DYNAMICS OF A 2D GEL AROUND ITS PERCOLATION TRANSITION

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Summary

- **MOTIVATIONS**
- **SAMPLE PREPARATION**

- **STRUCTURE: IN-SITU MICROSCOPY**

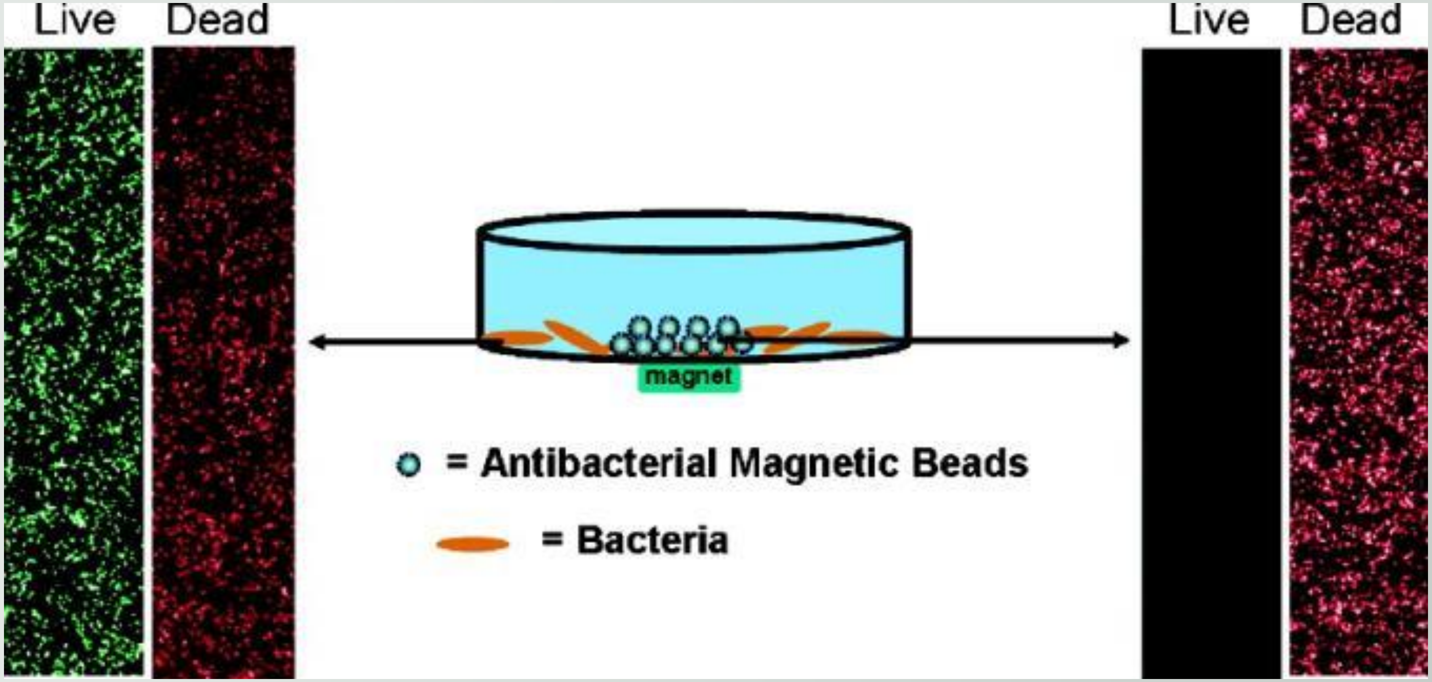
- **MECHANICAL RESPONSE: INTERFACIAL RHEOLOGY**

- **INTERNAL DYNAMICS: XPCS**

Nanoparticles at interfaces: applications

Antibacterial coatings

Ag nanocrystal coating of planar surfaces and colloidal particles – anctibacterial activity by release of Ag ions.
[Lee, Cohen, Rubner, **Langmuir** 21, 9651-9 (2011)]

