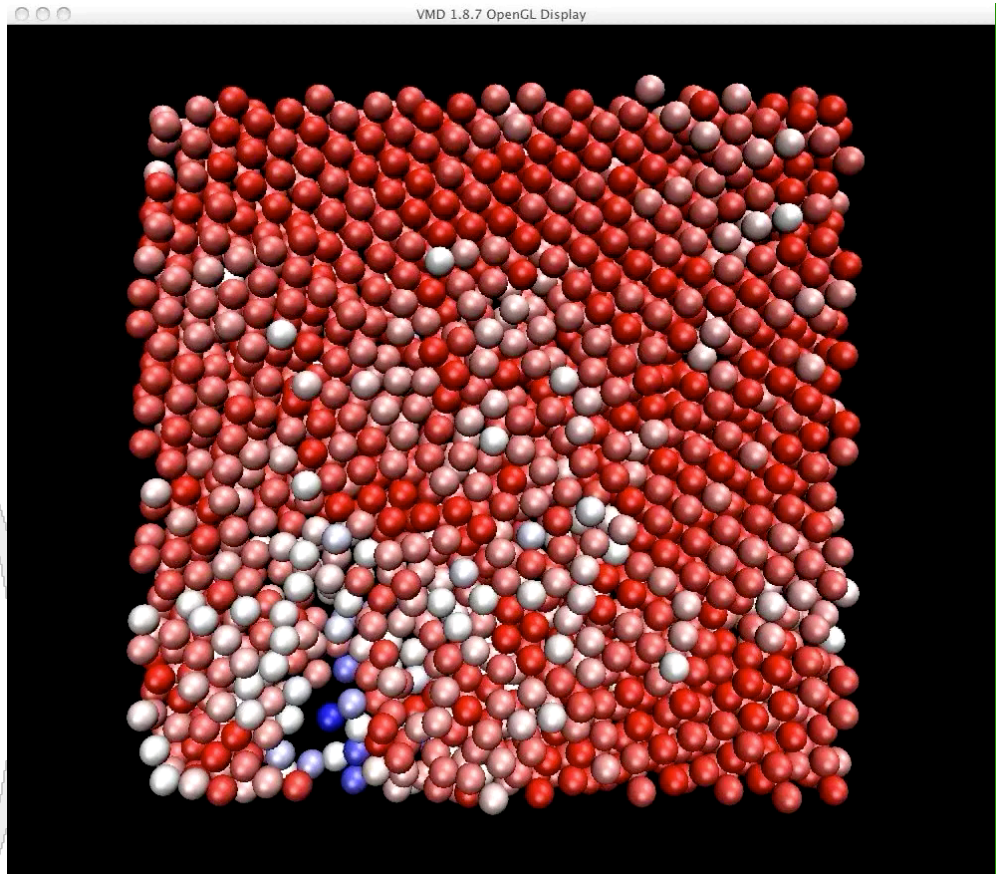
Generating defects in a crystal

Visualization or experiment

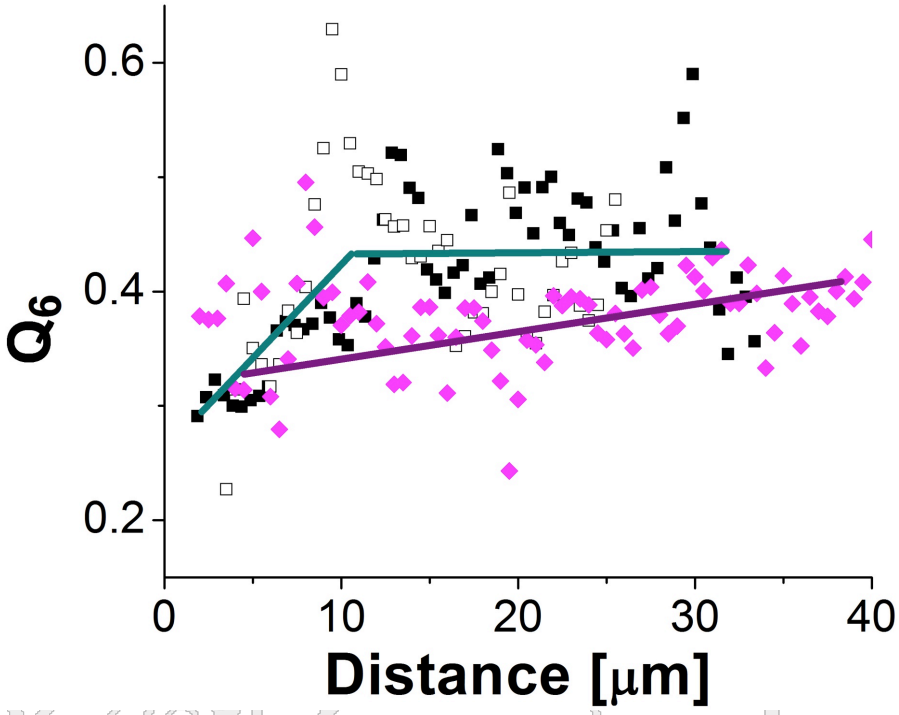
3D confocal sequence

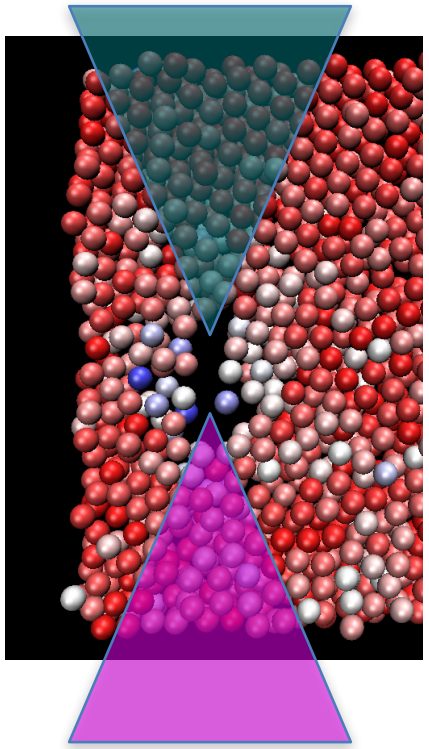
Chain of magnetic particles
in colloidal crystal

Magnetic field gradient



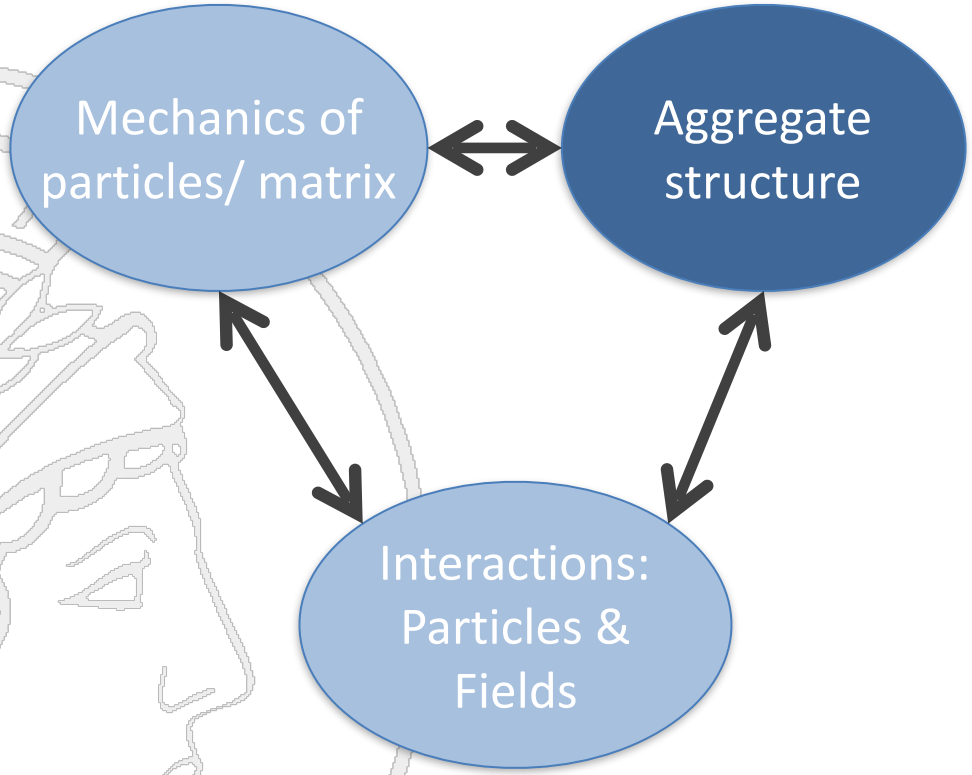
Crystal order vs. distance



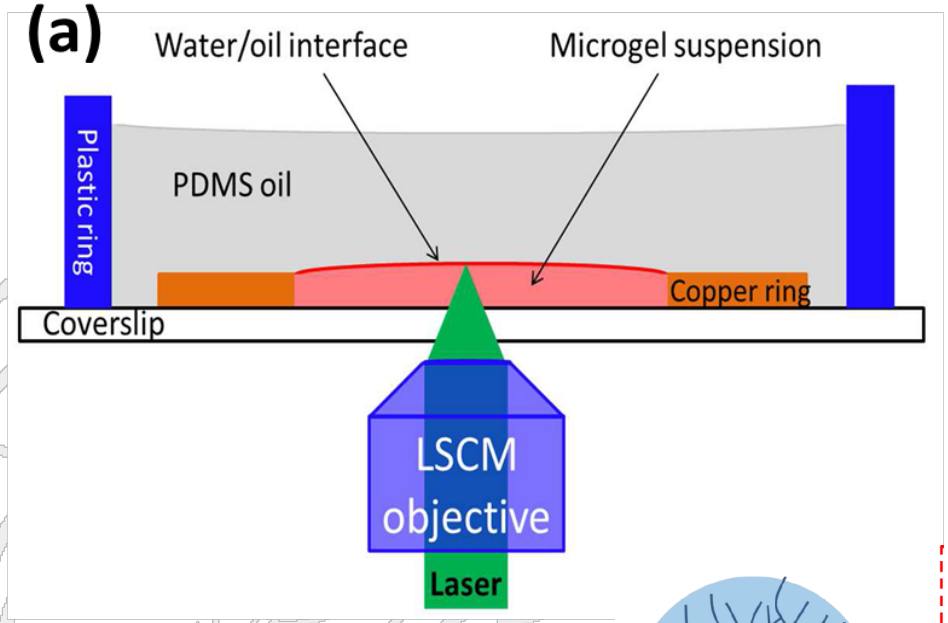


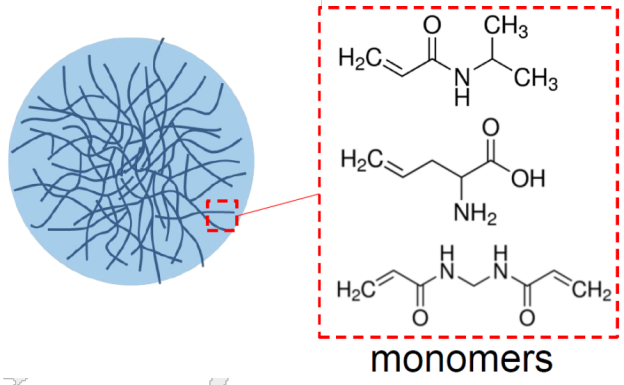
- Analysis of model atoms
- Colloidal crystal melts locally and recrystallizes slowly

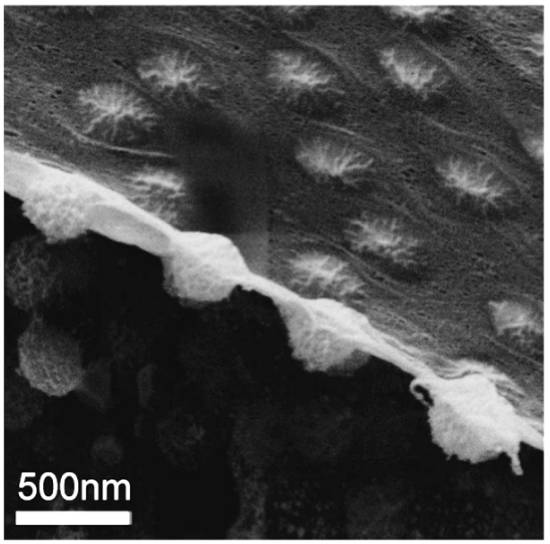
Structure vs. motion 2D



Soft particles at interfaces



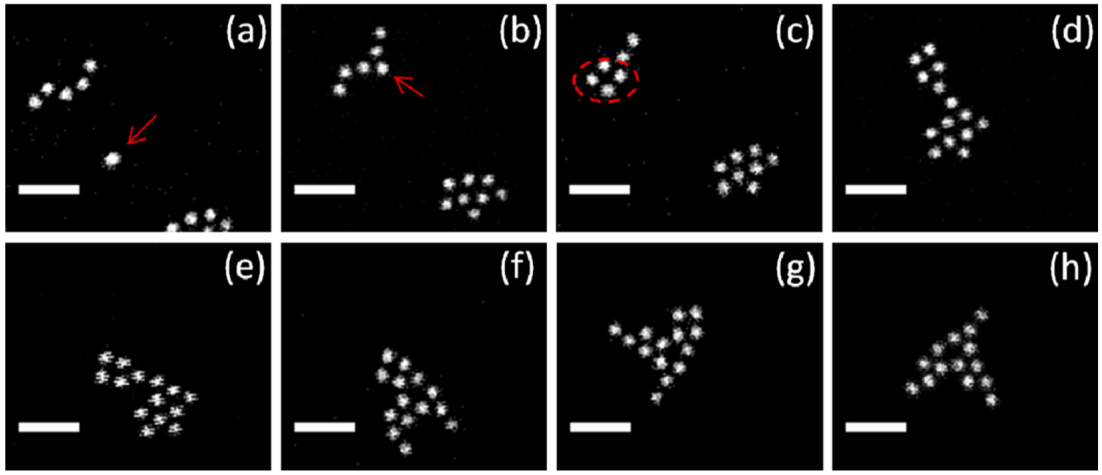


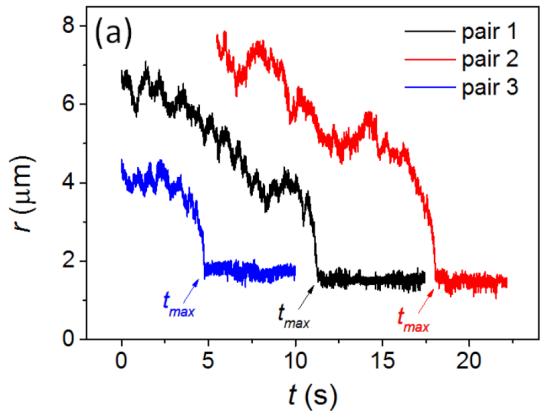


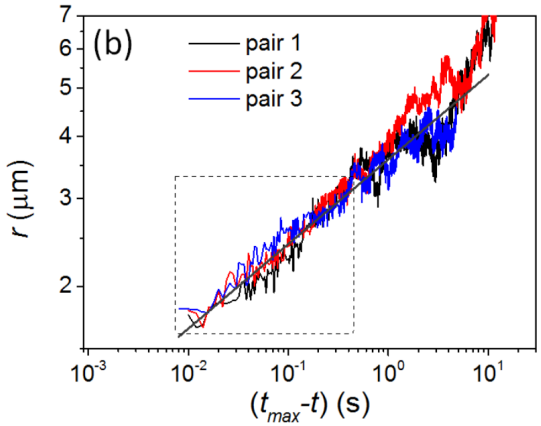
Style, R. W., et al. (2015). "Adsorption of soft particles at fluid interfaces." Soft Matter **11**(37): 7412-7419.

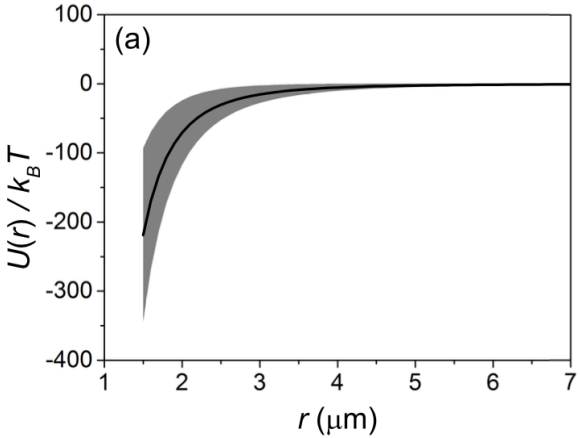
Huang, S., K. Gawlitza, R. von Klitzing, L. Gilson, J. Nowak, S. Odenbach, W. Steffen and G. K. Auernhammer (2016). Langmuir **32**: 712-722.

Attractive interaction



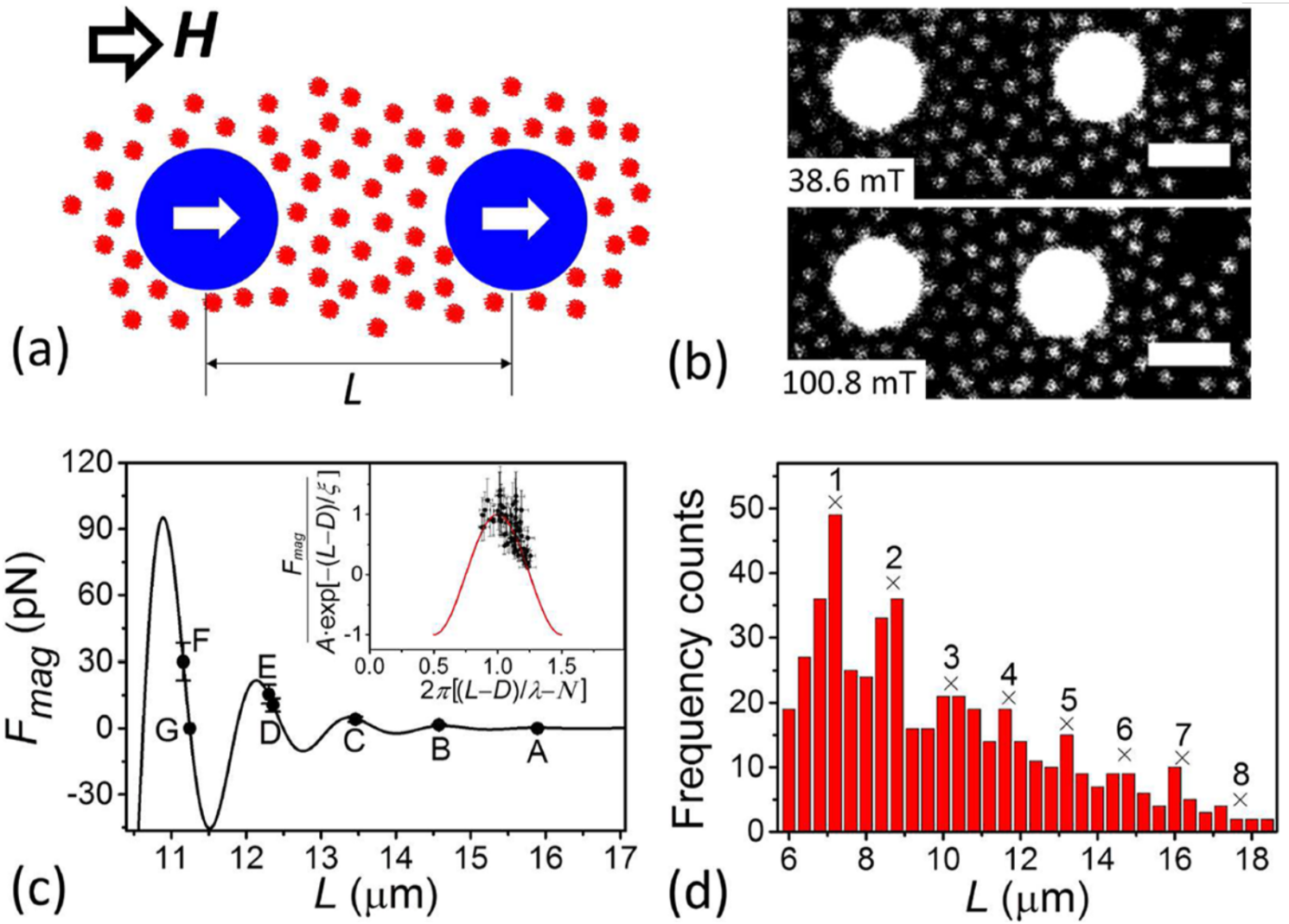




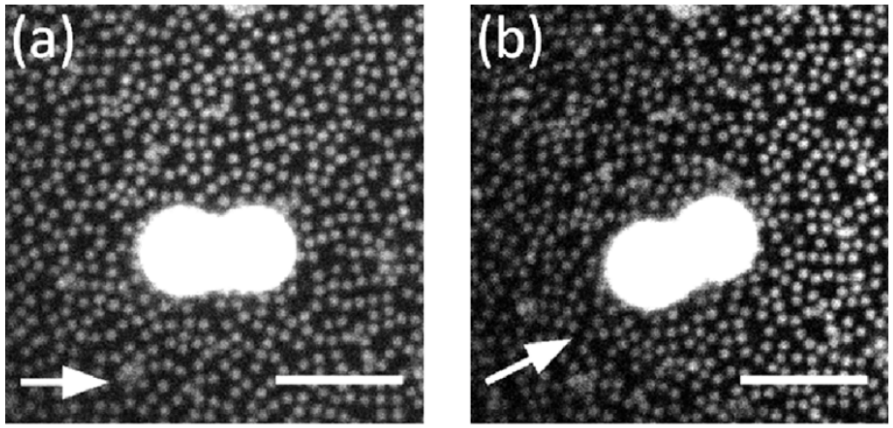


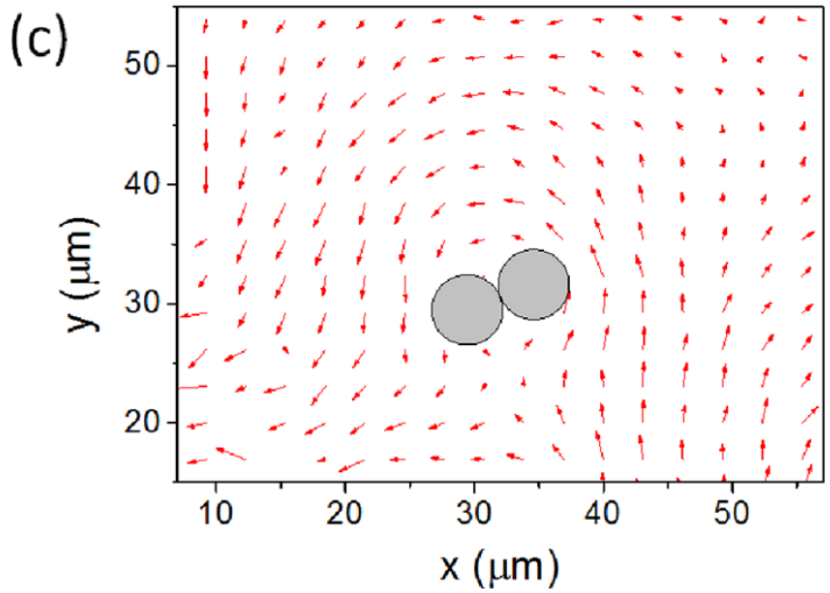
Huang, S., K. Gawlitza, R. von Klitzing, L. Gilson, J. Nowak, S. Odenbach, W. Steffen and G. K. Auernhammer (2016). Langmuir **32**: 712-722.