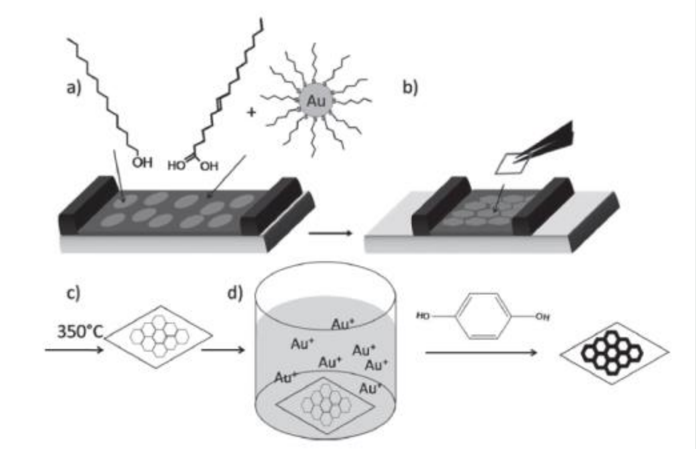


Nanoparticles at interfaces: applications

Electronics and optoelectronics

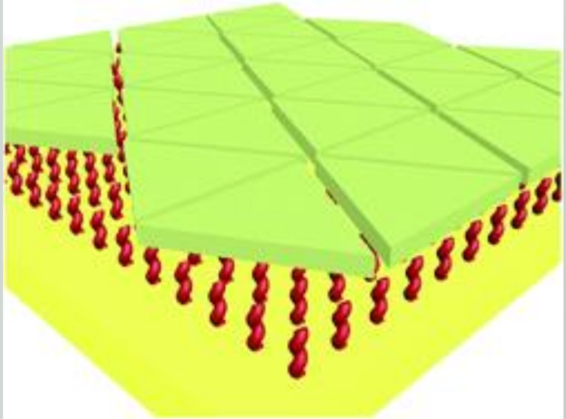
Thin, large and inexpensive Transparent Conducting Electrods by Langmuir-Schaeffer Deposition of monolayers of gold nanoparticles

[A. Morag et al. ***Advanced Materials*** *23, 4327−4331 (2011)]*



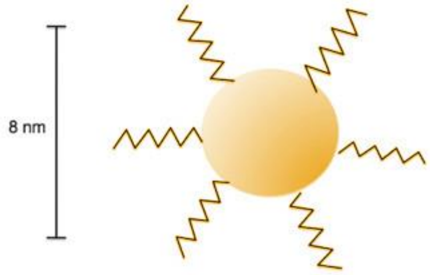
Langmuir Schaeffer deposition of SERS active planar assemblies of gold nanoparticles

[Lee et al. **Nanoscale**, 5, 6404-6412 (2013)]



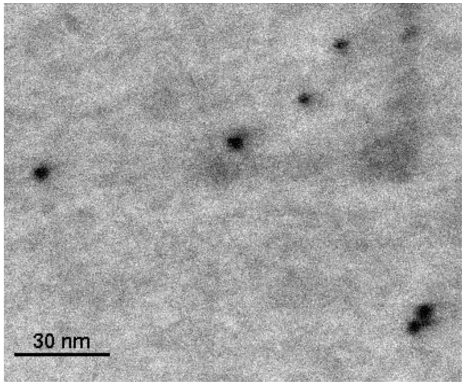
Our system

Gold nanoparticles (GNPs) stabilized by dodecanethiol coating

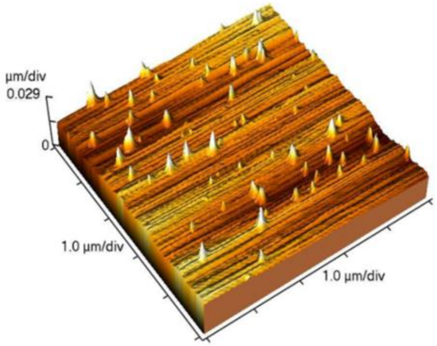


- Synthesized following *[Chen, Kimura, **Langmuir** 15, 1075 (1999)]*
- 8nm diameter
- Characterized by means of:

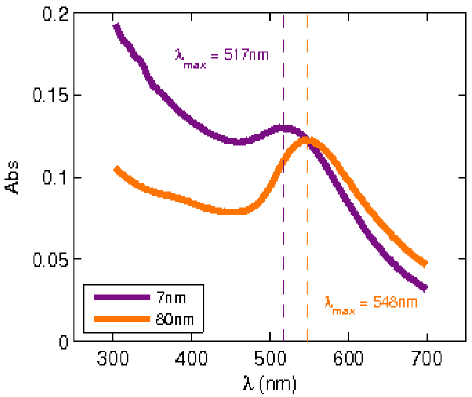
SEM



AFM



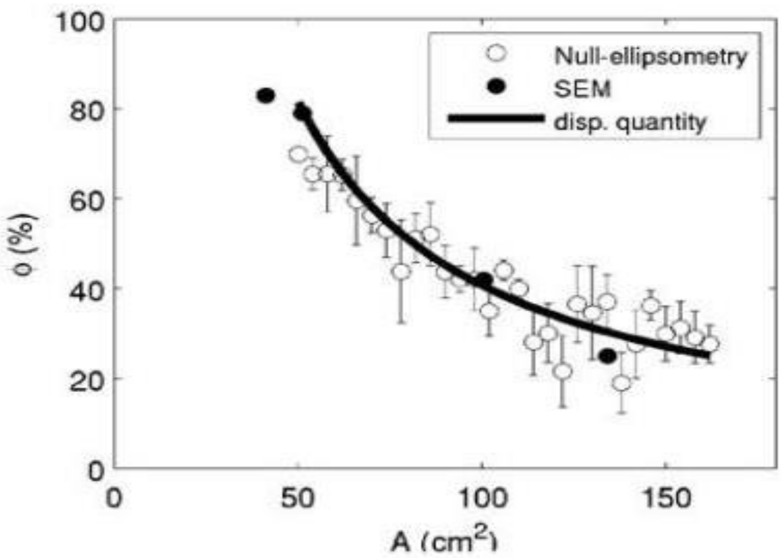
UV-Vis spectroscopy

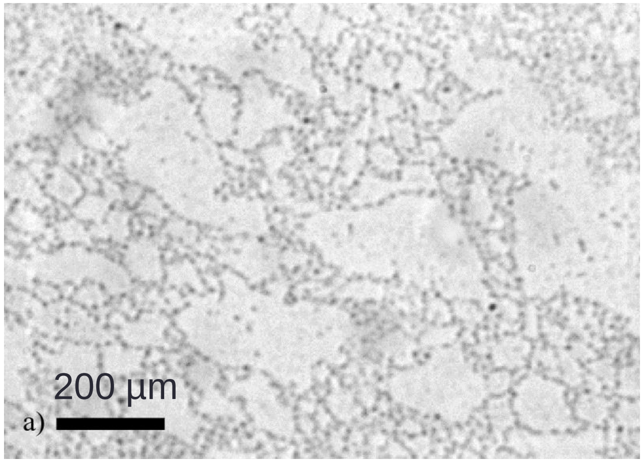


Langmuir films: preparation

- Film prepared by SLOW spreading of hexane solution at the air/water interface (Langmuir trough)
- The concentration is slowly increased by reducing the available area (trough barrier motion)
- Surface concentration Φ of GNPs measured by

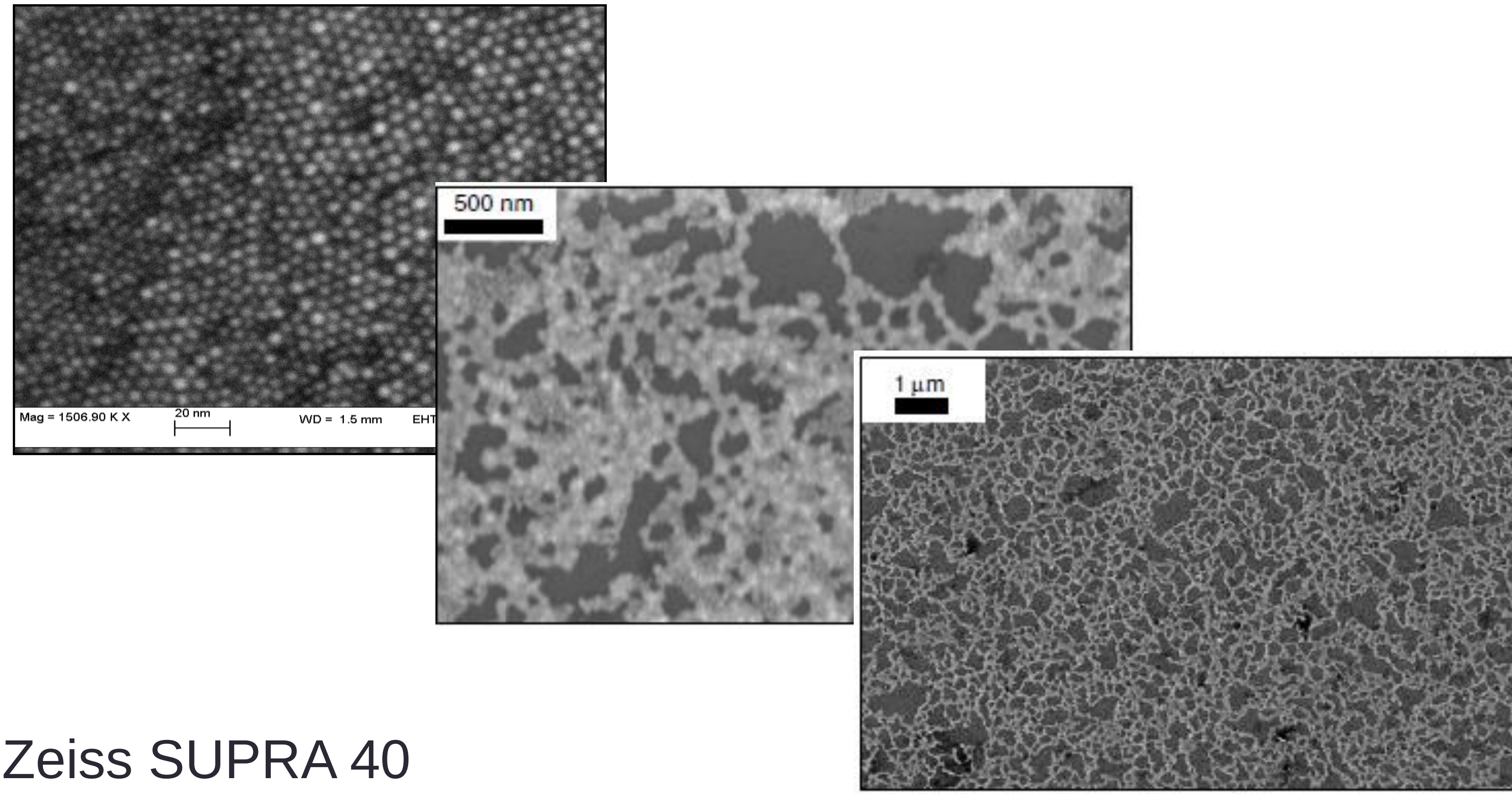
  - spreaded amount
  - In-situ microscopy
  - SEM imaging
  - Imaging ellipsometry