2D compression



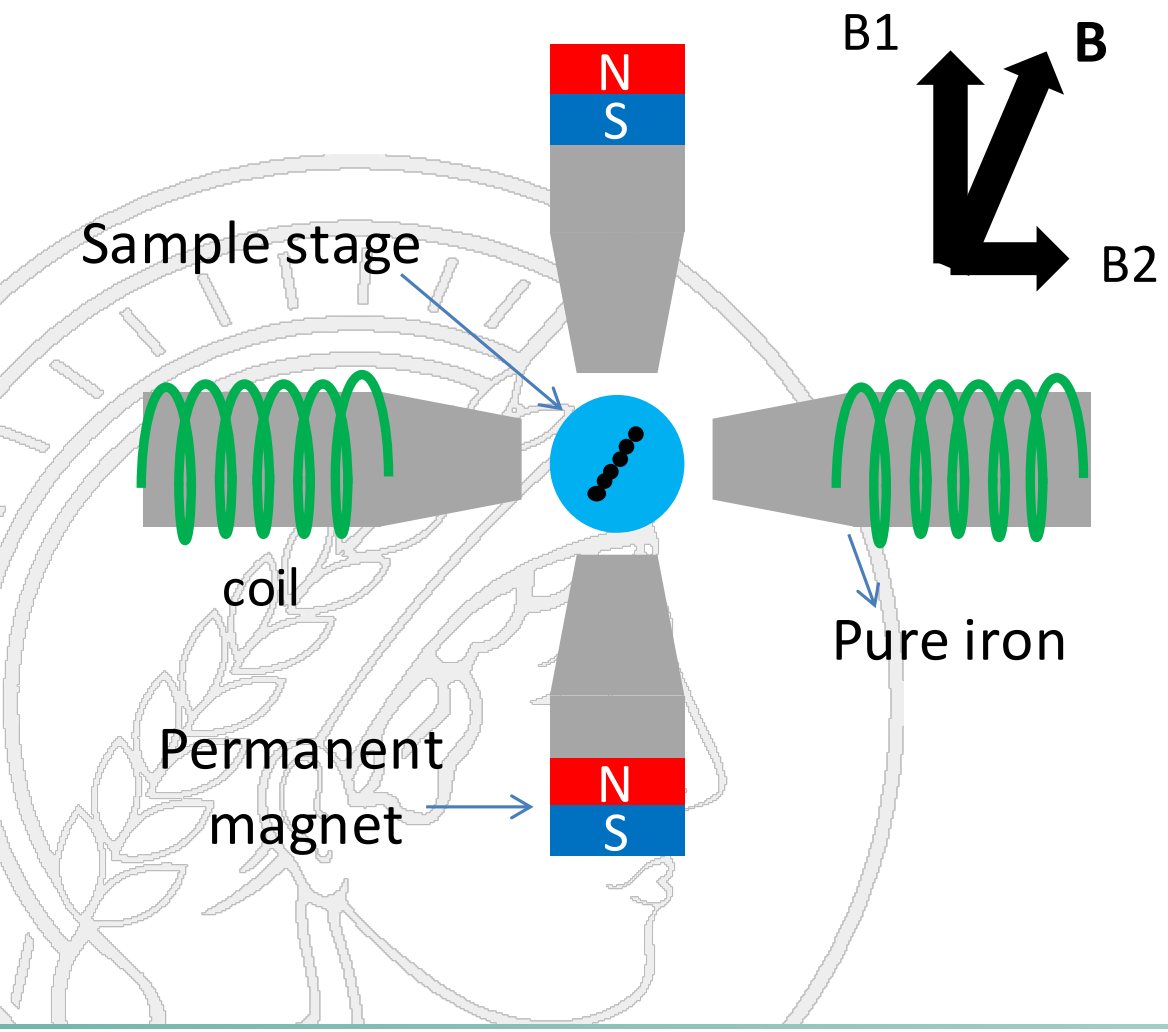
Deformation field in 2D

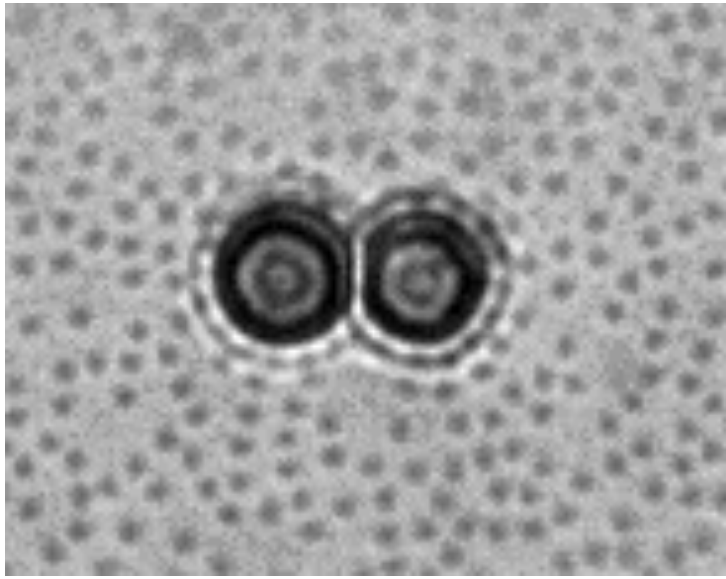




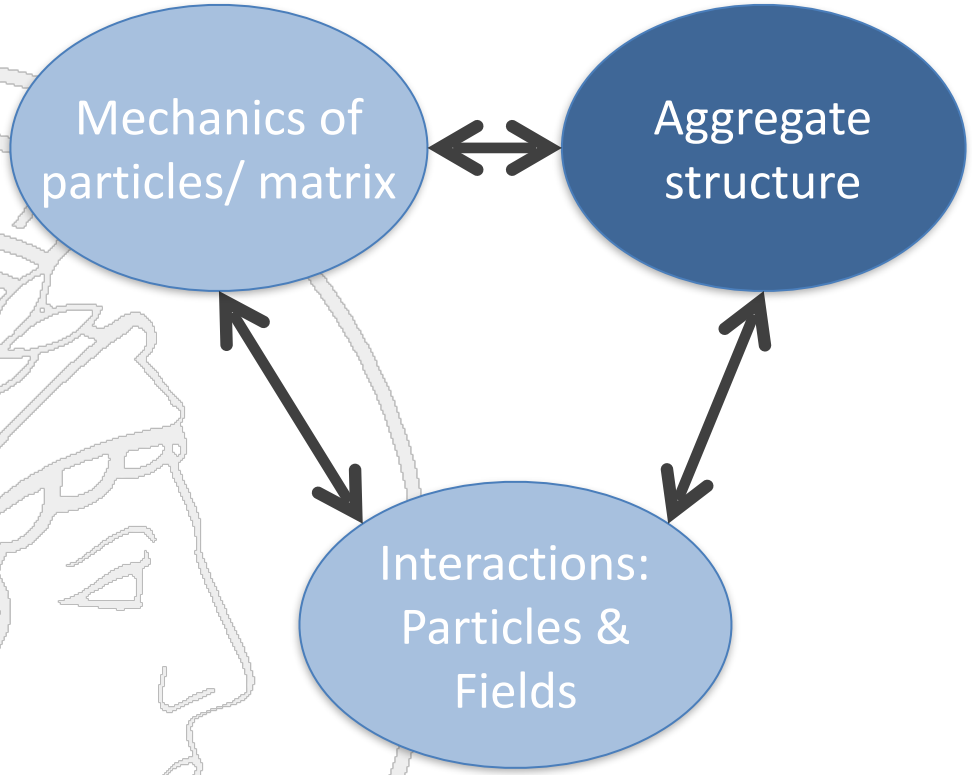
Step-wise rotation of the magnetic field.

Dynamic measurements (in progres)



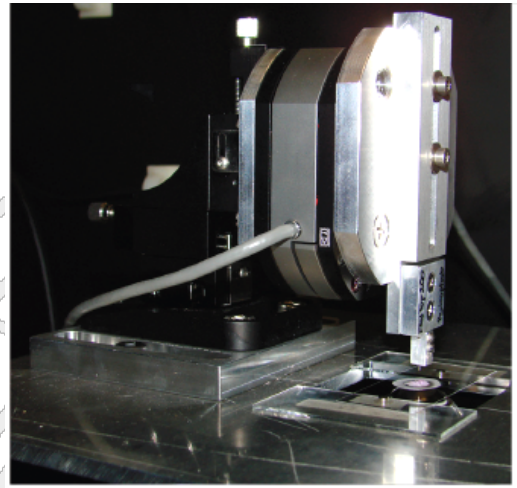


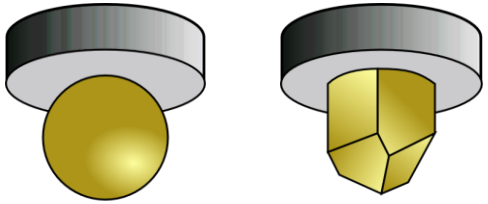
Structure vs. motion

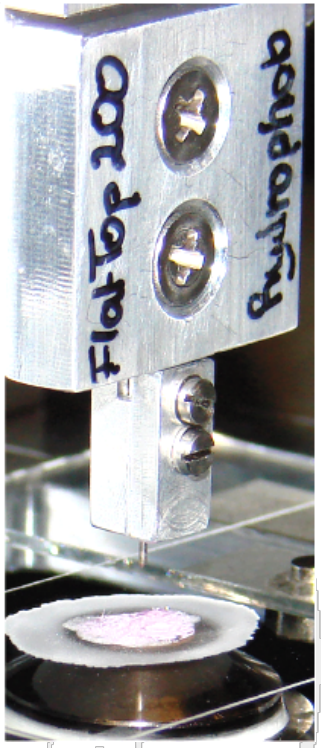


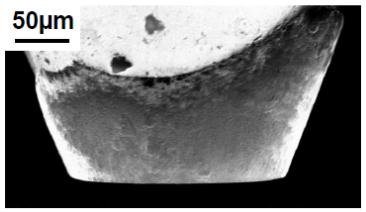
Nano-indentation

Displacement controlled

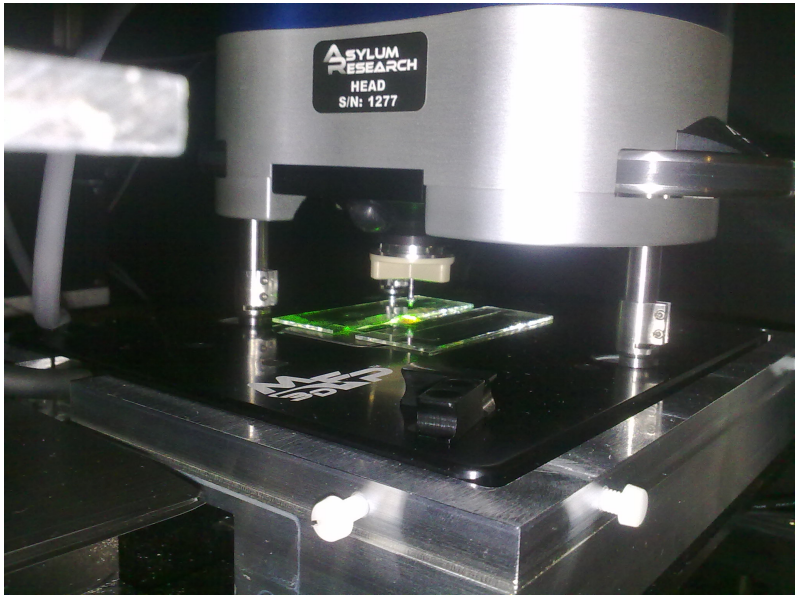








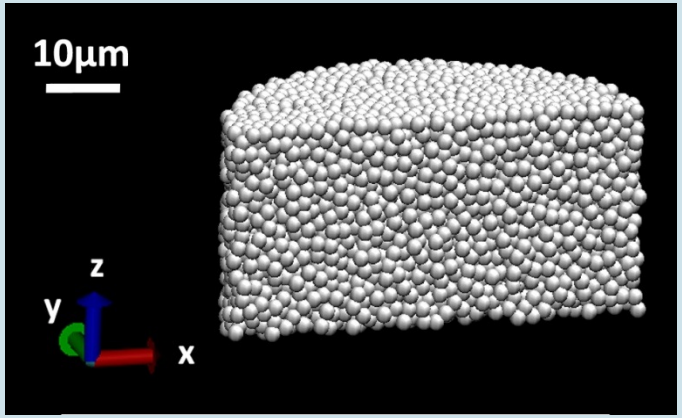
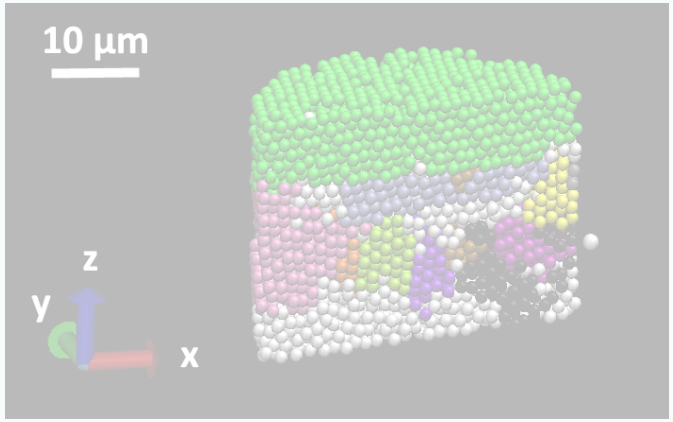
Force controlled



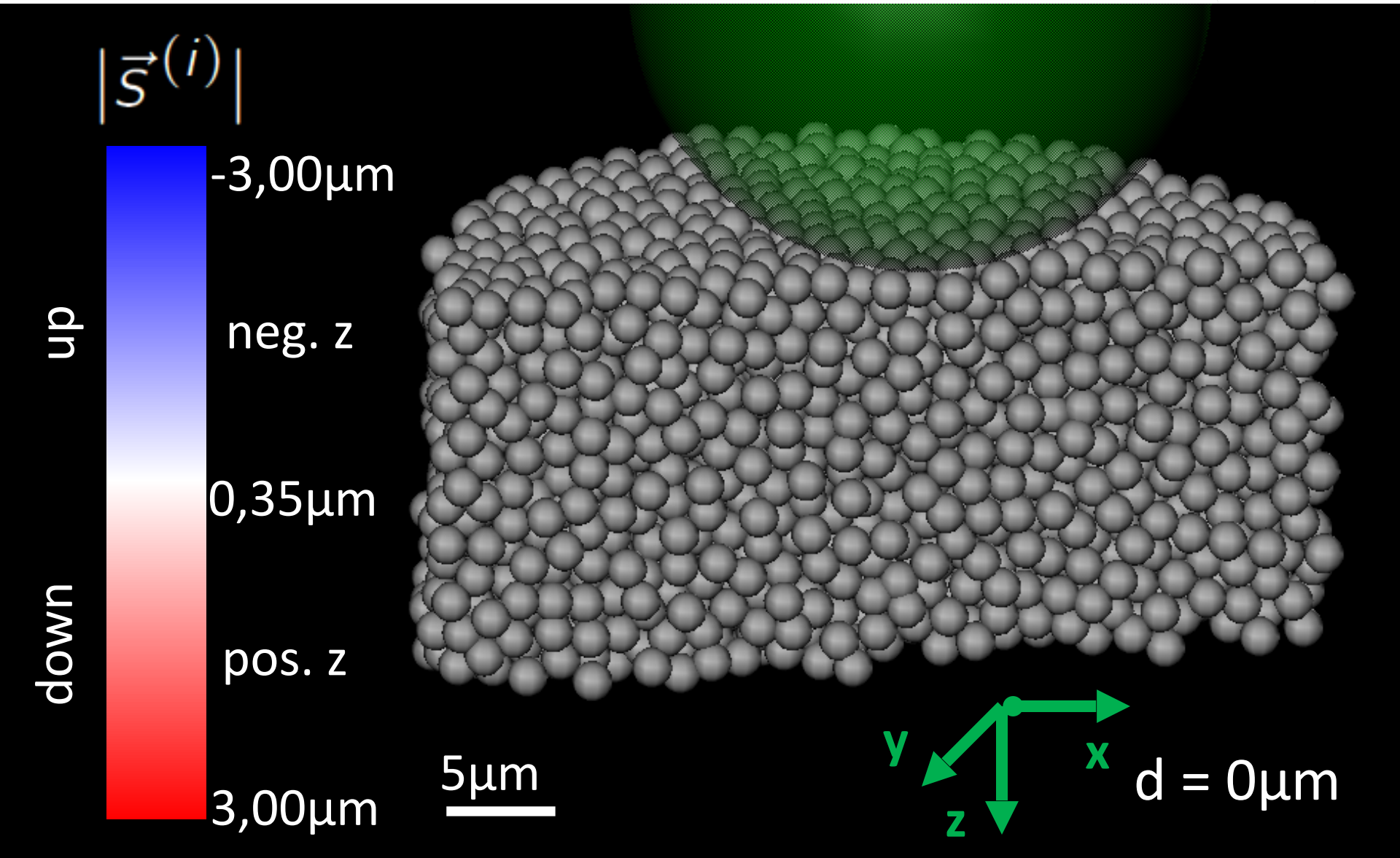
Displacement of the indenter:

- In x-direction (scretch)
- In z-direction (indentation)

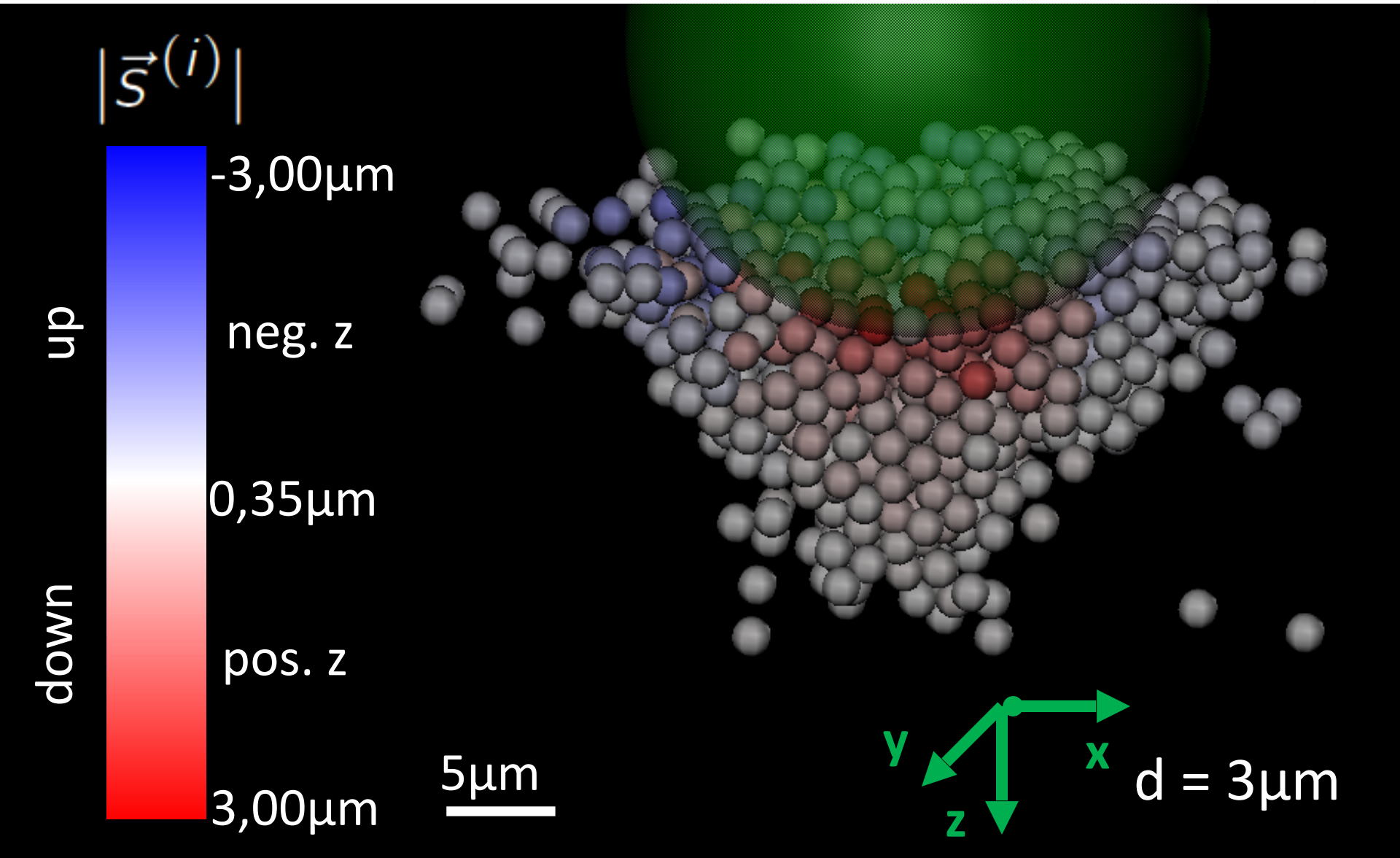
Samples

Process	Properties	Reconstruction
• PMMA (1.6 µm) • Fast drying from hexane @ 50°C • Slightly cohesive	• Amorphous • Random closed packing (63%) • Film thickness: 30µm	
		Auernhammer, Kwade et al. Eur. Phys. J. E (2012) ***35,*** *124;*
• PMMA (1.6 µm) • Slow drying from hexane @ RT • Slightly cohesive	• Crystalline (66%) • Crystalline closed packing (74%) • Film thickness: 30µm	
		Auernhammer, Kwade et al. Chem. Lett. ***41*** *(10), 1110-1112 (2012).*

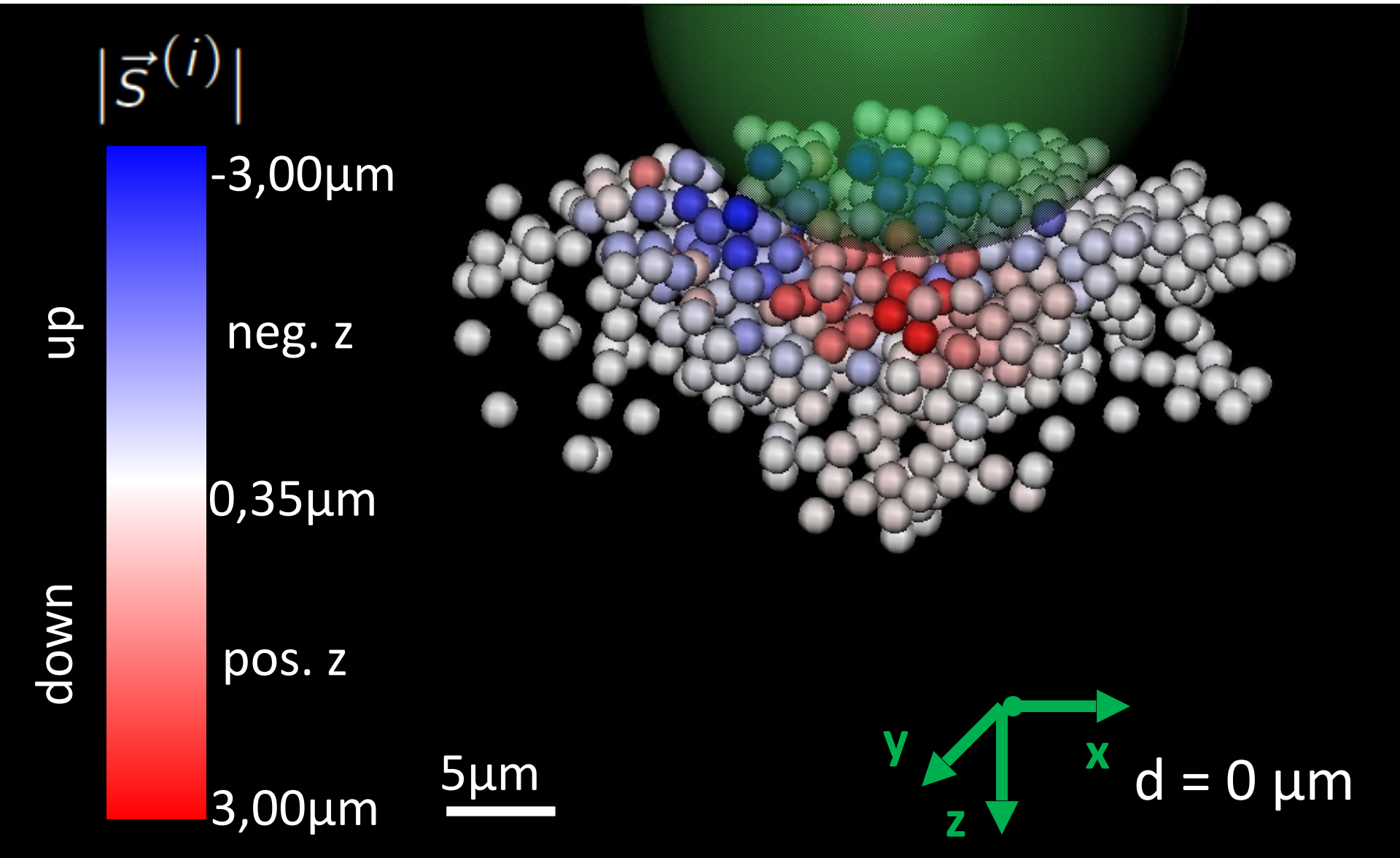
Imaging indentation



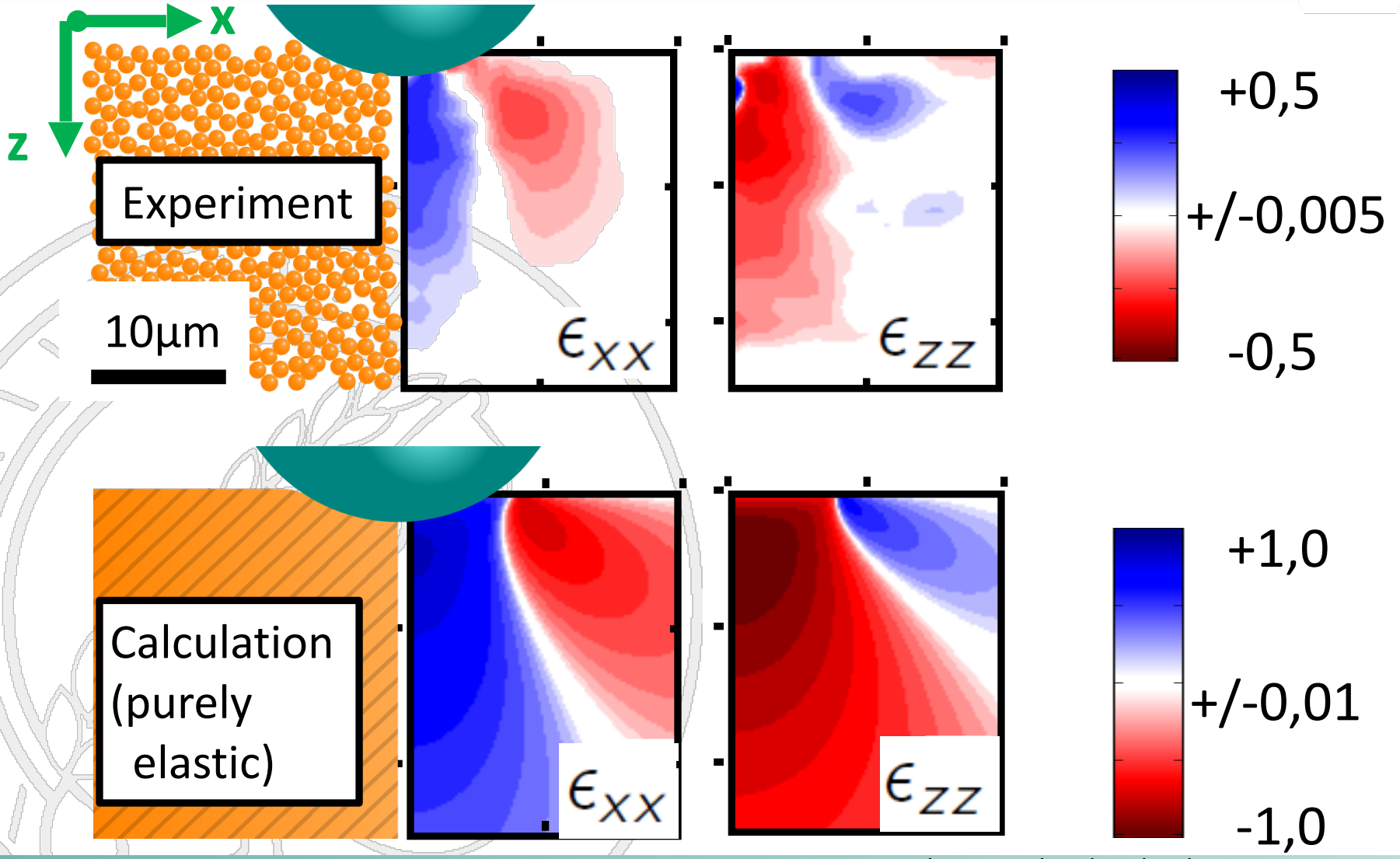
Imaging indentation



Imaging indentation



Comparison to continuum mechanics



Huber, Annalen der Physik, **2006**, *316*, 153-163

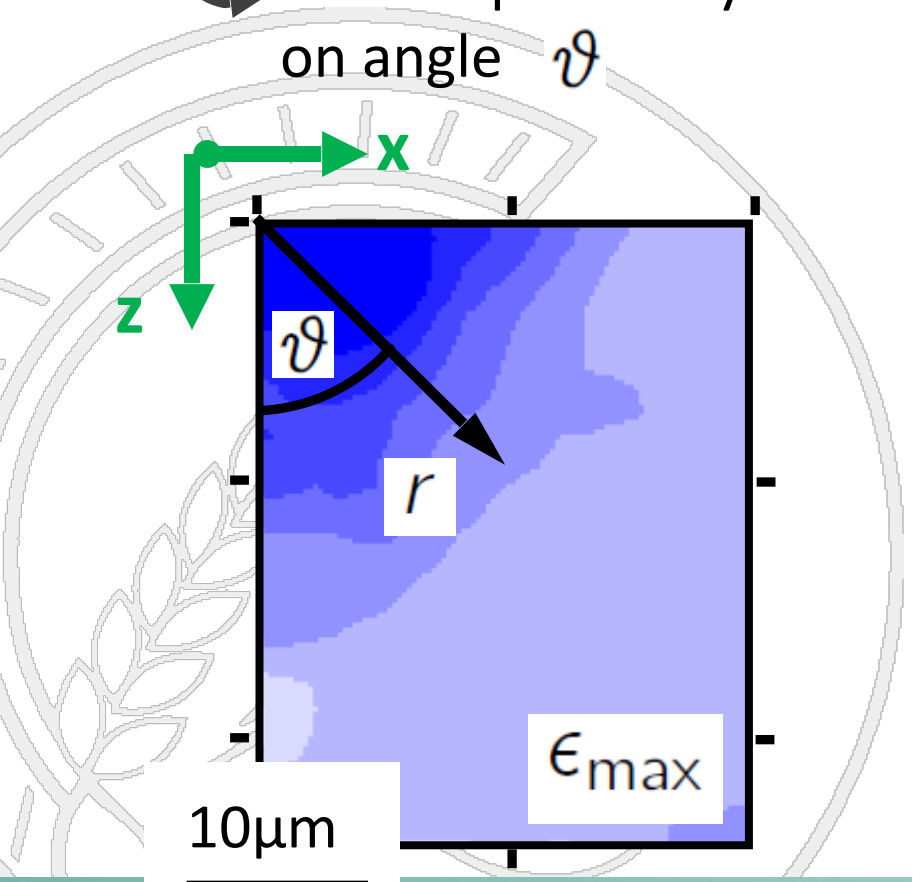
Comparison to continuum mechanics

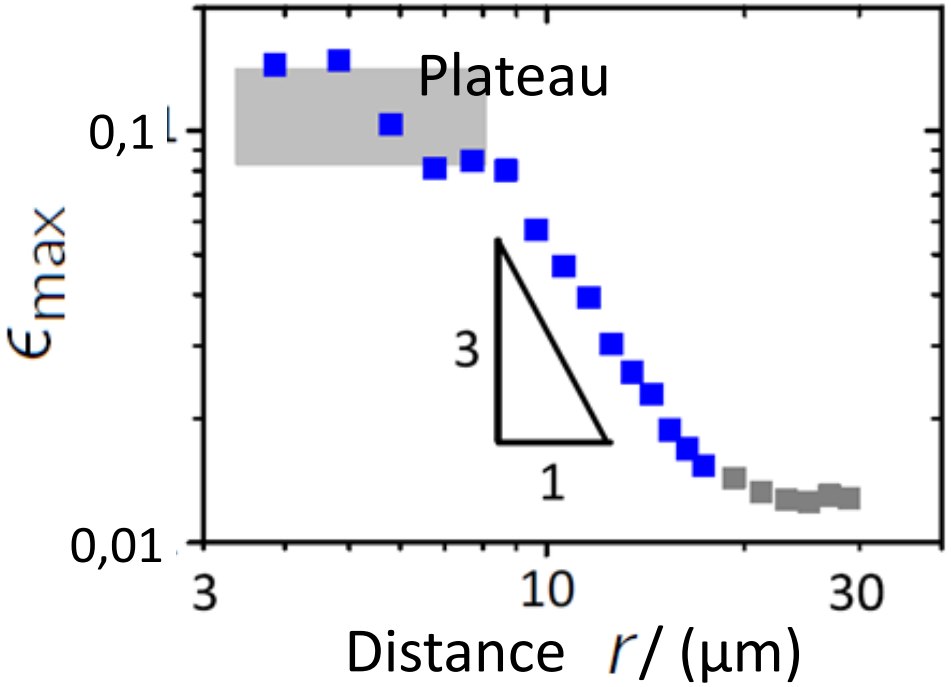
Plastic vs. elastic deformation

$$\epsilon_{max} = \sqrt{(\epsilon_{xx} - \epsilon_{zz})^2/4 + \epsilon_{xz}^2}$$

Little dependency on angle ϑ

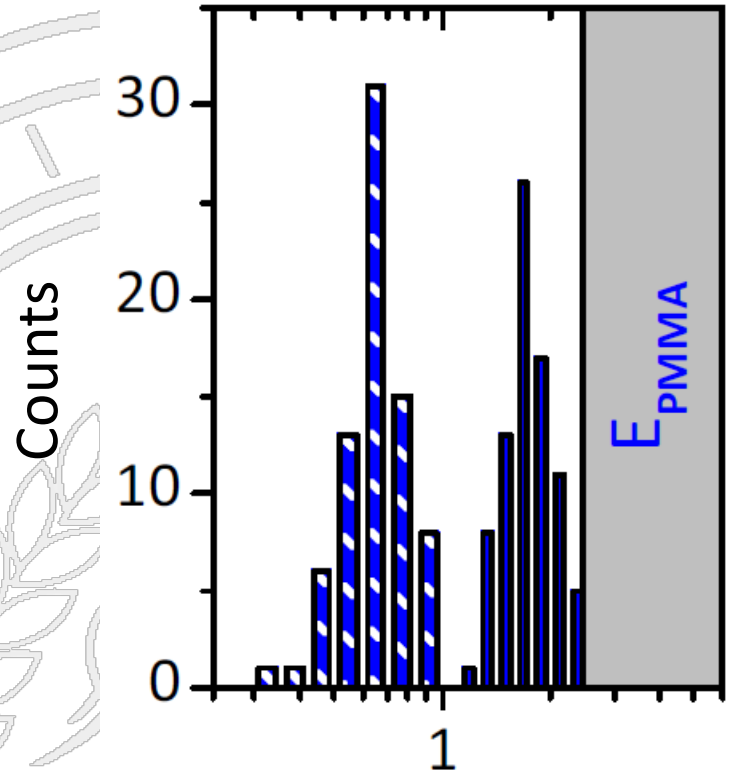
Elastic deformation for „large“ distances to indenter

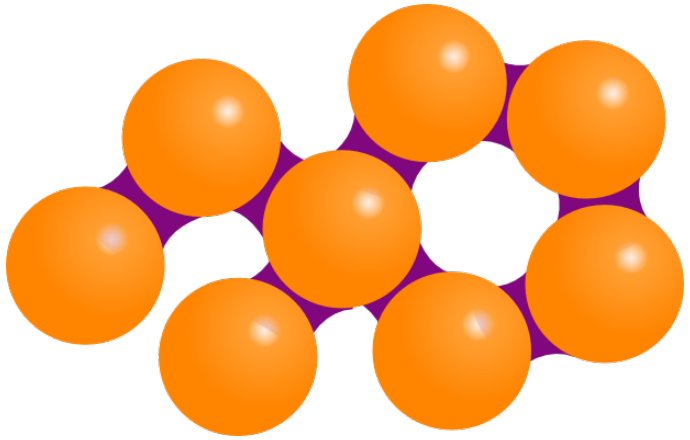




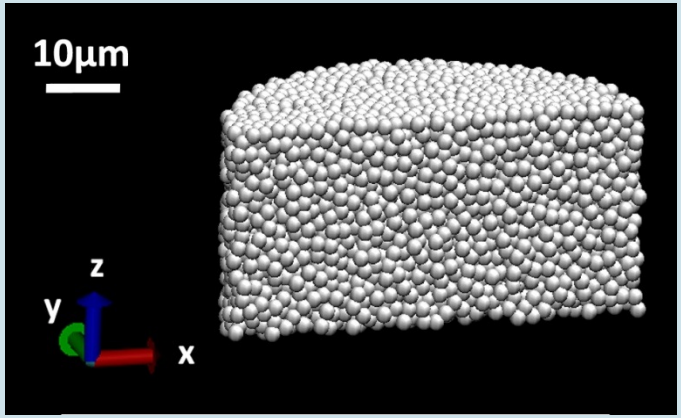
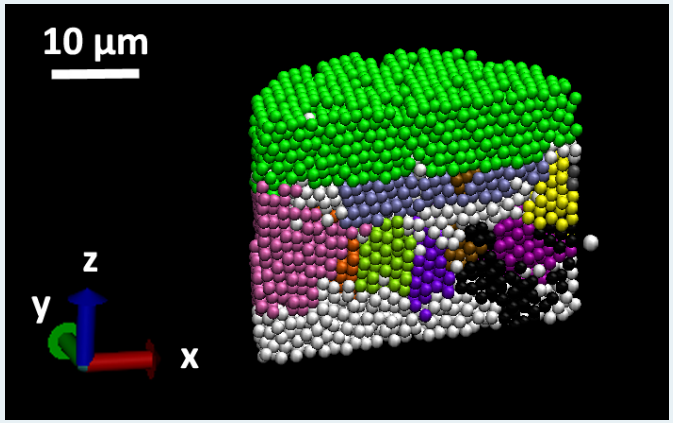
Effect of added polymer

Introducing solid bridges between polymer colloids

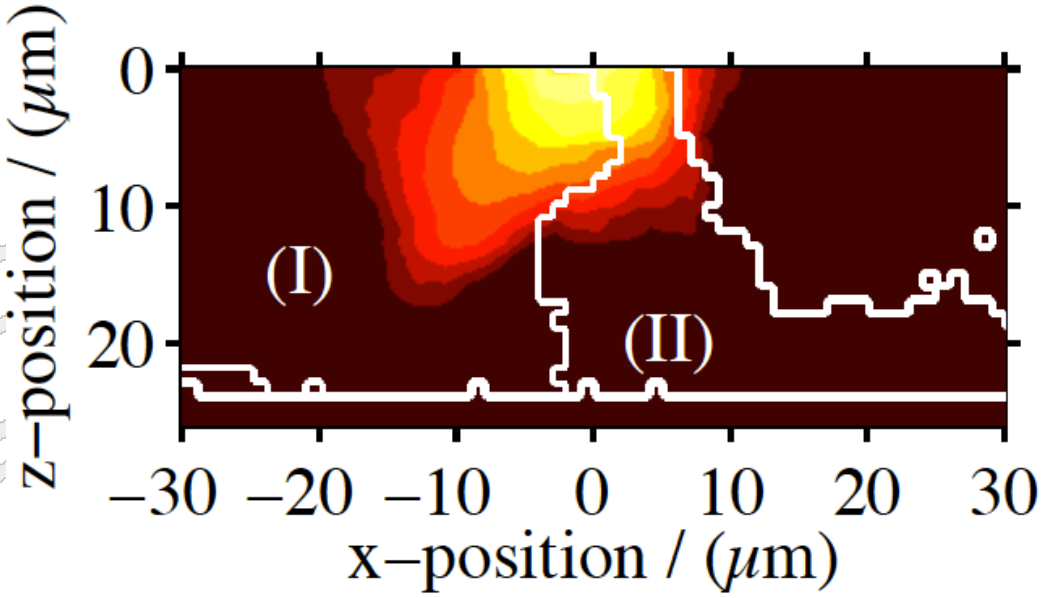




Samples

Process	Properties	Reconstruction
• *PMMA (1.6 µm)* • • *Fast drying from hexane @ 50°C* • • *Dominant effect: Hydrodynamics*	• *Amorphous* • • *Random closed packing (63%)* • • *Film thickness: 30µm*	 *Auernhammer, Kwade et al. Eur. Phys. J. E (2012)* ***35,*** *124;*
• *PMMA (1.6 µm)* • • *Slow drying from hexane @ RT* • • *Dominant effect: Sedimentation*	• *Crystalline (66%)* • • *Crystalline closed packing (74%)* • • *Film thickness: 30µm*	 *Auernhammer, Kwade et al. Chem. Lett.* ***41*** *(10), 1110-1112 (2012).*

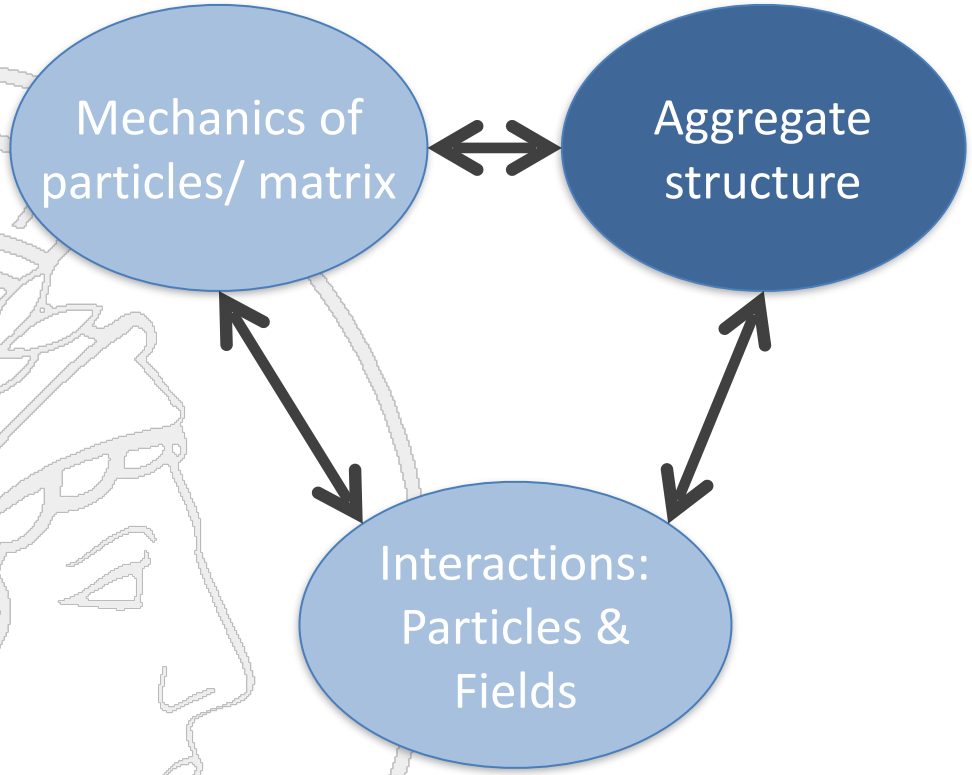
Effect of crystallinity



- Deformation longer ranged in crystalline region (I)
- Stronger reorganization (plastic deformation) in amorphous region (II)
- Largest microscopic structure is crystallite size

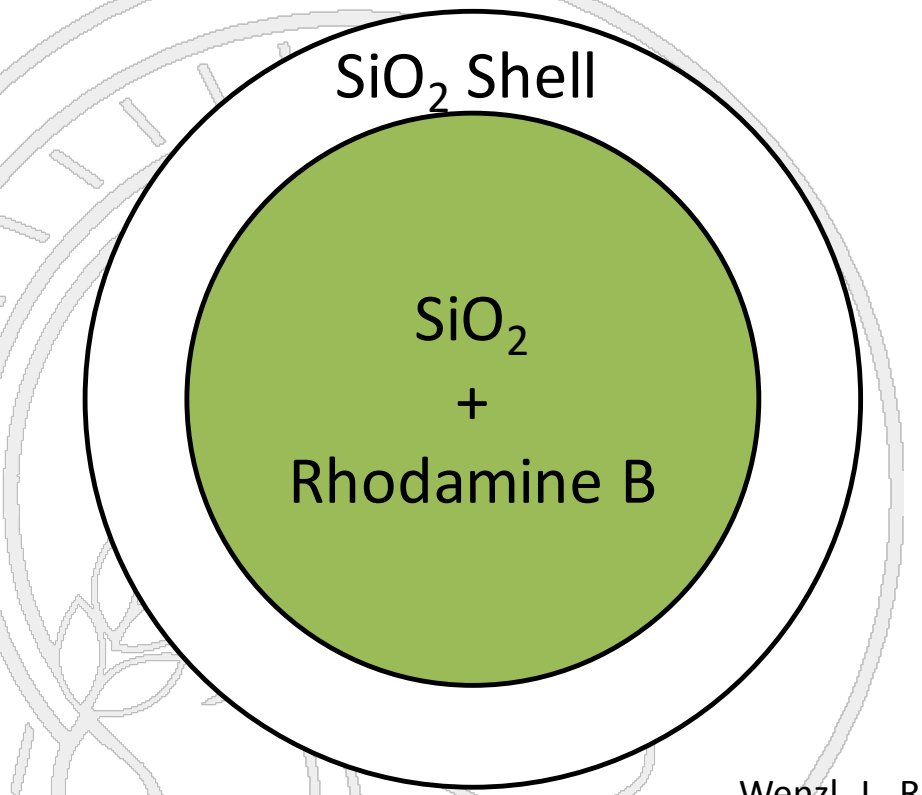
→ Particle systems as model for amorphous/semi-crystalline solids → Additives may dominate behavior

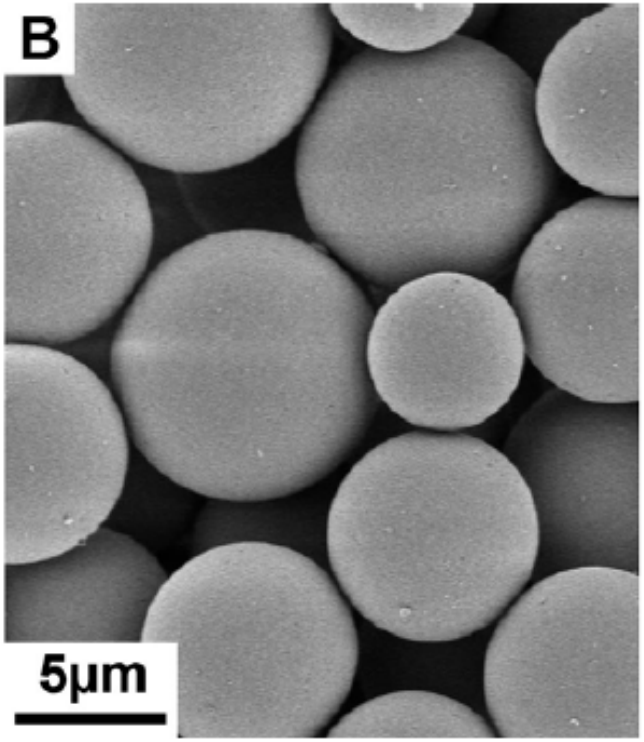
Shearing model sand



Model granular particles

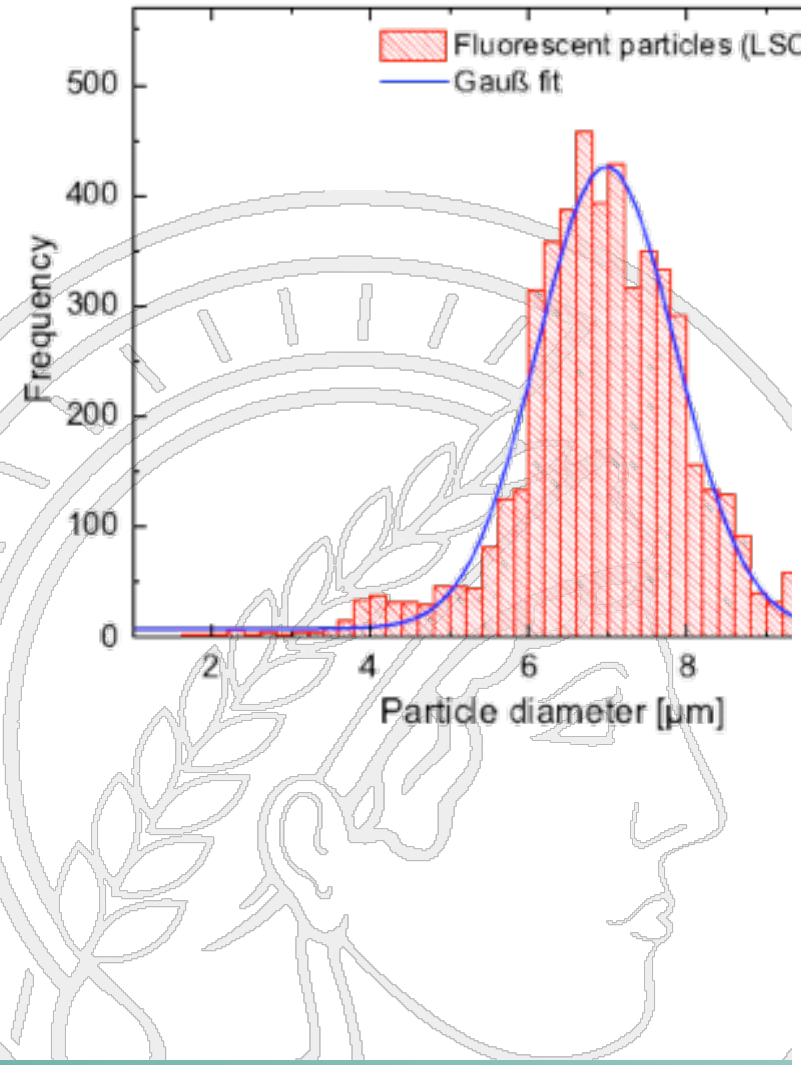
- 7 µm spherical silica particles
- Core-shell particles

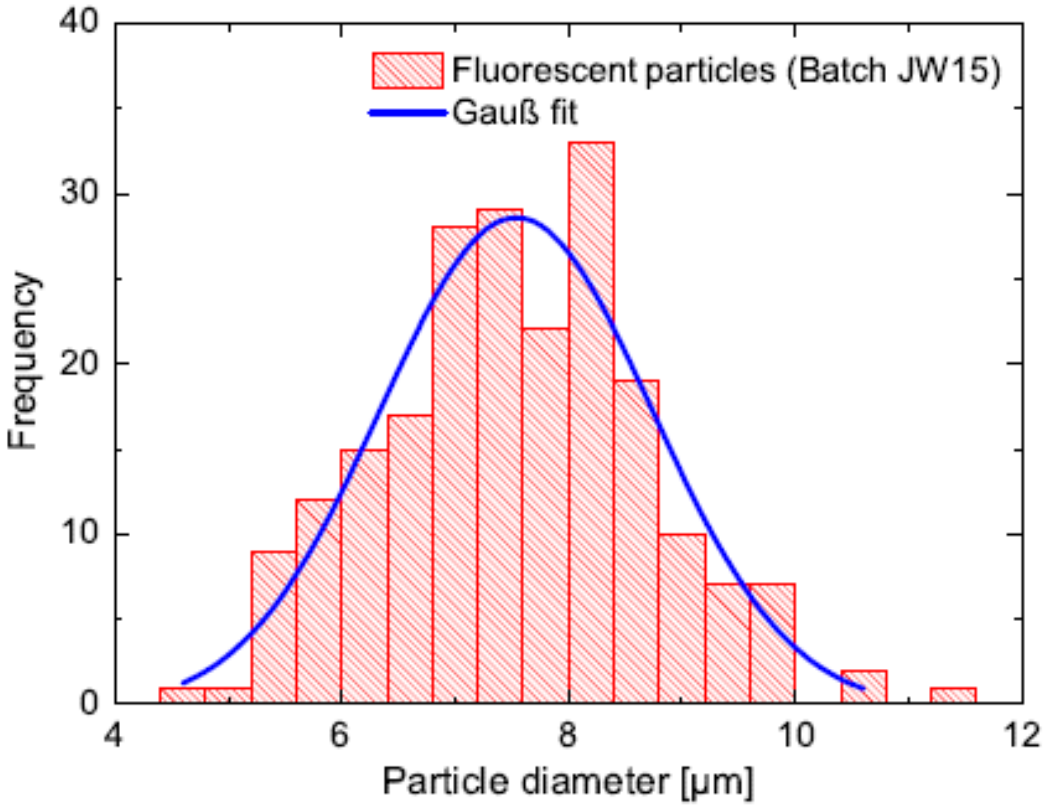




Wenzl, J., R. Seto, M. Roth, H.-J. Butt and G. Auernhammer (2013). Granular Matter **15**: 391-400.