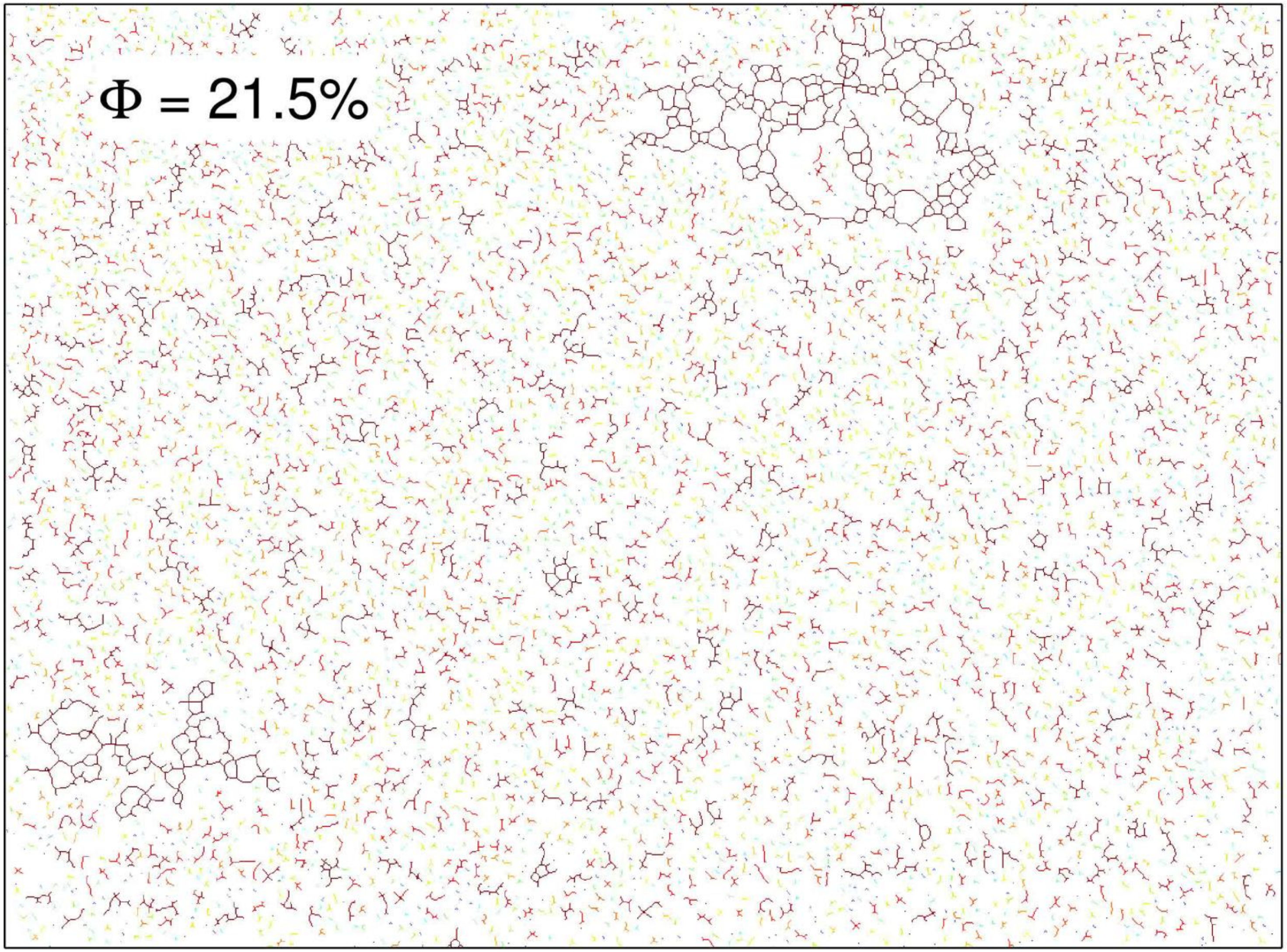
Langmuir films: SEM Characterization

Transferred film (Langmuir Schaeffer) on silicon substrate

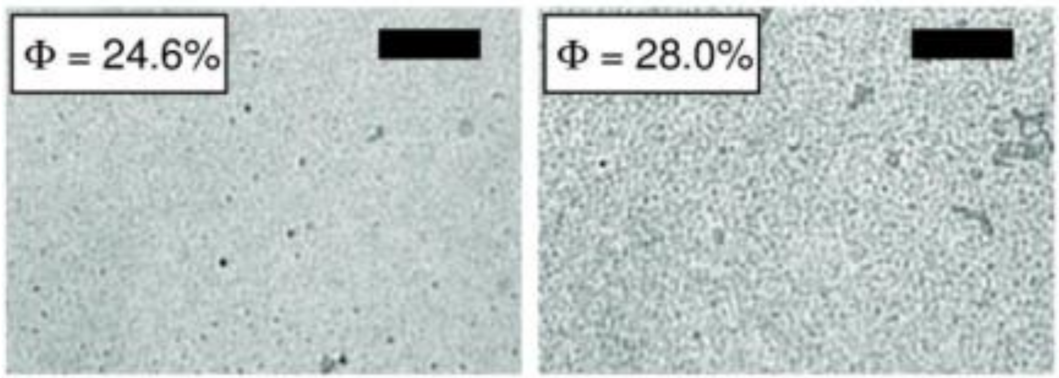


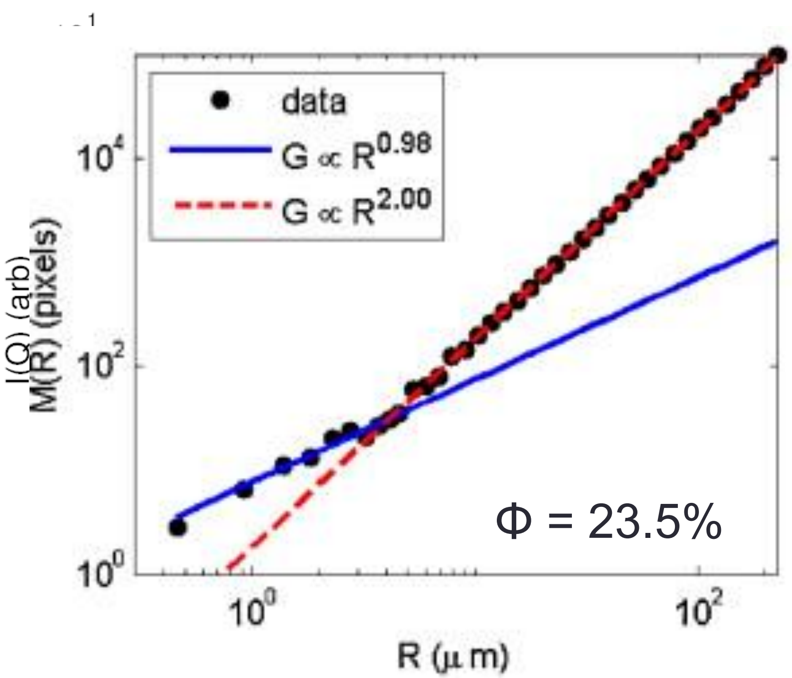
Zeiss SUPRA 40

Gel formation: in-situ microscopy



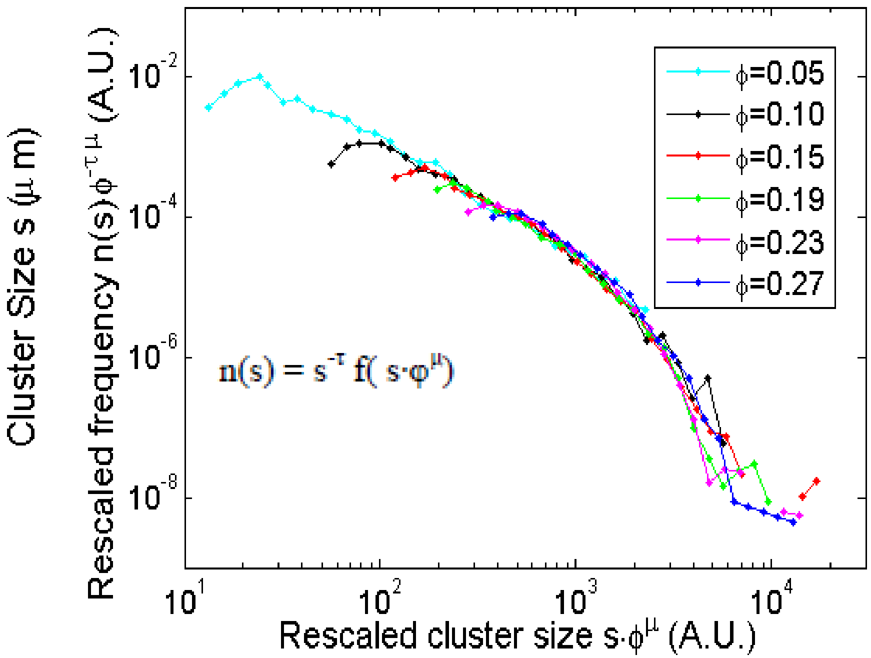
Gel formation – 1° step: flocculation

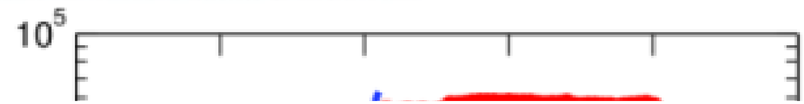




- crossover (around 4–5 μm) between a linear and a quadratic growth of the mass
- Small and quasi 1D objects organize in a large scale homogeneous 2D film

Gel formation – 2° step: percolation





The size distribution scale in a fashion similar to percolation theory

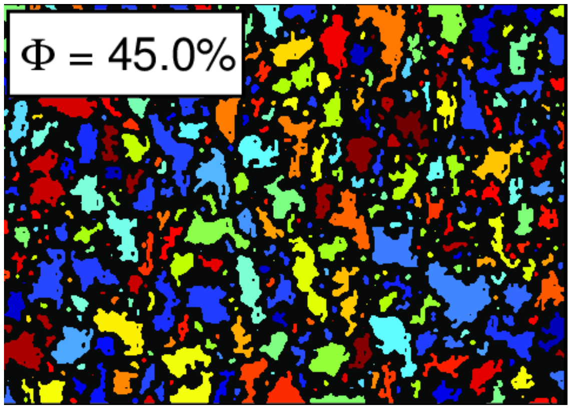
EXPERIMENTS: $\mu = 1.8 \pm 0.2$ $\tau = 1.6 \pm 0.2$

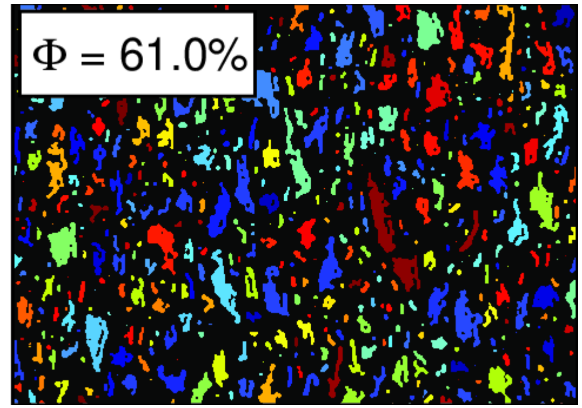
THEORY: $\mu_c = 91/36 \approx 2.5$ $\tau_c = 187/91 \approx 2.05$

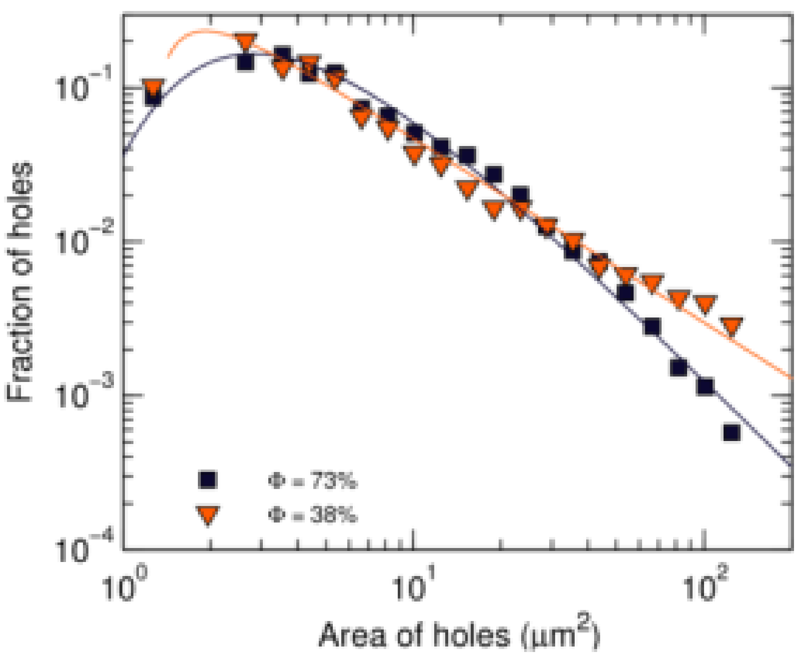
The exponents are **not compatible** with the analytical ones expected for 2D percolation