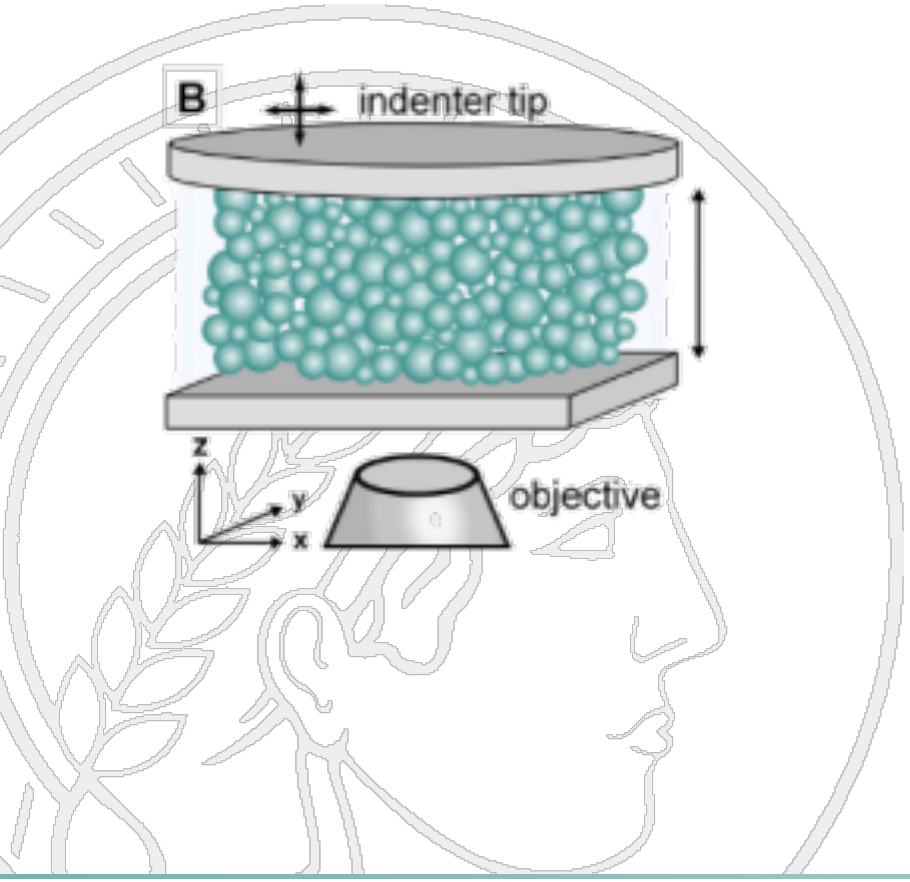
Polydisperse silica spheres

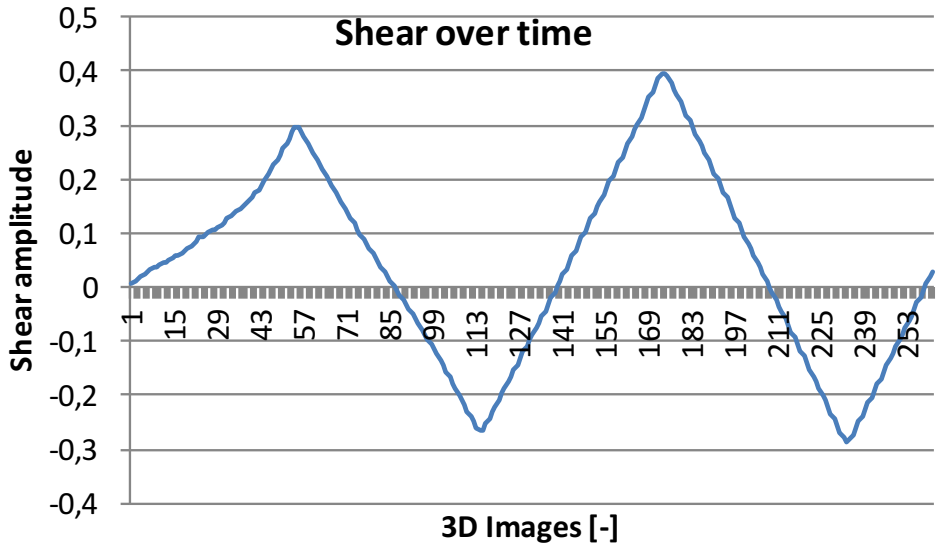




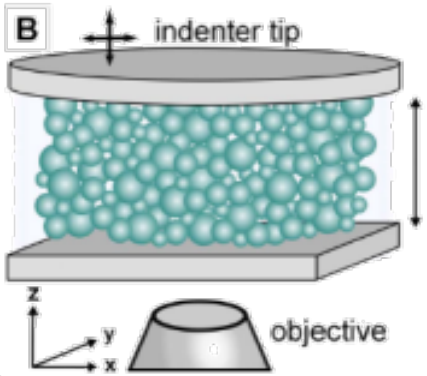
Wet and dry model granulates under mechanical load – a confocal mocroscopy study, Phd thesis 2013, JGU Mainz, Jennifer Wenzl

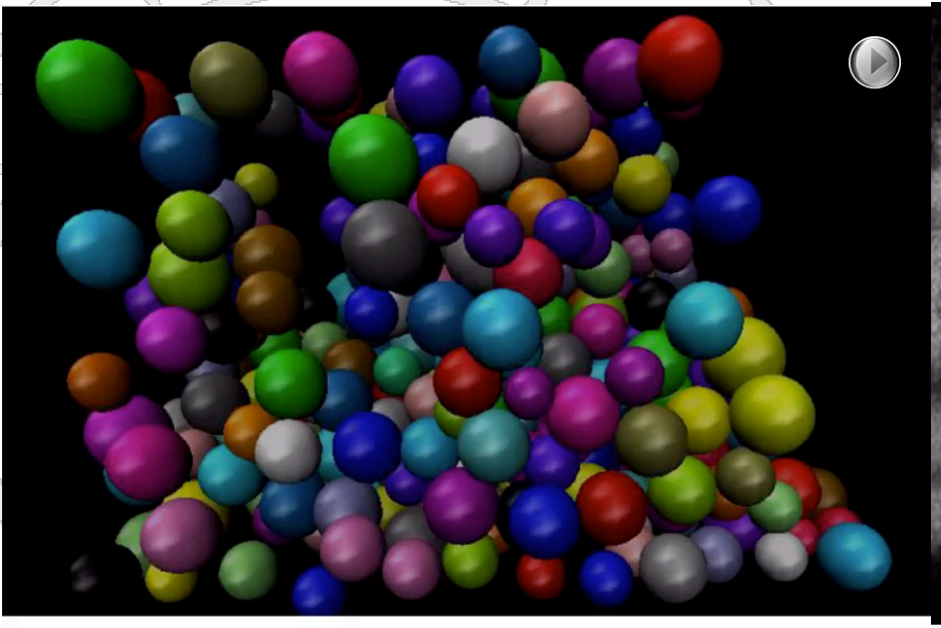
Typical shear experiment

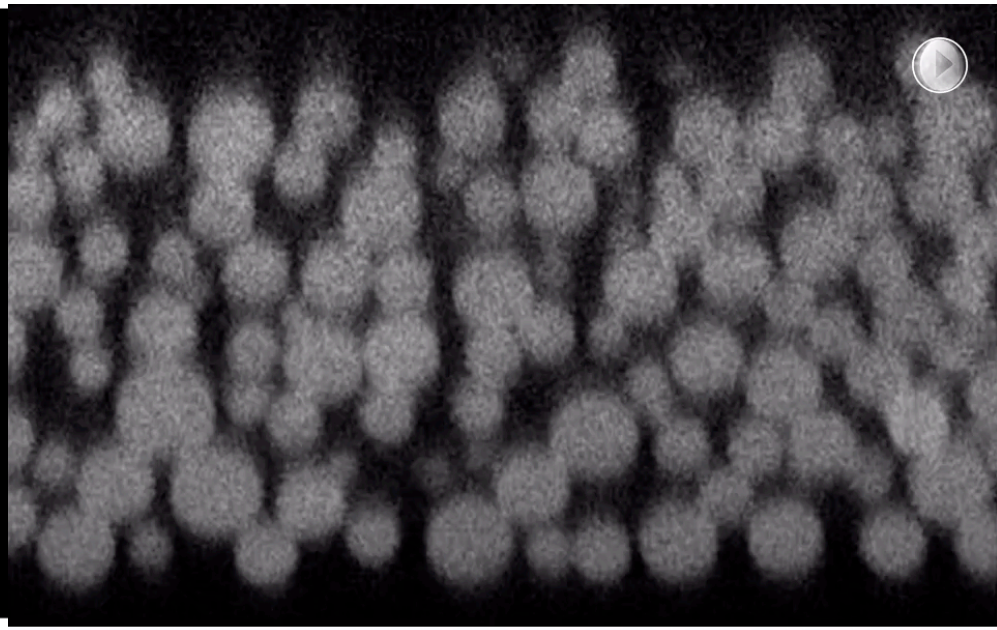




Trajectories of all particles

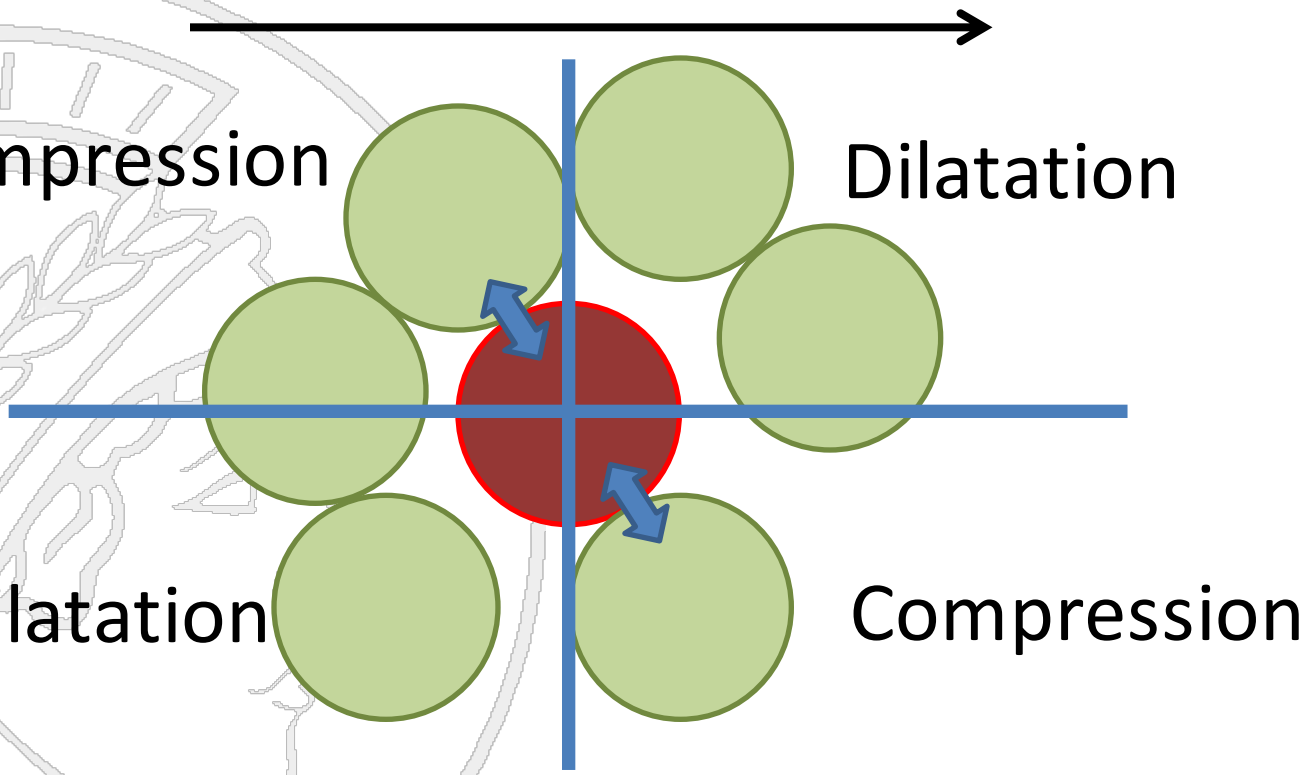




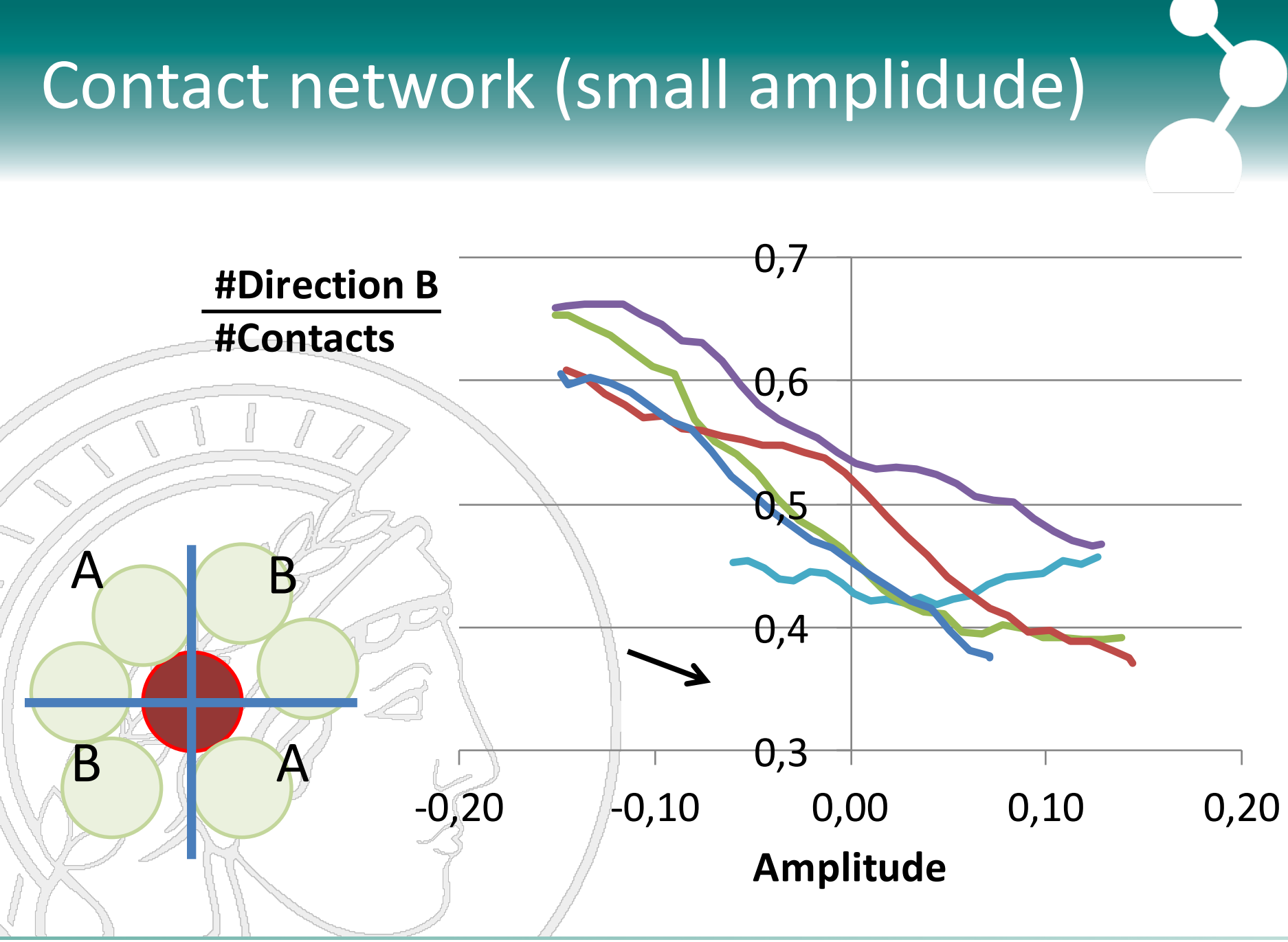


Contact network

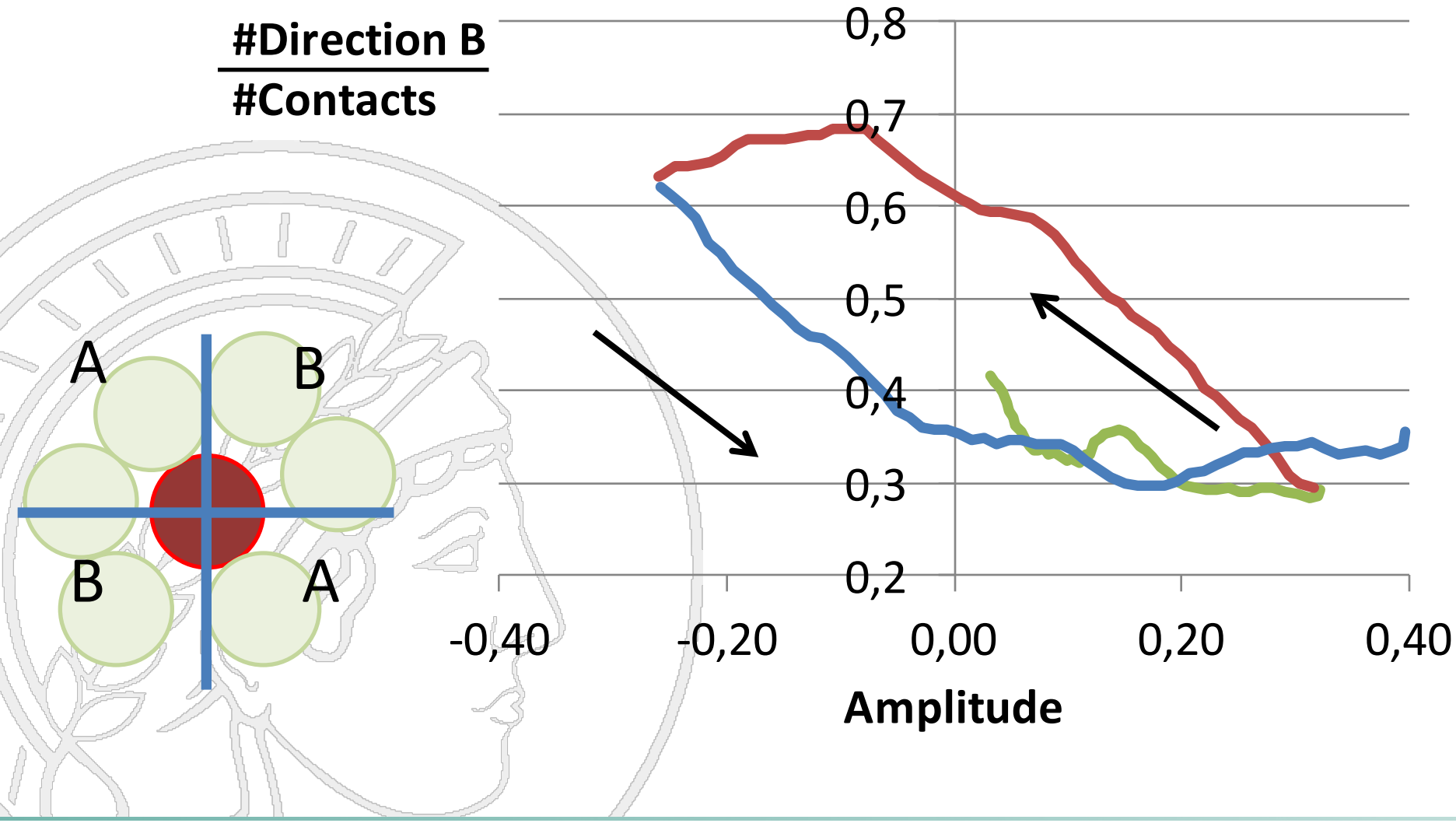
- Anisotropic contact network
- Force chain network



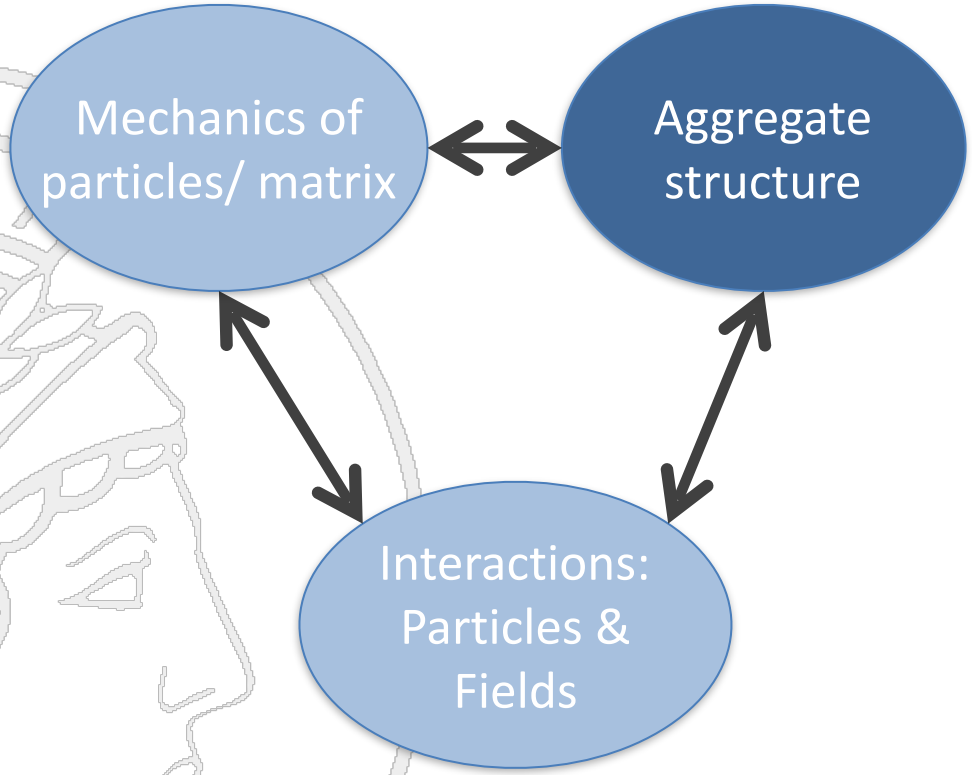
Contact network (small amplidude)



Contact network (large amplidude)

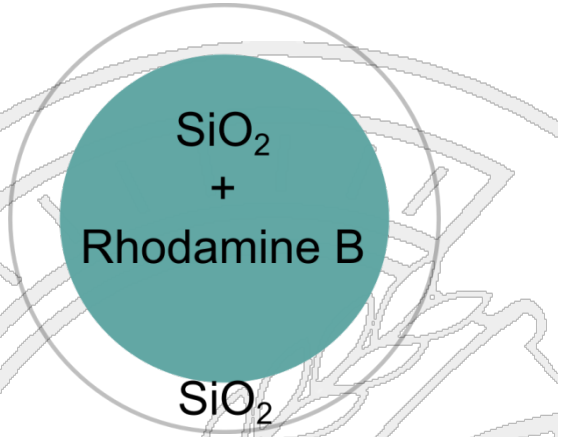


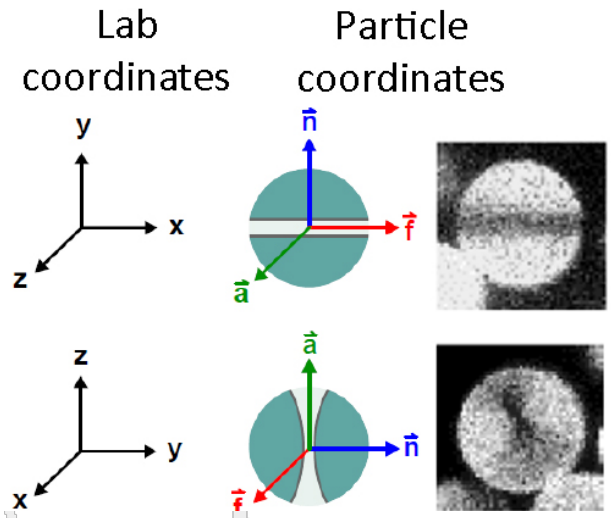
Orientation of spheres

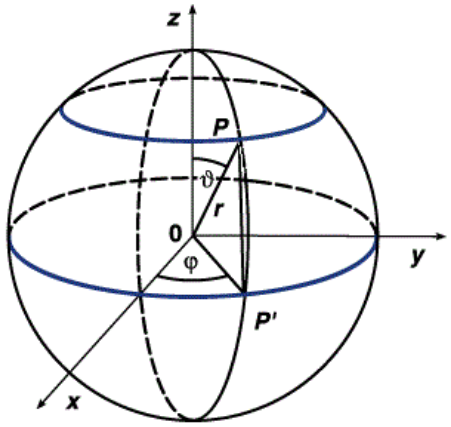


Particle rotation

Optically anisotropic particles: Photobleaching of internal structure







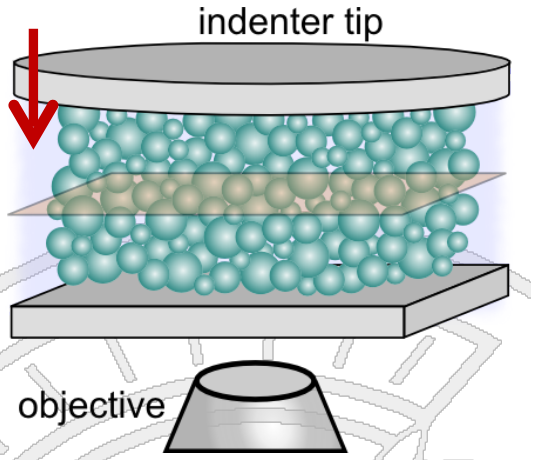
- Core-shell particles: Isotropic interaction
- Bleaching generates plane in particle
- Particle coordinate system
- Rotates in lab system

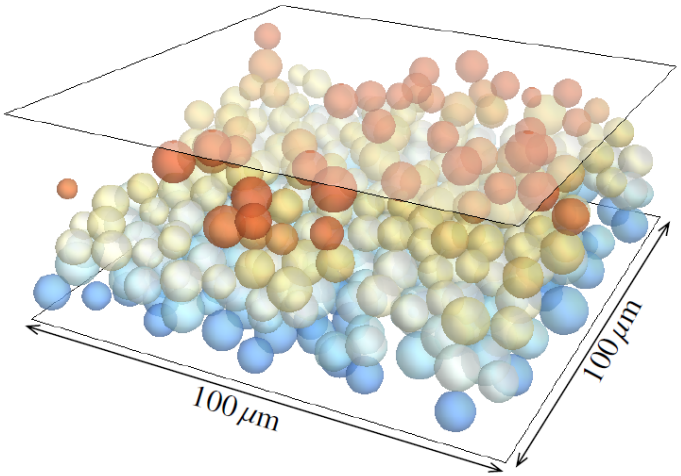
Set of 3 independant angles, describes particle orientation in 3D

Wenzl, et al., Granul Matt **(2012)** DOI 10.1007/s10035-012-0383-7

Roth, et al., Arxiv cond-mat.soft **(2011)** 1106.3623v2

Compression measurement



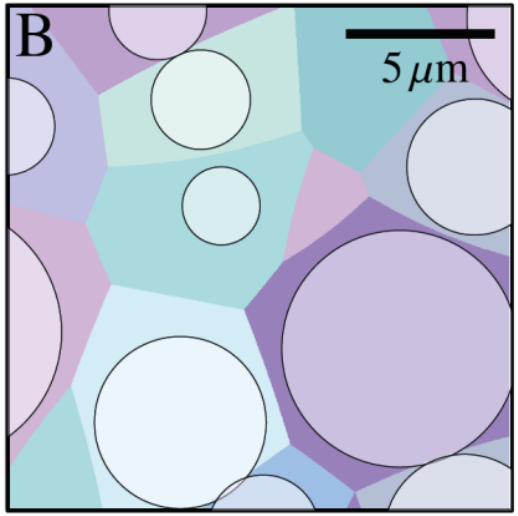


Starting configuration:

- sedimented bed
- Volume fraction ϕ~45%
- 8 compression steps

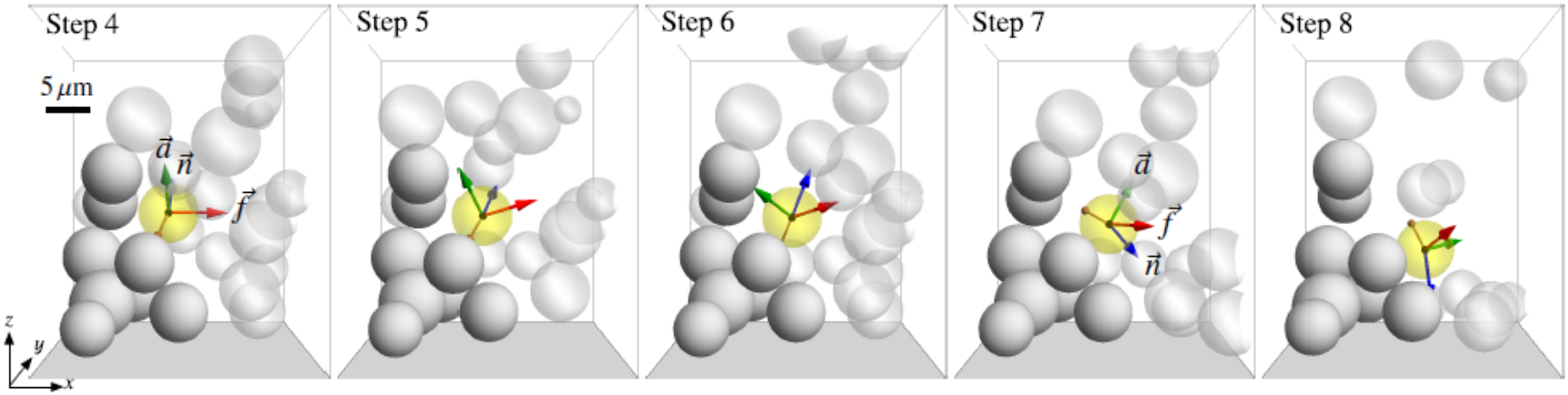
For each compression step:

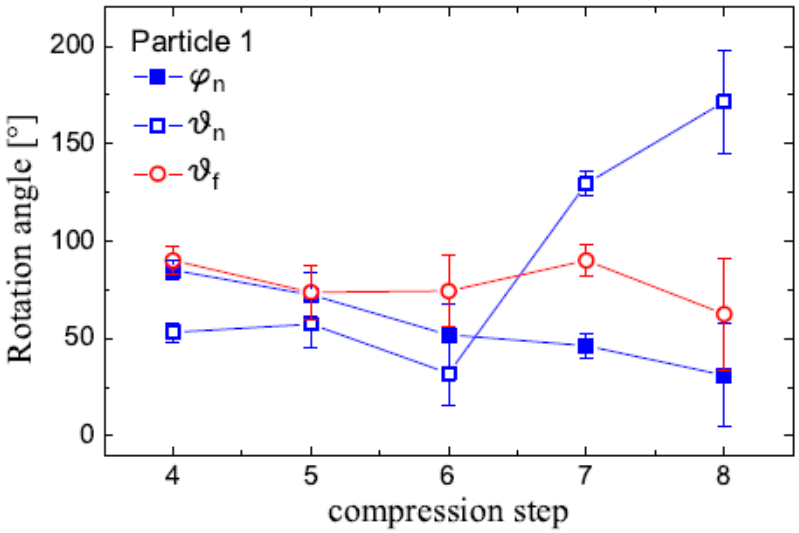
- Position (coordinates) of particles
- Voronoi cell volume
- Trajectories of anisotropic particles



Wenzl, et al., Granul Matt **(2012)** DOI 10.1007/s10035-012-0383-7

3D reconstruction



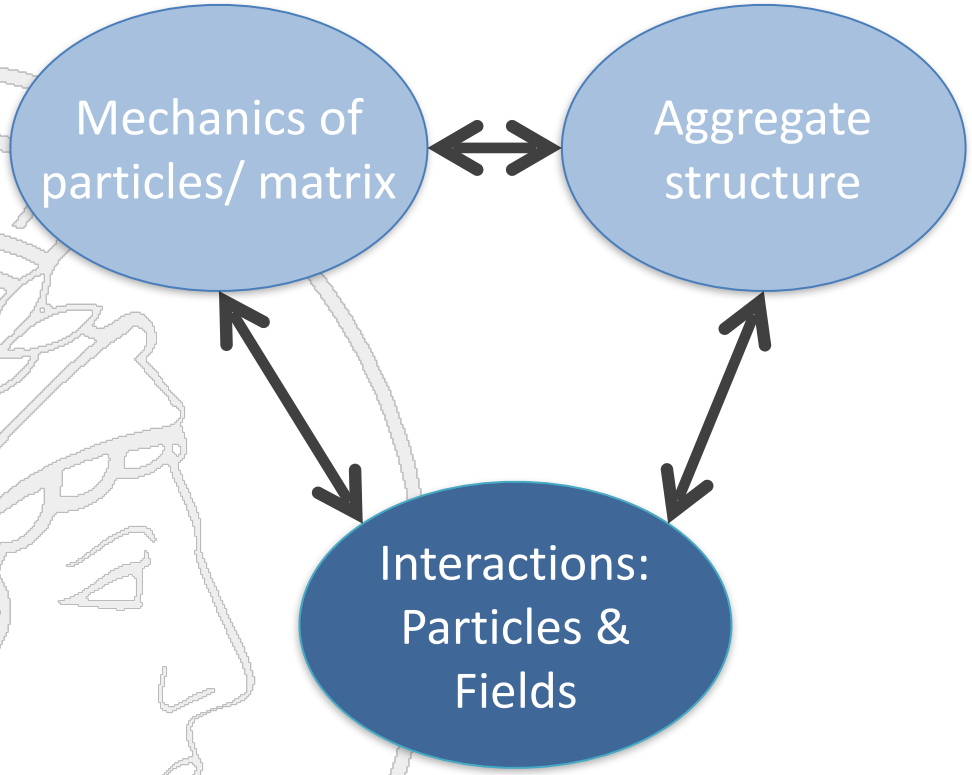


- Step 4 - 6: Only rotation
- Step 6/7: Bond breaking
- Step 7 & 8: Additional sliding motion

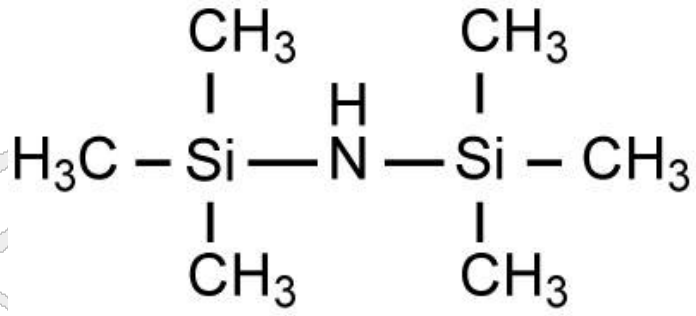
Full description needs
translation and rotation

Now: Automatic orientation detection

Attractive colloids

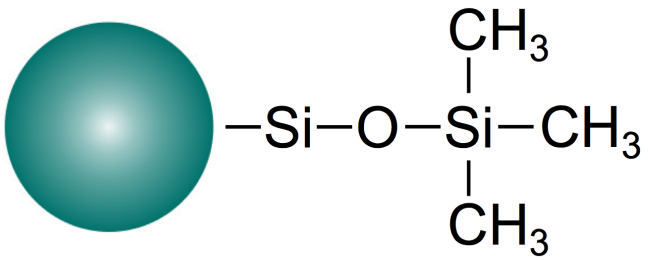


Hydrophobization of silica



HDMS

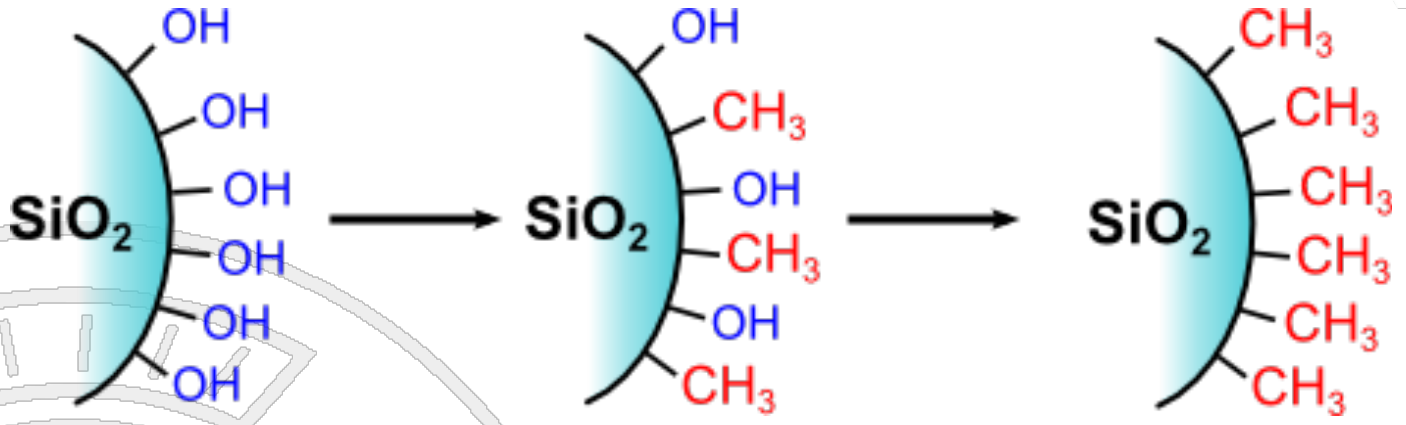
Hexamethyldisilazane



- Slow binding

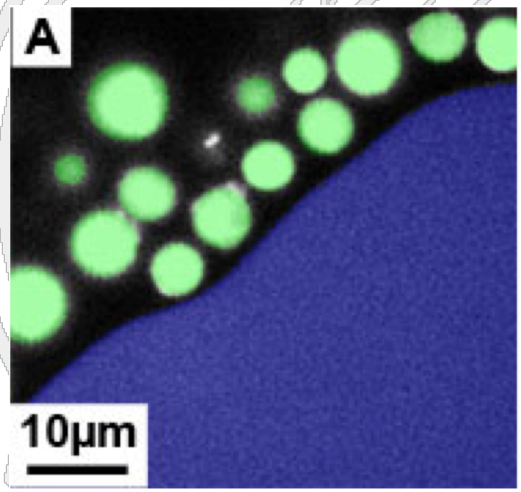
Hair, M. L. and W. Hertl (1971). J. Phys. Chem. **75**(14): 2181-2185.

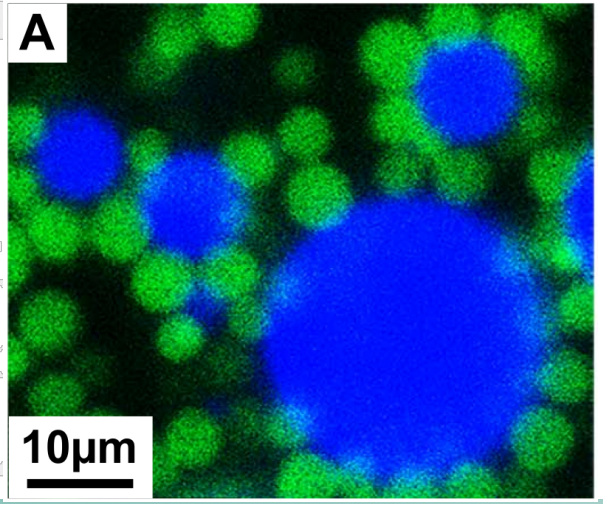
Wet model granulates

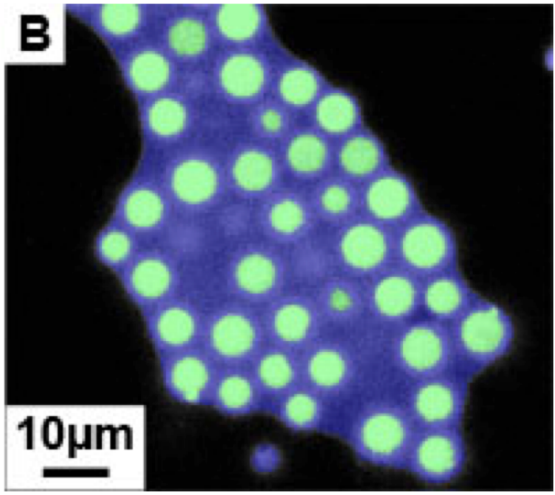


Phase separation

Phase separation

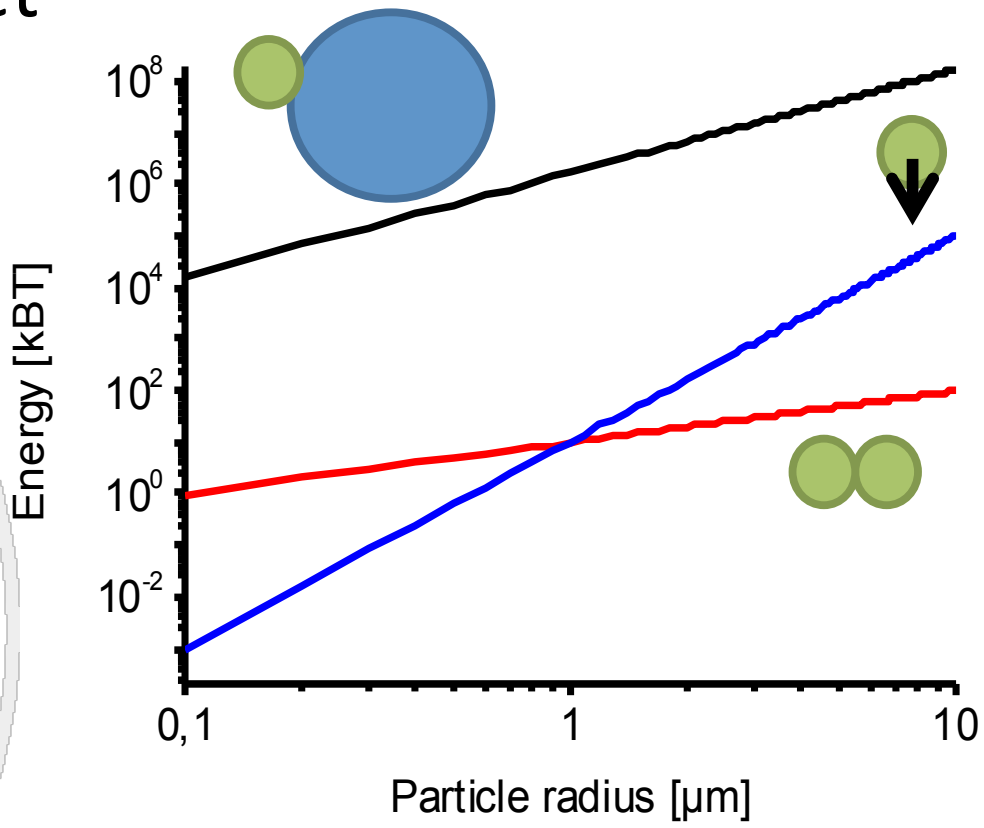






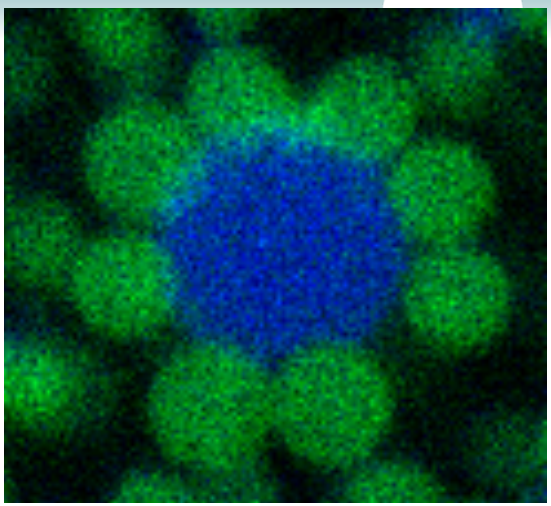
Energy scales

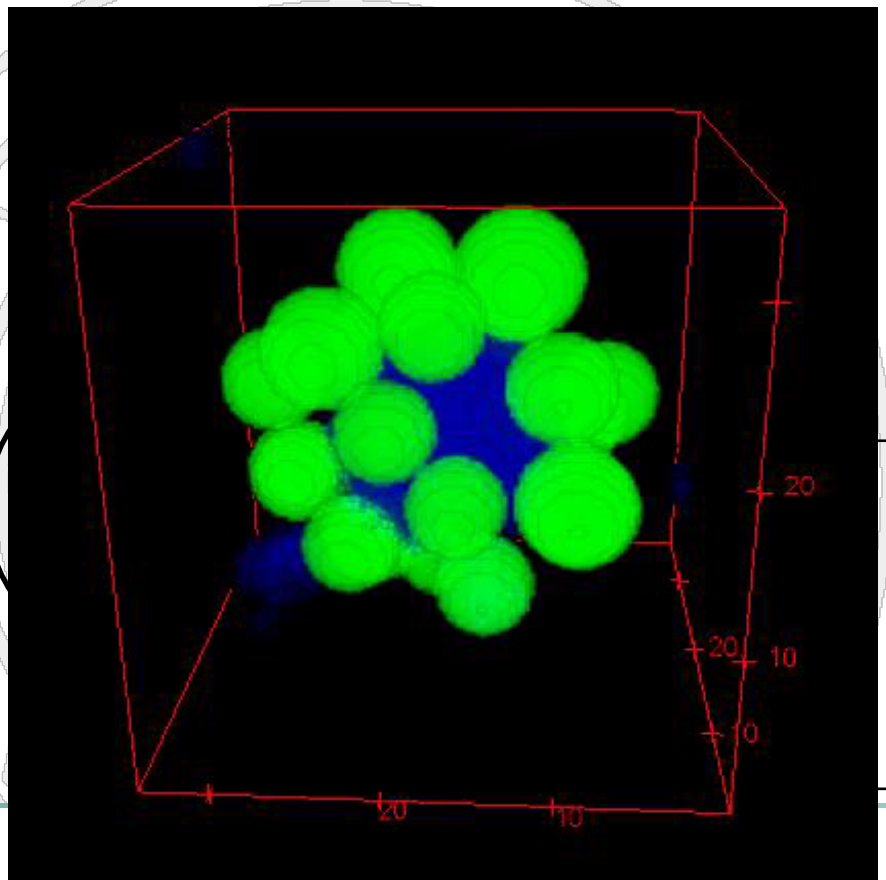
- Model system for wet granular matter
- Single particle resolution
- Binding force dominant
- Droplet – particles ensembles