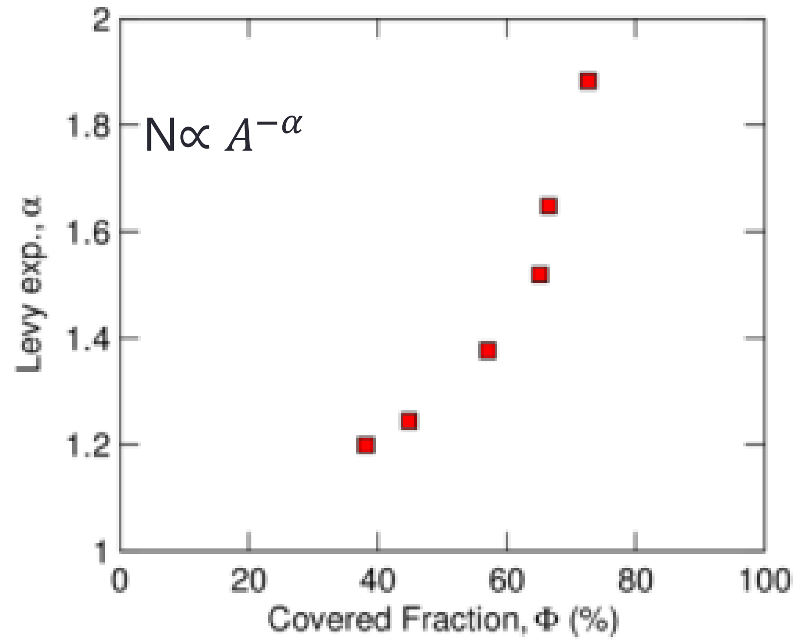
D. Orsi, A. Vezzani, R. Burioni, A. Pucci, G. Ruggeri, and L. Cristofolini, **Colloids Surfaces A Physicochem. Eng. Asp.** 441, 912 (2014)