Drop sizing and deformation

- Particle fixed to interface
- Drop position and diameter





$r_{D,i}$

$r_{p,i}$: Radius particle i

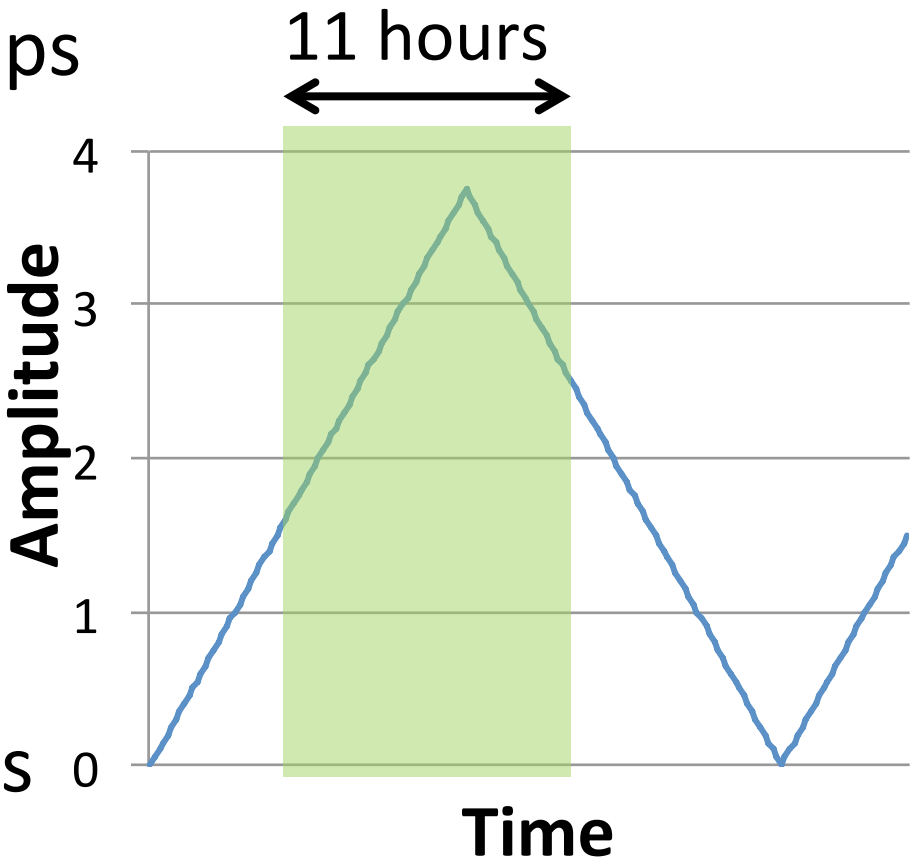
$r_{D,i}$: Radius drop i

$sub_{p,i}$: submerged part i

Minimise StdDev($r_{D,i}$)

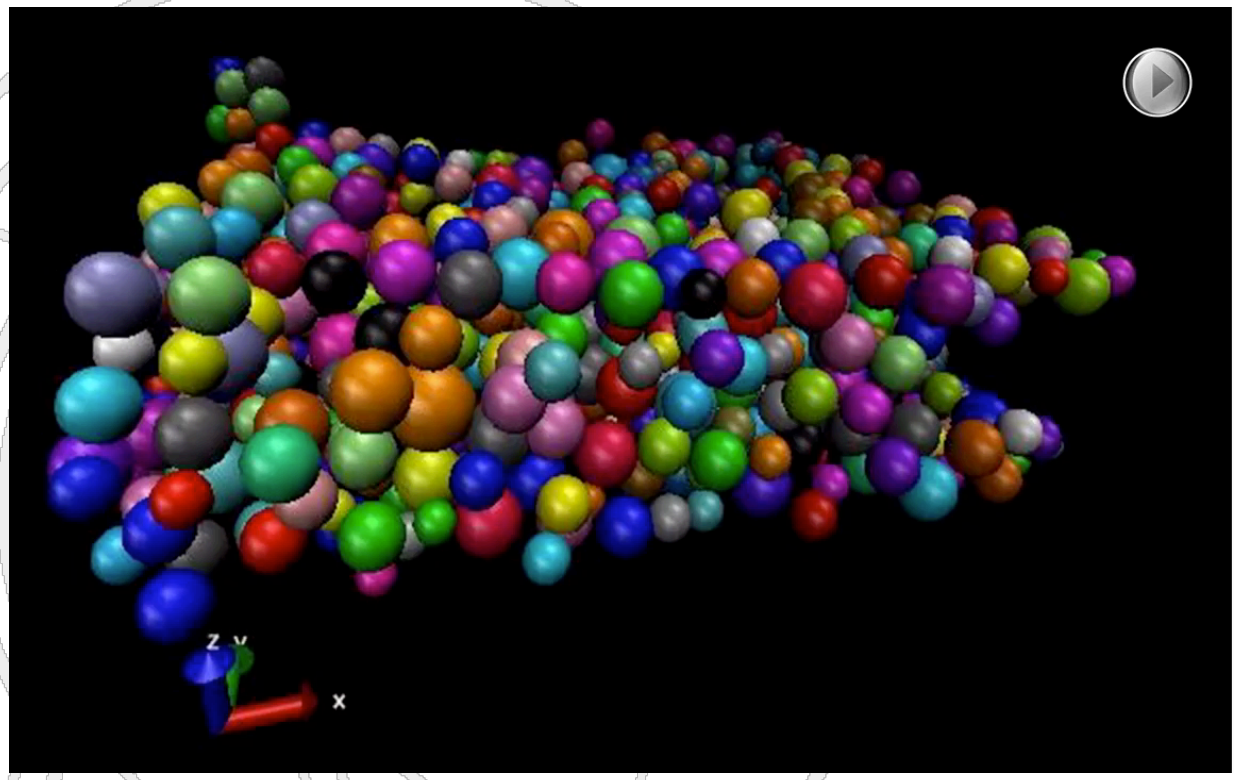
Long shear experiment

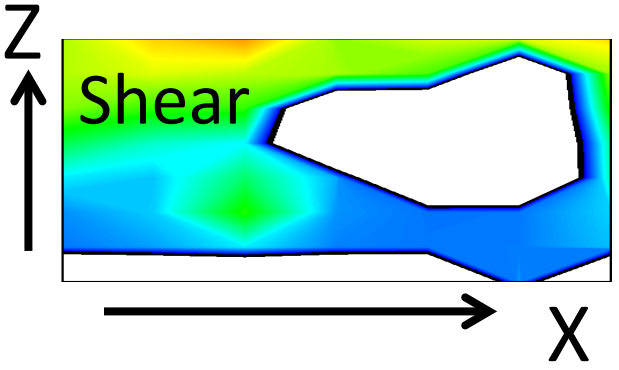
- 150x150x50µm volume
  ~1400 particles, 87 drops
- Oscillatory shear
- 3.75 shear amplitude
- Observed:
  1.75 – max – 2.5
- 320 3D images
- Position, size and tracks

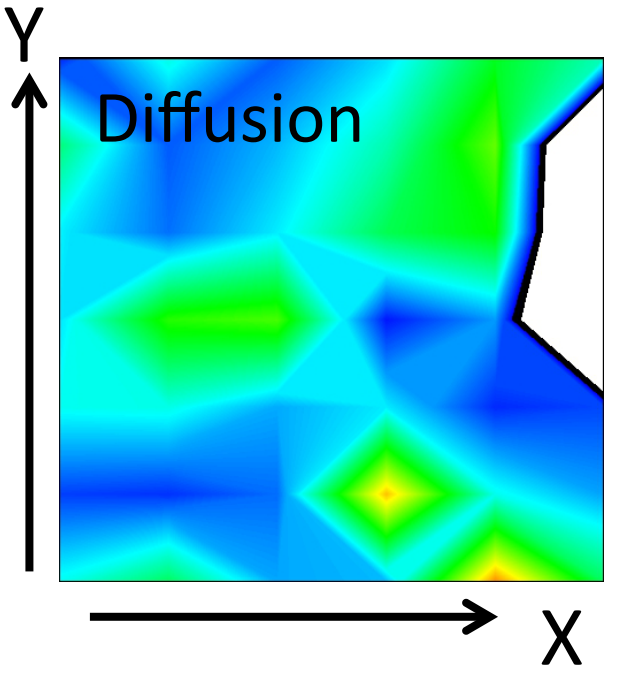


Results

- Temporal and spatial resolved movement in 3D

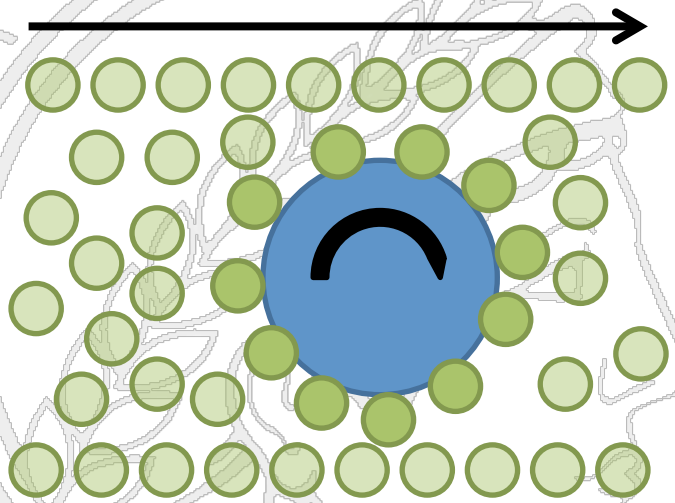


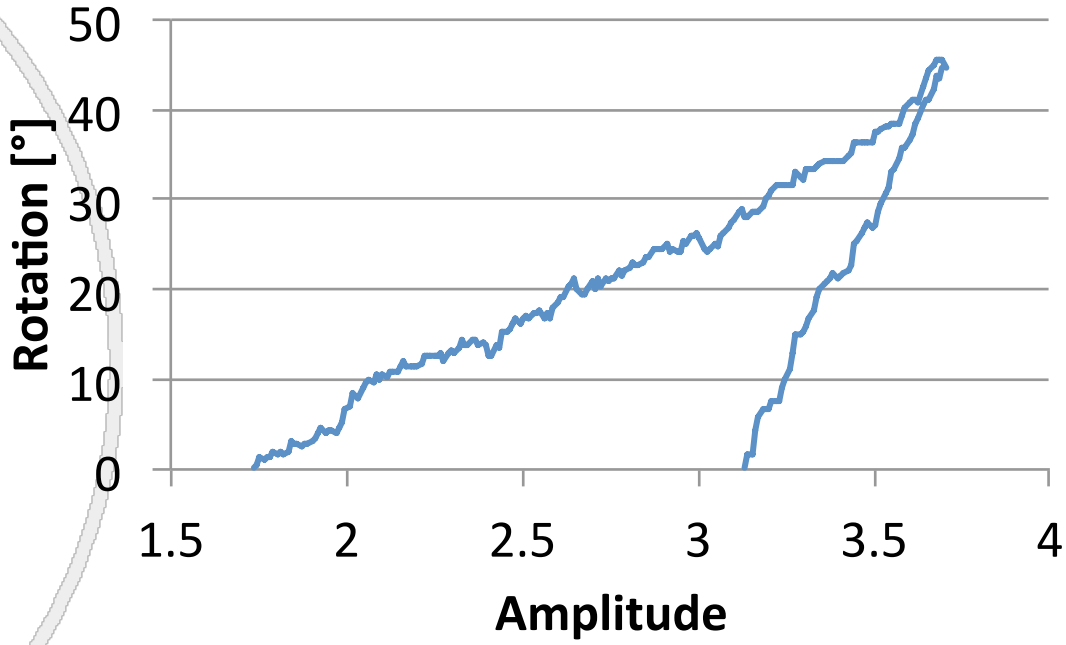




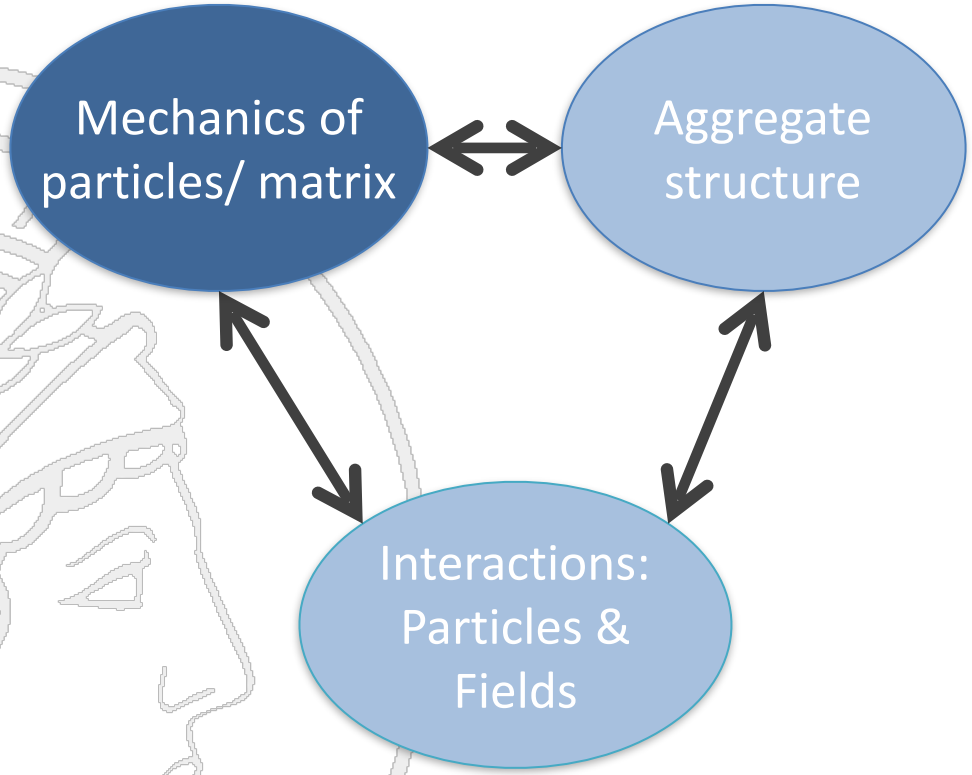
Rotation of drops

- Particles trapped at surface
- Droplet with particles forms one entity
- Energy stored in droplet

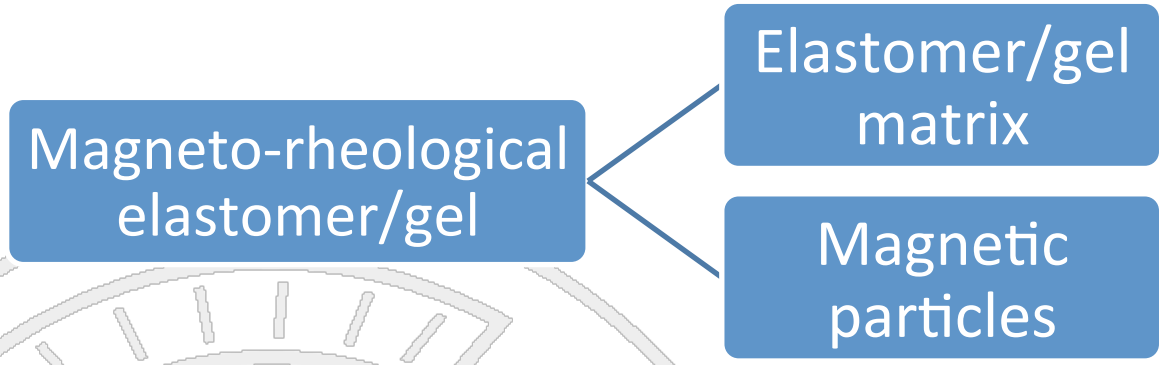




Magnetic fields



Magnetic gels



Damper
Actuator
…

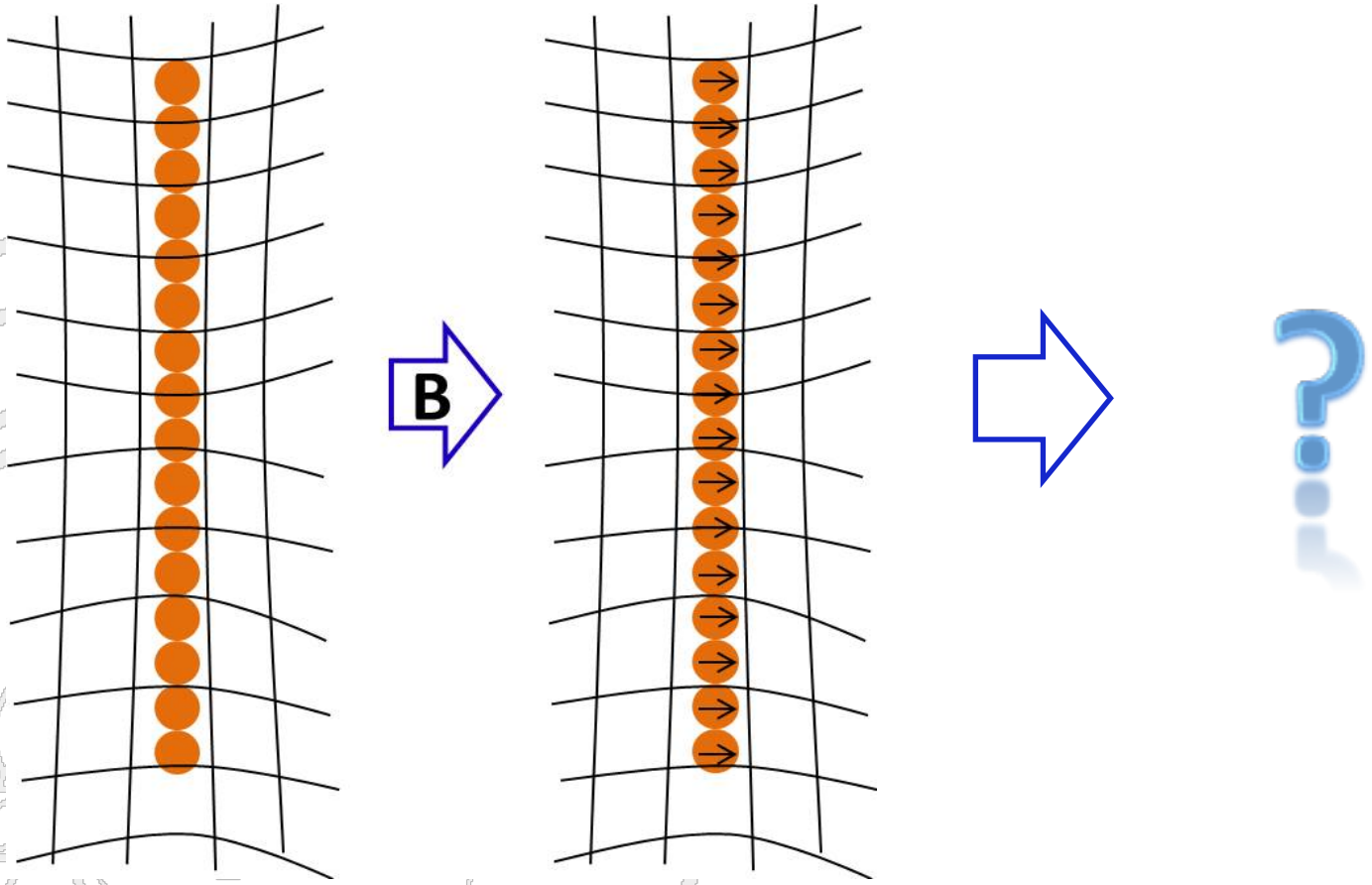
Magneto-elastic coupling:

- Magnetic interaction of magnetic particles → Particle distribution
- Elasticity of matrix → Deformation field of matrix

Aim:

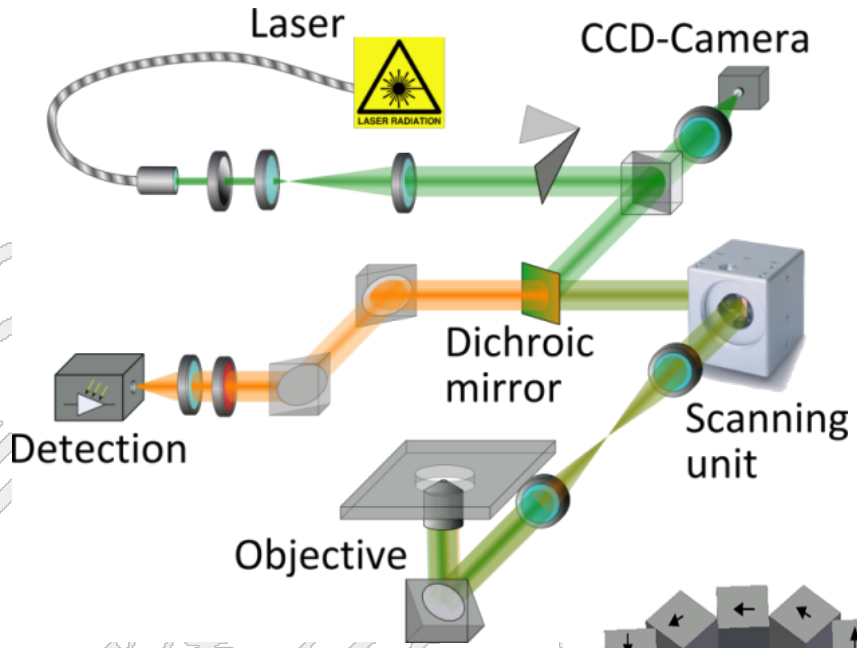
- understand magneto-elastic coupling at ***microscopic level***

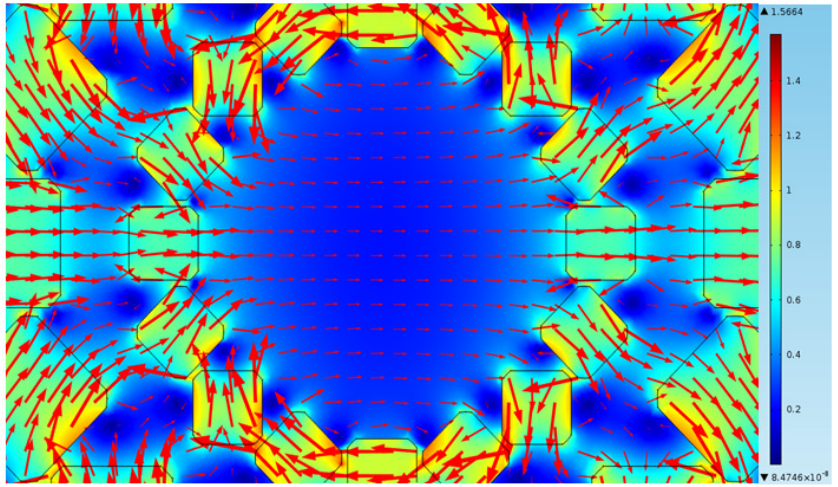
Basic question

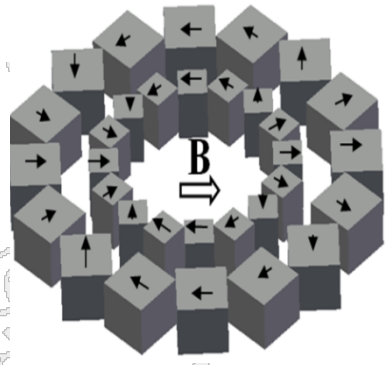


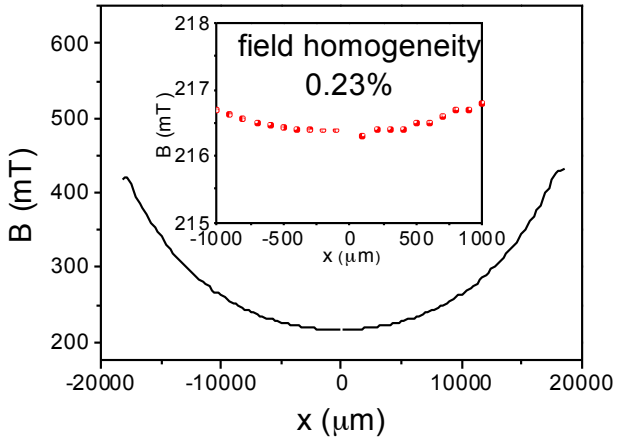
Single chain behavior

Magnetic fields



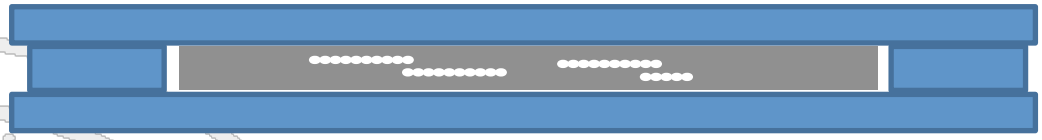




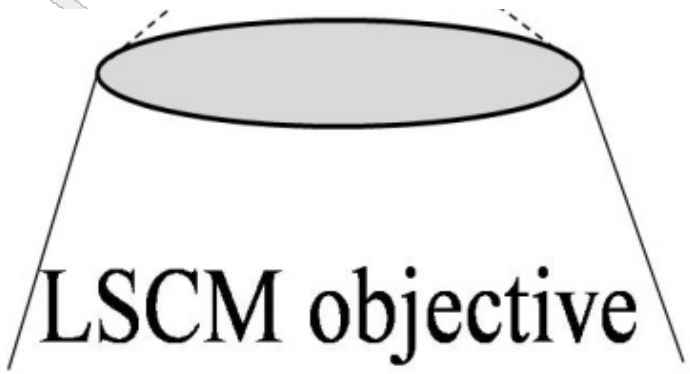


Huang, S., G. Pessot, P. Cremer, R. Weeber, C. Holm, J. Nowak, S. Odenbach, A. M. Menzel and G. K. Auernhammer (2016). Soft Matter **12**: 228-237.

Sample geometry



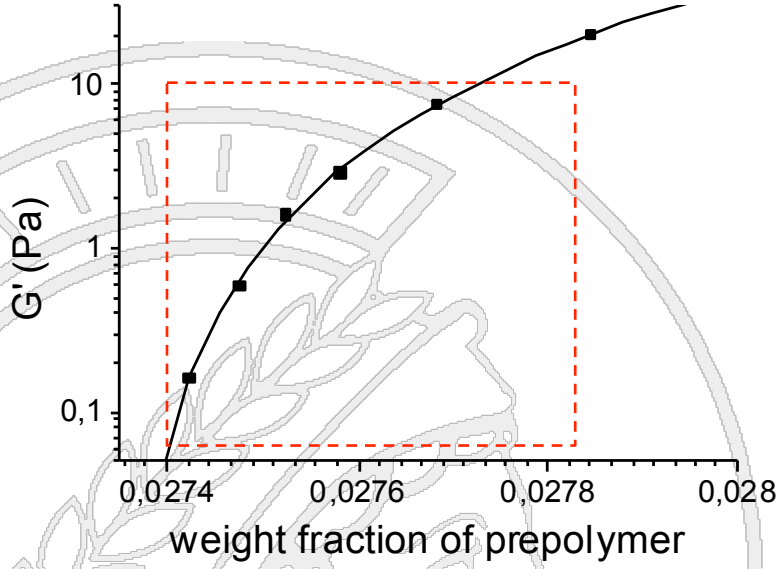
Sample chamber



No.1 standard coverslip
≈ 160 µm

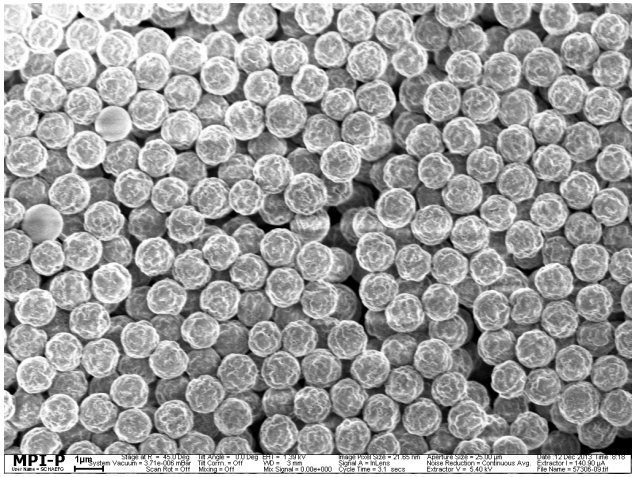
Sample

Matrix: PDMS gel



Crosslinking:
Hydrosilation with platinum catalyst

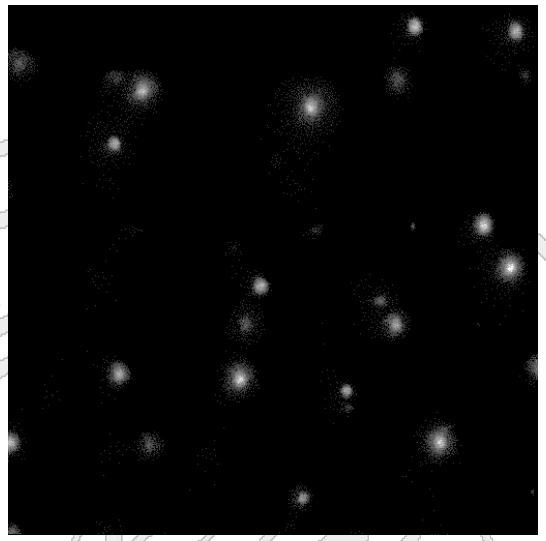
Magnetic particles



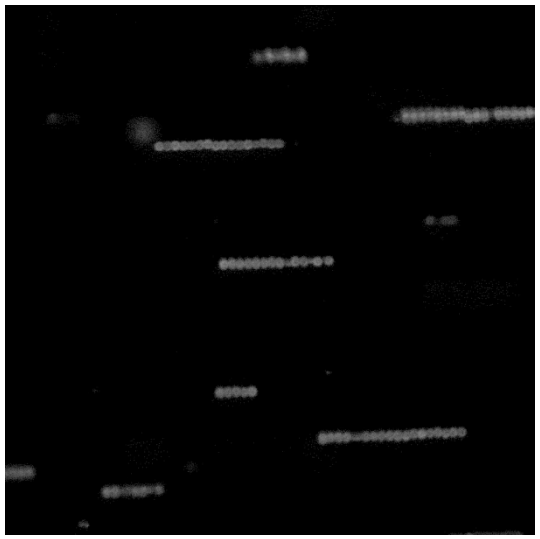
Superparamegnetic
Fluorescent-labeled

0.1 wt%

Confocal images

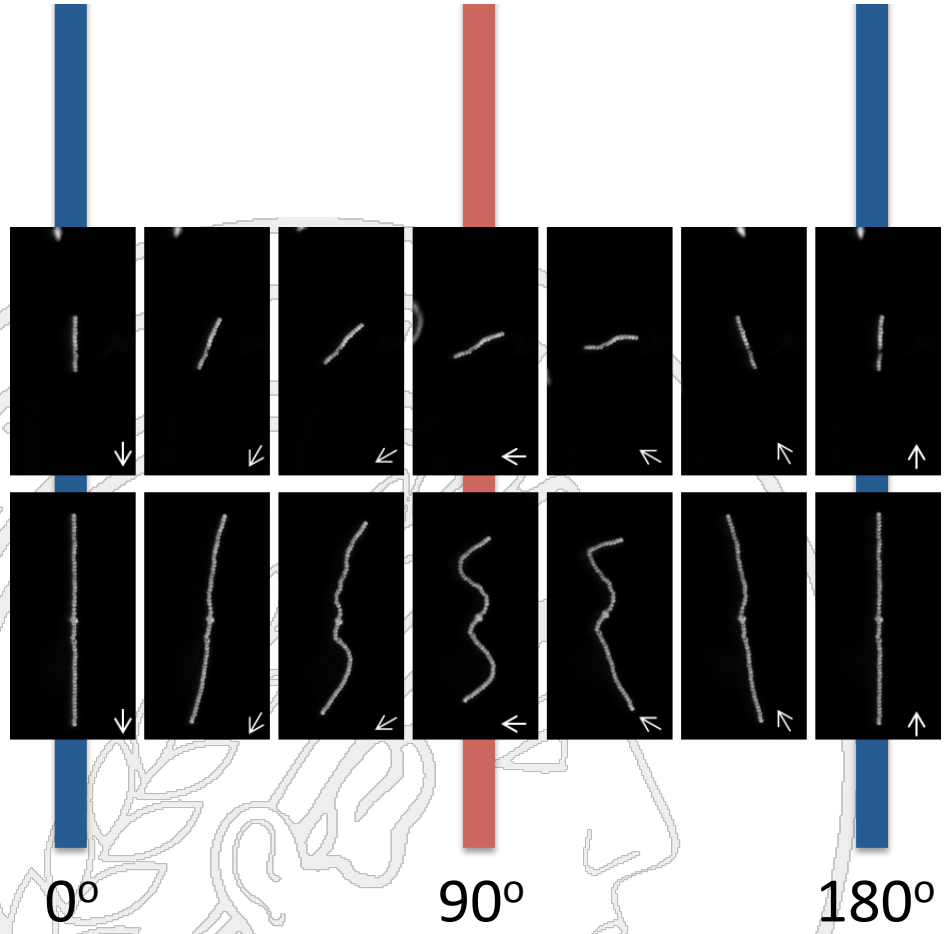


Crosslinked without applied field

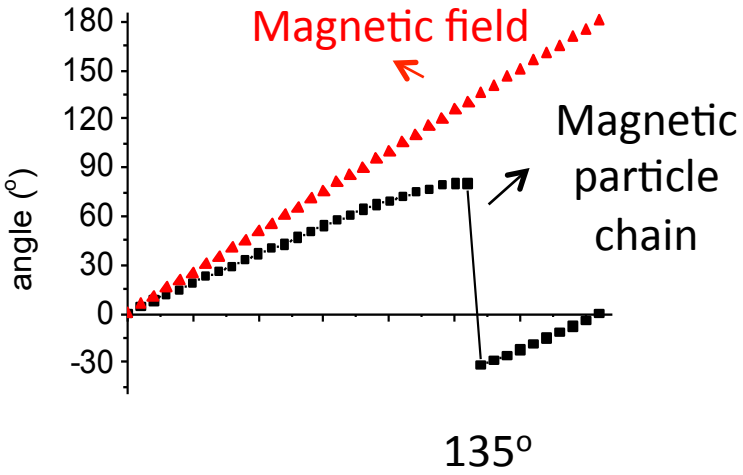


Crosslinked with applied field

Rotating field



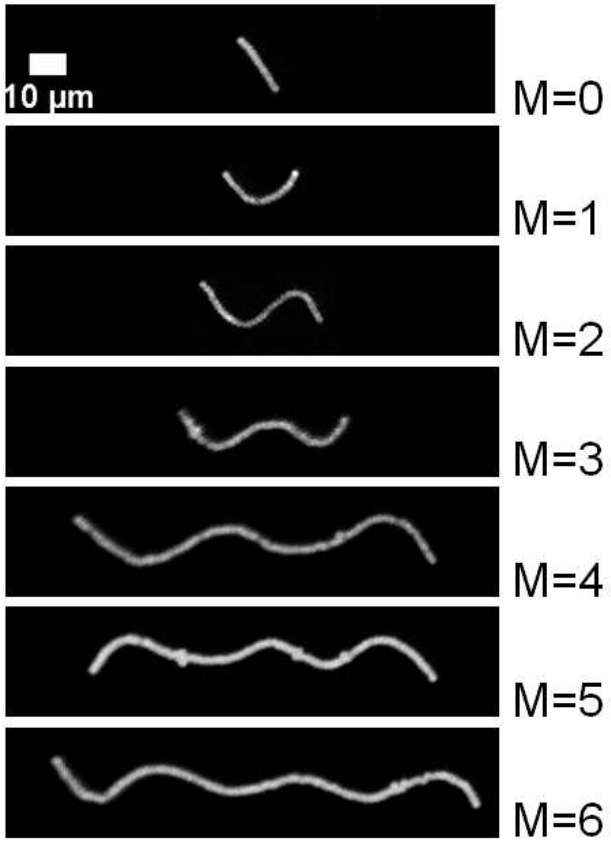
- Short chains rotate
  Long chains buckle
- Hysteresis



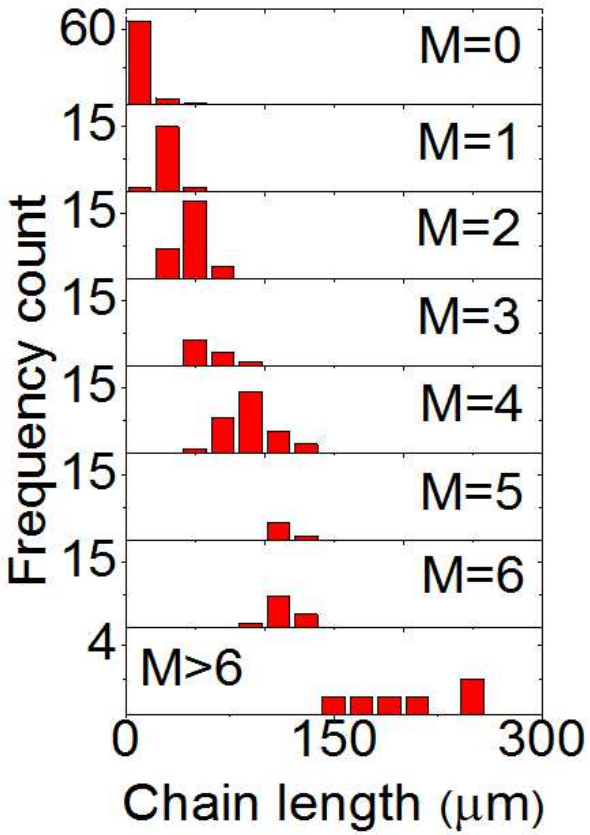
G'≈ 0.2 Pa, B = 216 mT

Huang, S., G. Pessot, P. Cremer, R. Weeber, C. Holm, J. Nowak, S. Odenbach, A. M. Menzel and G. K. Auernhammer (2016). Soft Matter **12**: 228-237.

Modes of deformation



(a)



(b)

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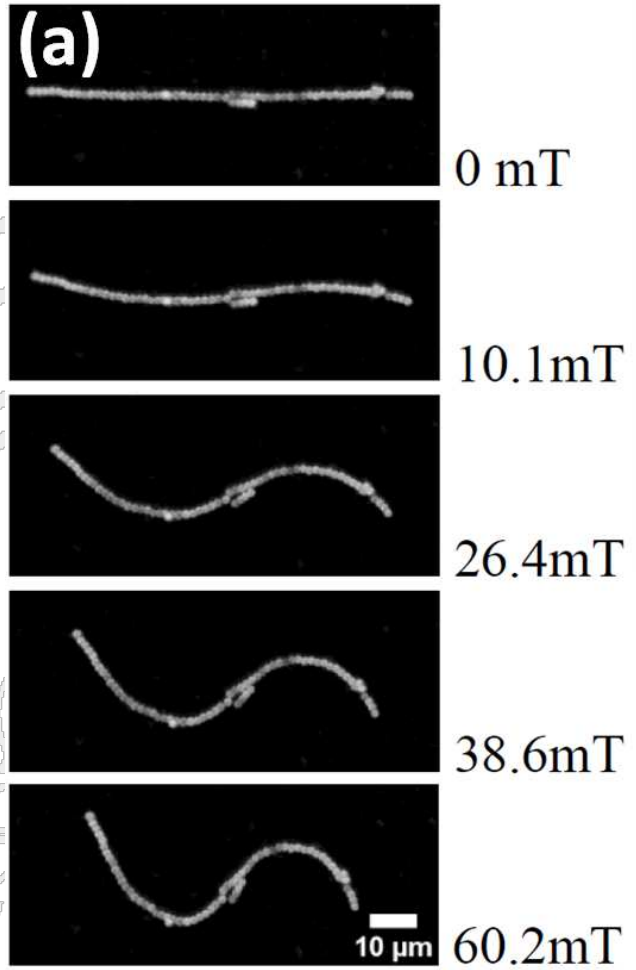
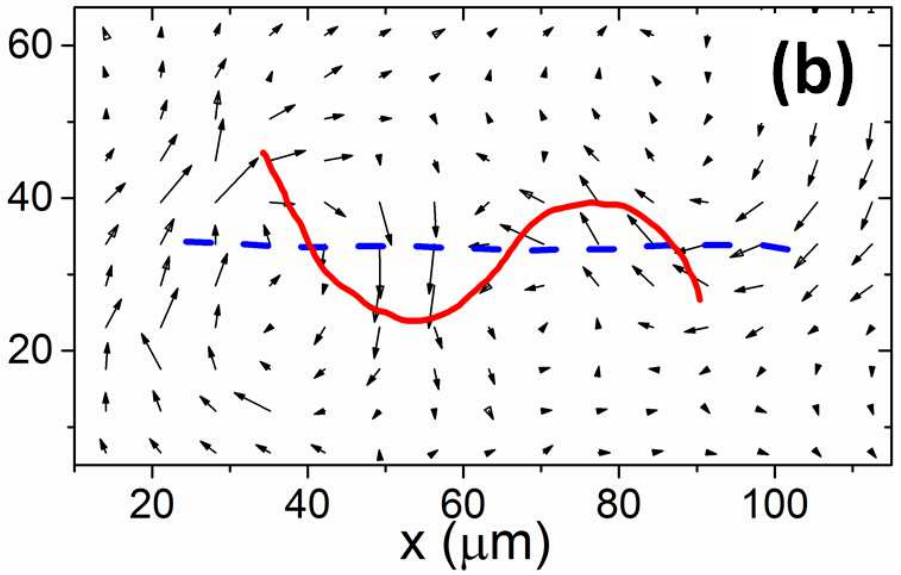
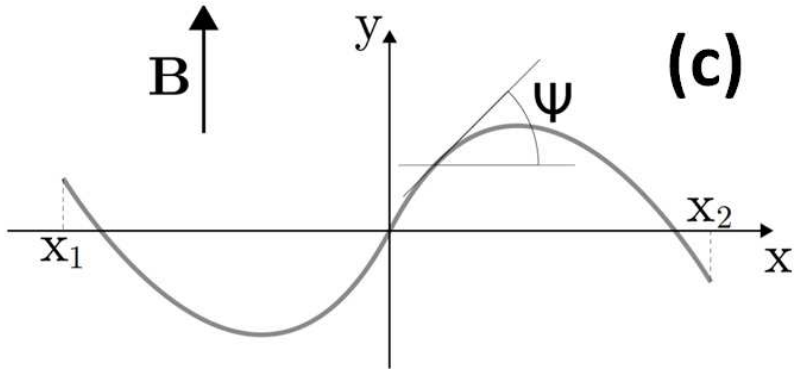
Deformation field







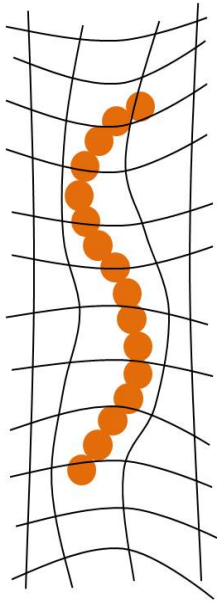
Huang, S., G. Pessot, P. Cremer, R. Weeber, C. Holm, J. Nowak, S. Odenbach, A. M. Menzel and G. K. Auernhammer (2016). Soft Matter **12**: 228-237.

Modelling

Magnetic chain tends to align to magnetic field direction to decrease magnetic energy.

buckling

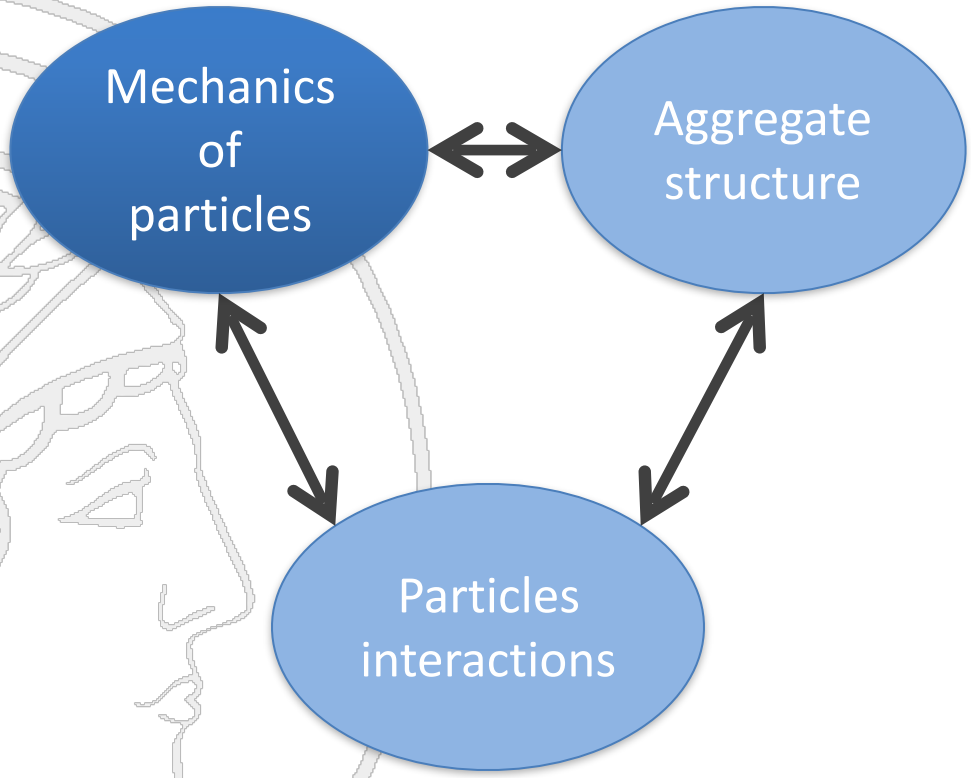
Surrounding elastic network increases elastic energy due to deformation.



Wave length = $f(G', H_0, l_0)$
Amplitude = $g(G', H_0, l_0)$

$$E_{total} = E_{elastic} + E_{magnetic}$$

Soft Colloids

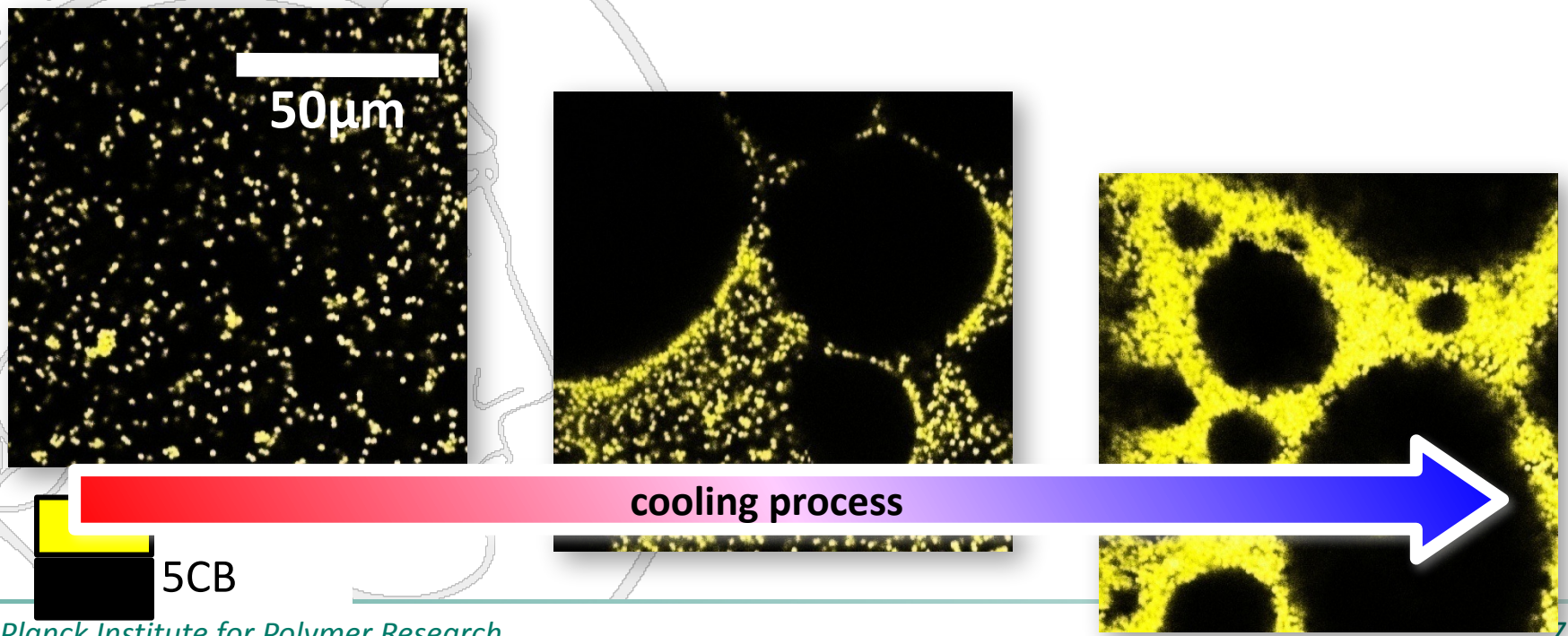


Colloids in liquid crystals

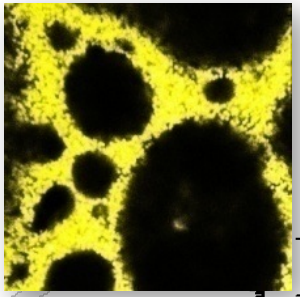
Network formation

- Colloids dispersed in isotropic phase
- Coexistence of nematic and isotropic phase
- Interaction of nematic liquid crystal, impurities and colloids

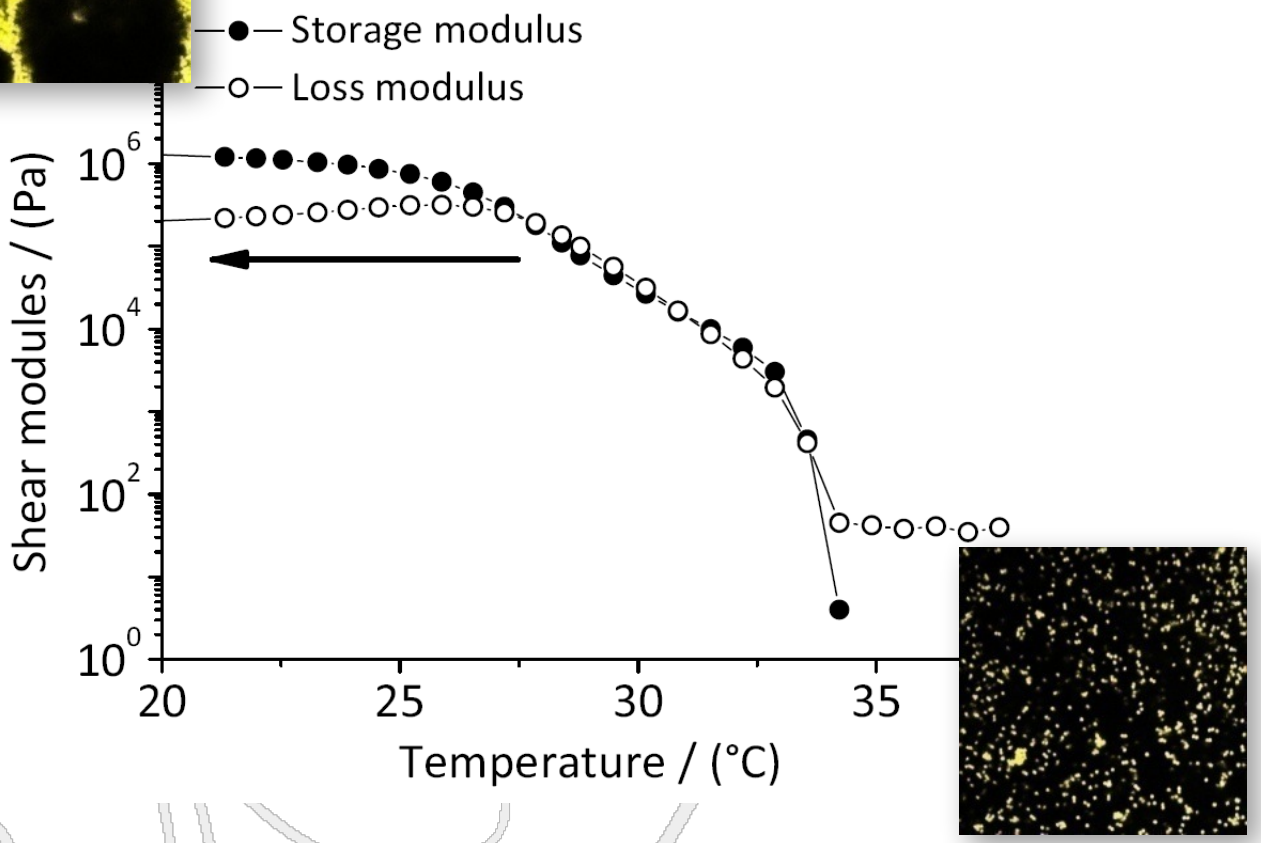
Stark, Phys. Rep. ***(2001)*** *351, 387*
Meeker et al., Phys. Rev. E ***(2000)*** *61, R6083*
Vollmer et al., Langmuir ***(2005)*** *21, 4921*

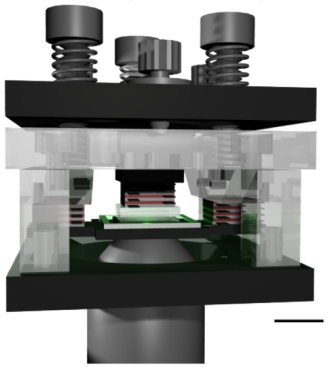


Rheological properties



Temperature dependency



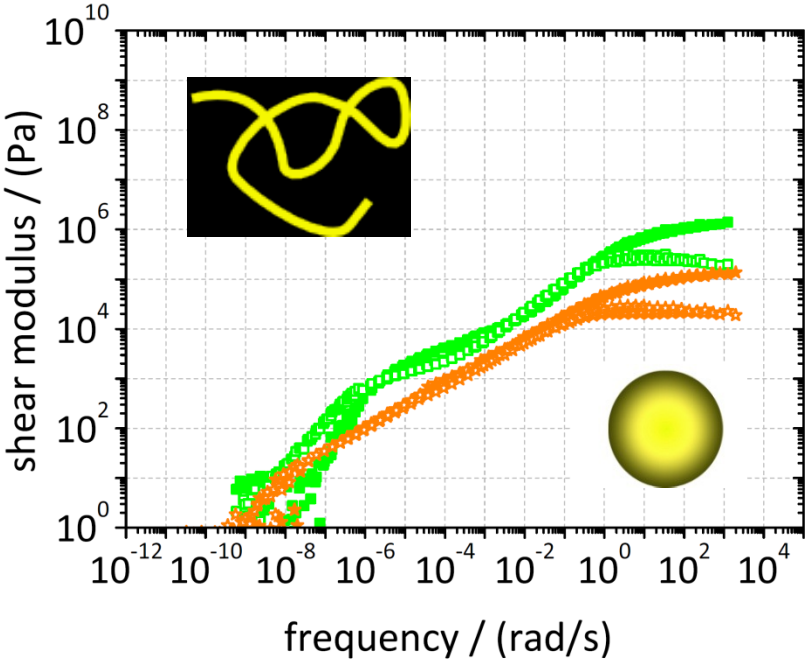


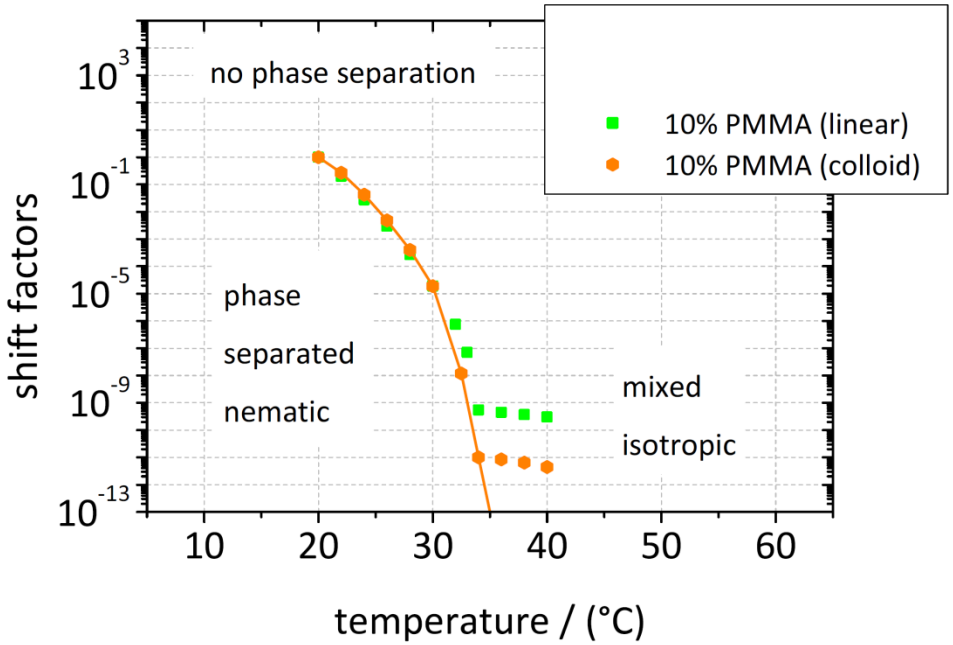
- frequency dependency gives further physical insight

G.K. Auernhammer et al., J. Chem. Phys. ***132****, 124702 (2010).*

Superposition

Phase separation master curves and shift factors

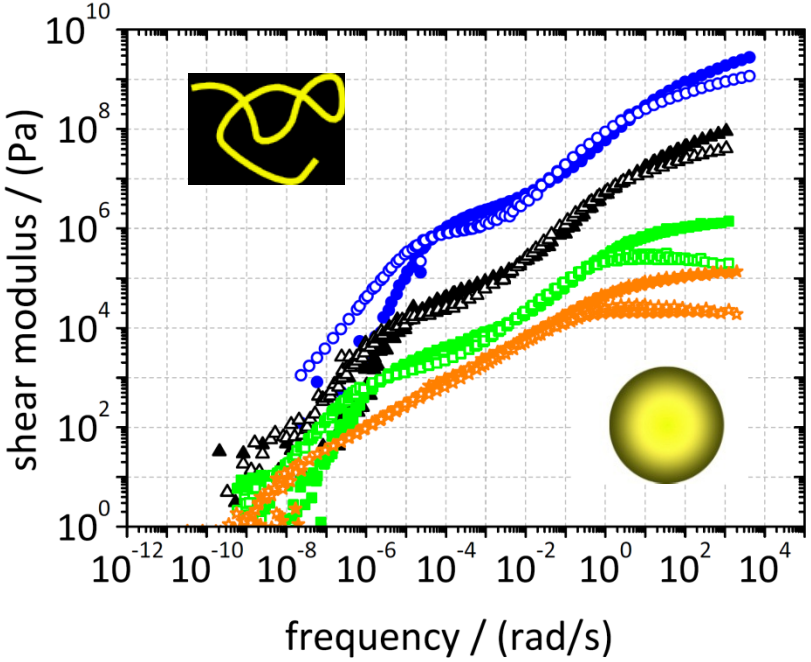


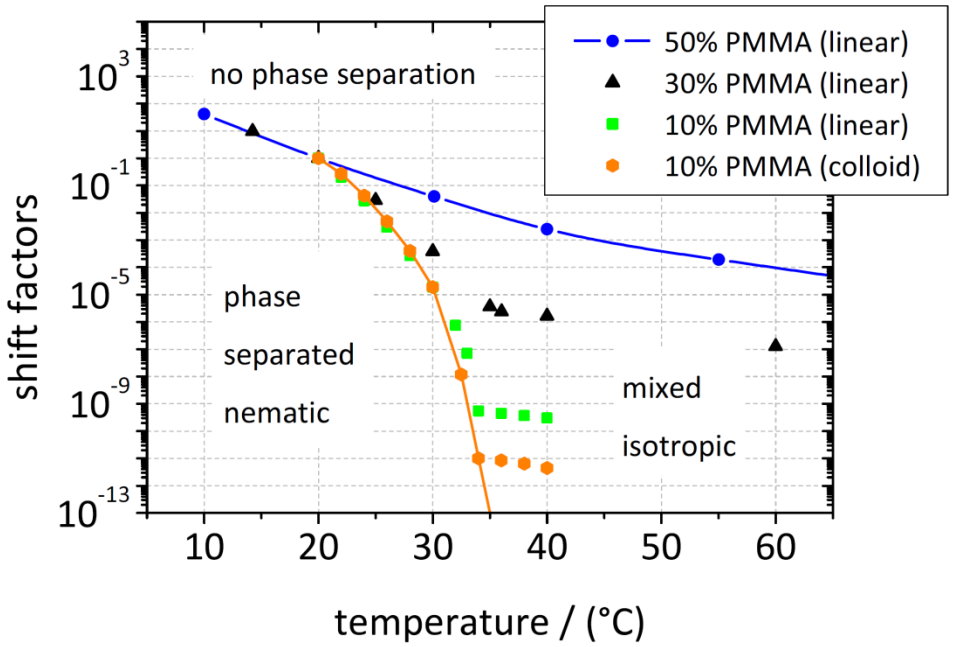


- Hard core reflected in suppressed rubbery plateau
- Shift factors universal, therefore bound to the phase diagram
- Rheology dominated by plastizied PMMA, compare polymer dispersed LC

Superposition

Phase separation master curves and shift factors



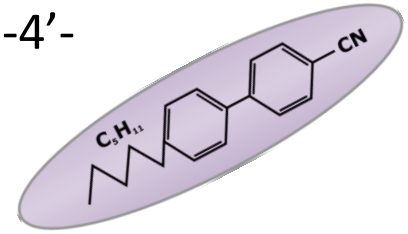


- Hard core reflected in suppressed rubbery plateau
- Shift factors universal, therefore bound to the phase diagram
- Rheology dominated by plastizied PMMA

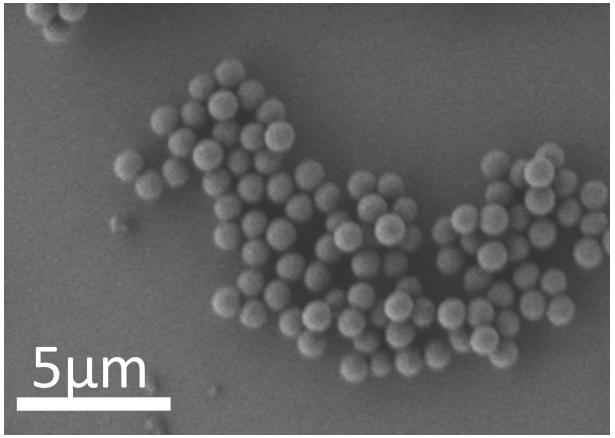
Experimental: Sample system

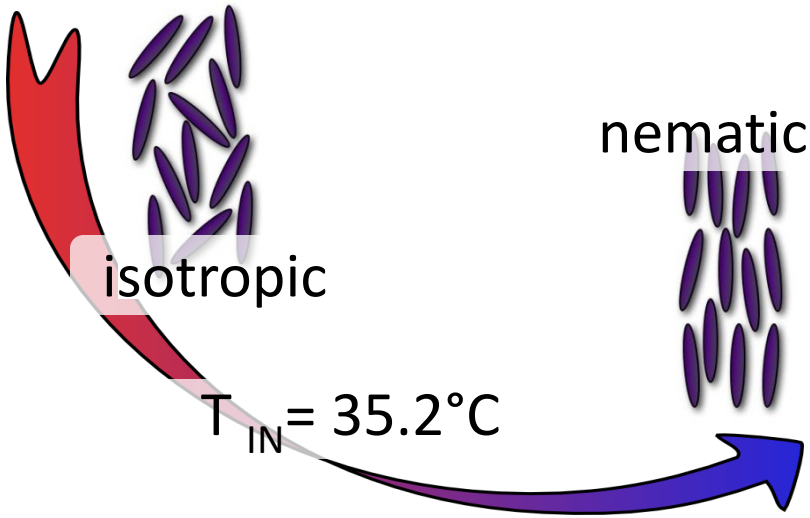
Composition

- Thermotropic liquid crystal 5CB (4-n-pentyl-4'-cyanobiphenyl)



- PMMA– particles, partially crosslinked, sterically stabilized (poly 12-hydroxy stearic acid)

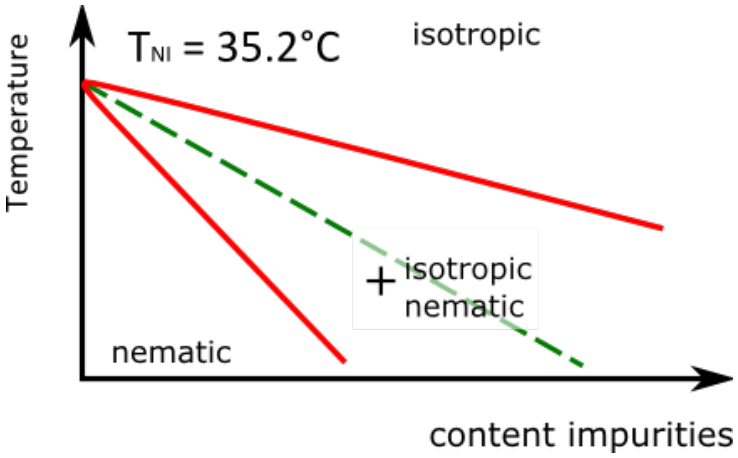




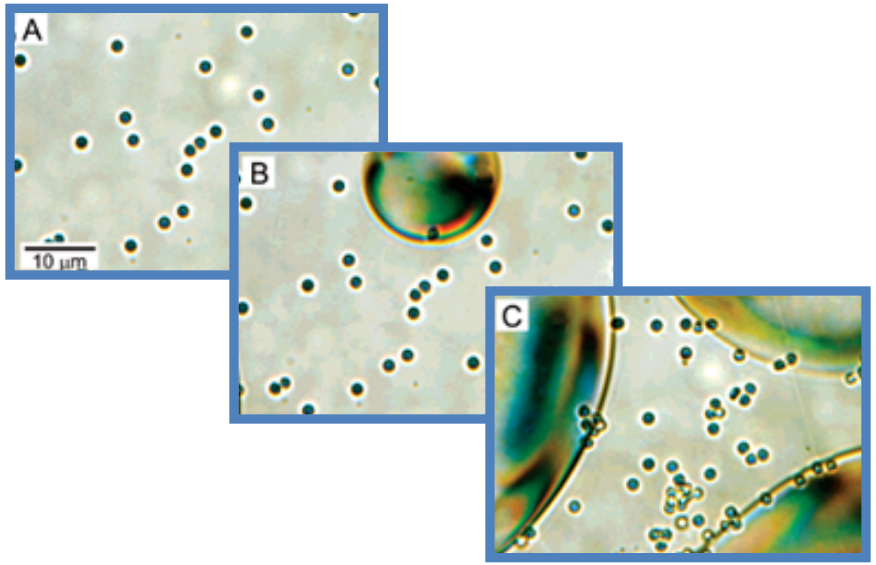
Colloids at NI Interface

- Kinetics and mechanisms at the phase transition

➔Coexistence of nematic and isotropic phase due to impurities

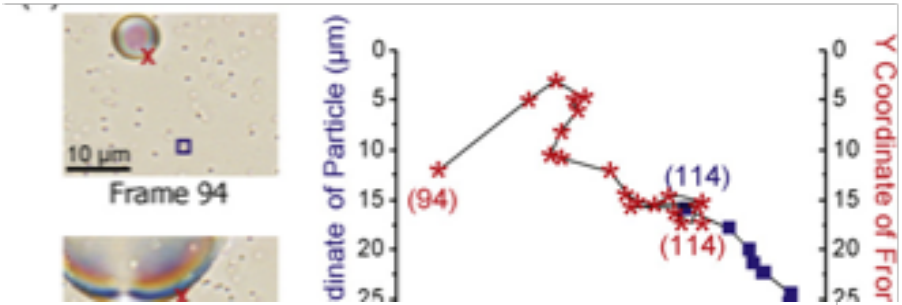


➔Interaction with NI interface and impurities

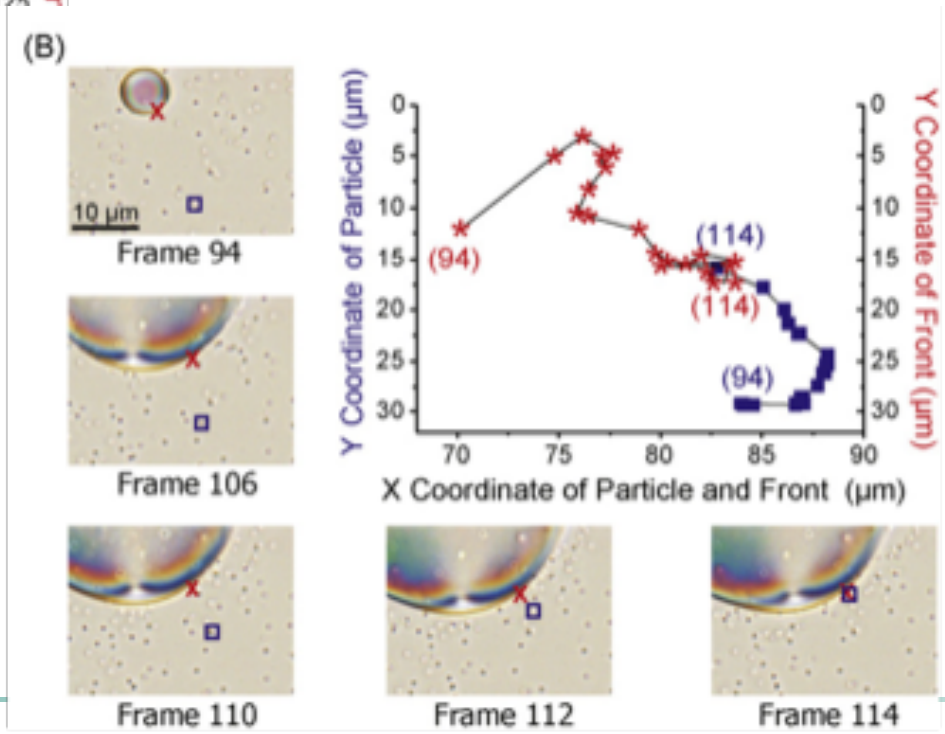


*B. Ullrich, GKA, E. M. Sam, D. Vollmer, Colloids and Surfaces A: **354**, 298-307 (2010)*

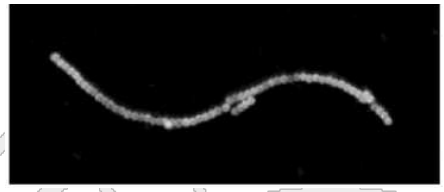
Colloids at NI Interface



Interaction with the interface?



Summary

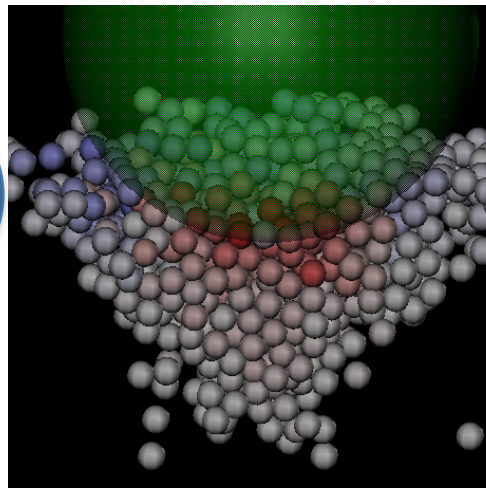


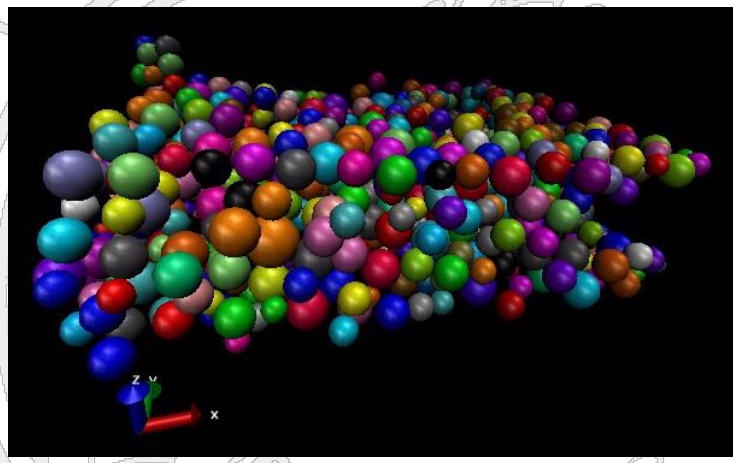
26.4mT

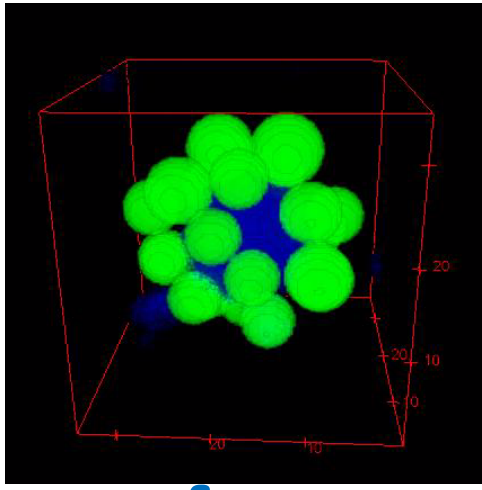
Mechanics of particles/ matrix

Aggregate structure

Interactions: Particles & Fields







Understanding of single particle properties

=> tunable macroscopic properties

Thank you for your attention