Gel formation – 3° step: compaction









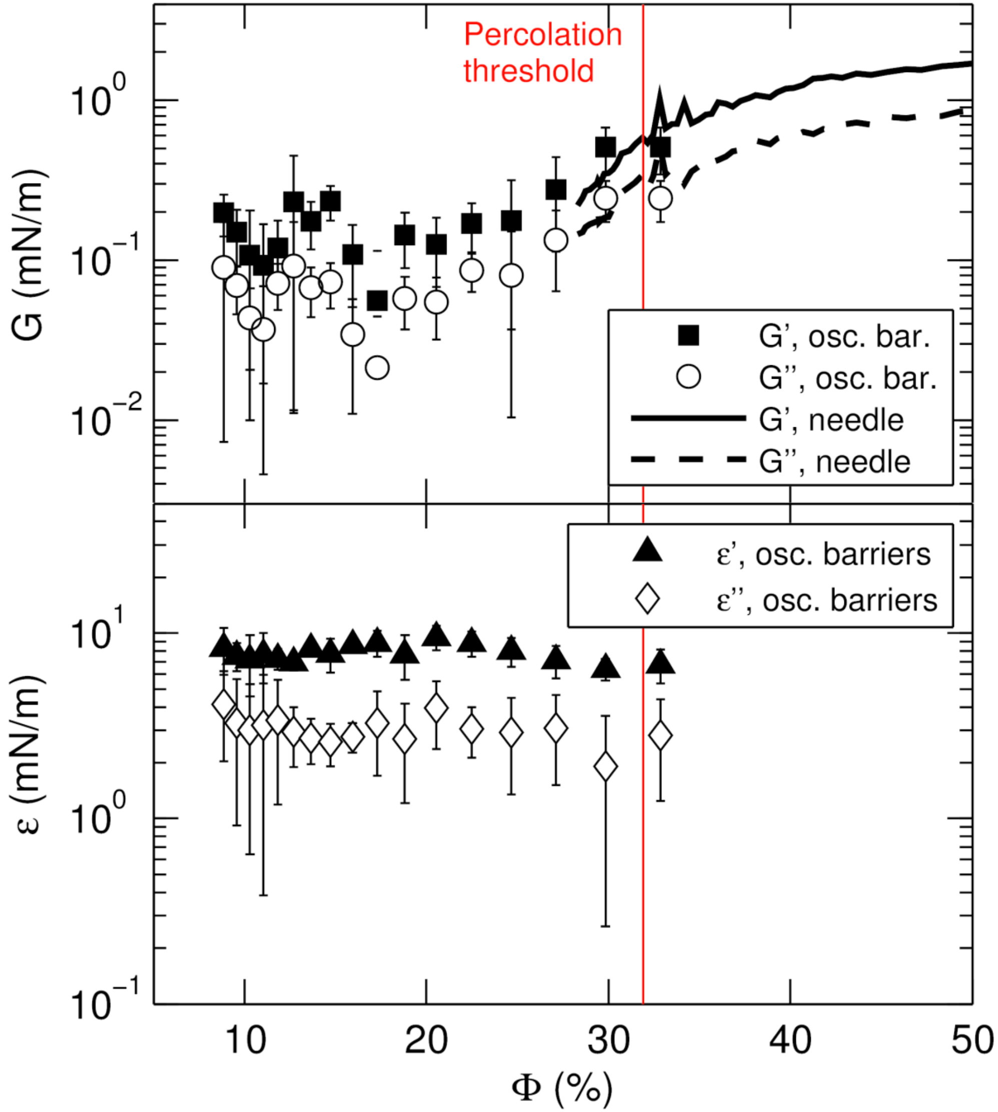
The gel shows elastic response

Shear G and compression ε moduli measured by means of 2 techniques:

- Oscillating needle
- Oscillating barriers

We find:

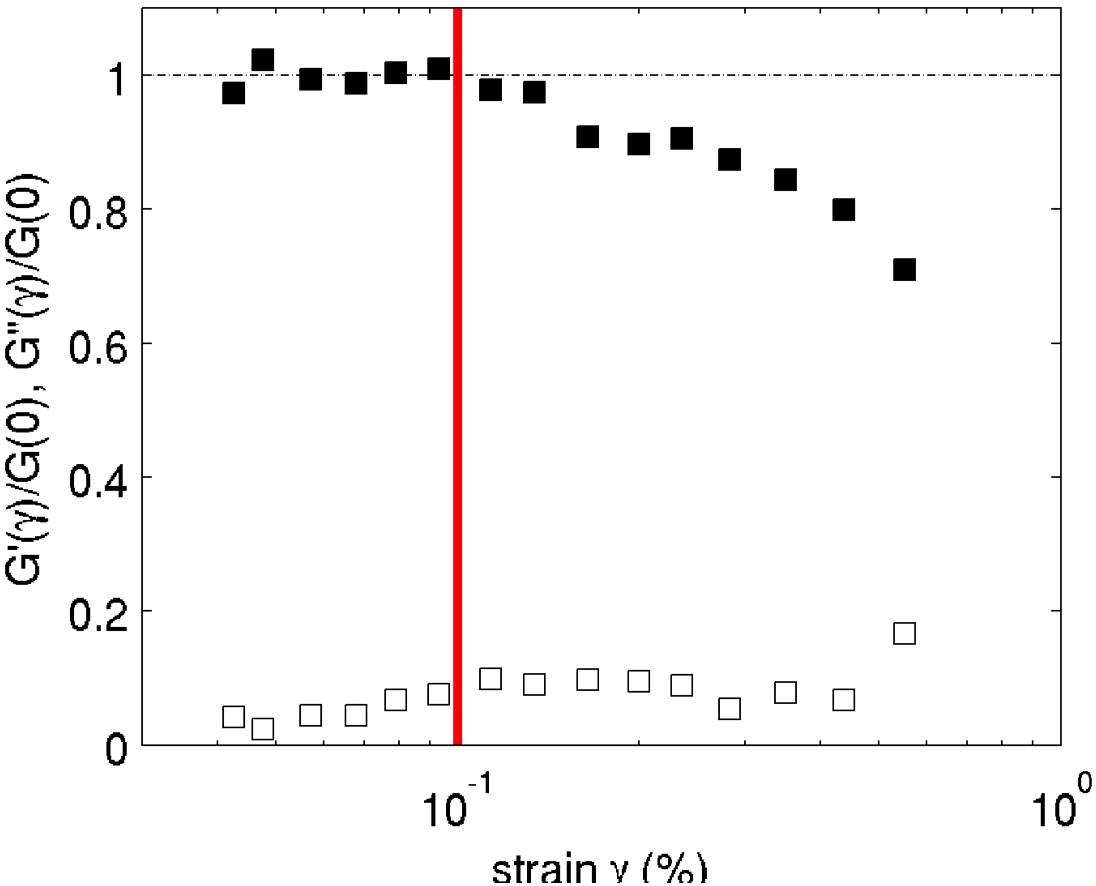
- An mainly elastic response (G' > G'', ε' > ε'')
- The compression moduli are constant in the probed Φ range
- G increases approaching the percolation transition



Shear softening

The network structure is very brittle: we have shear softening even at γ<0.1%

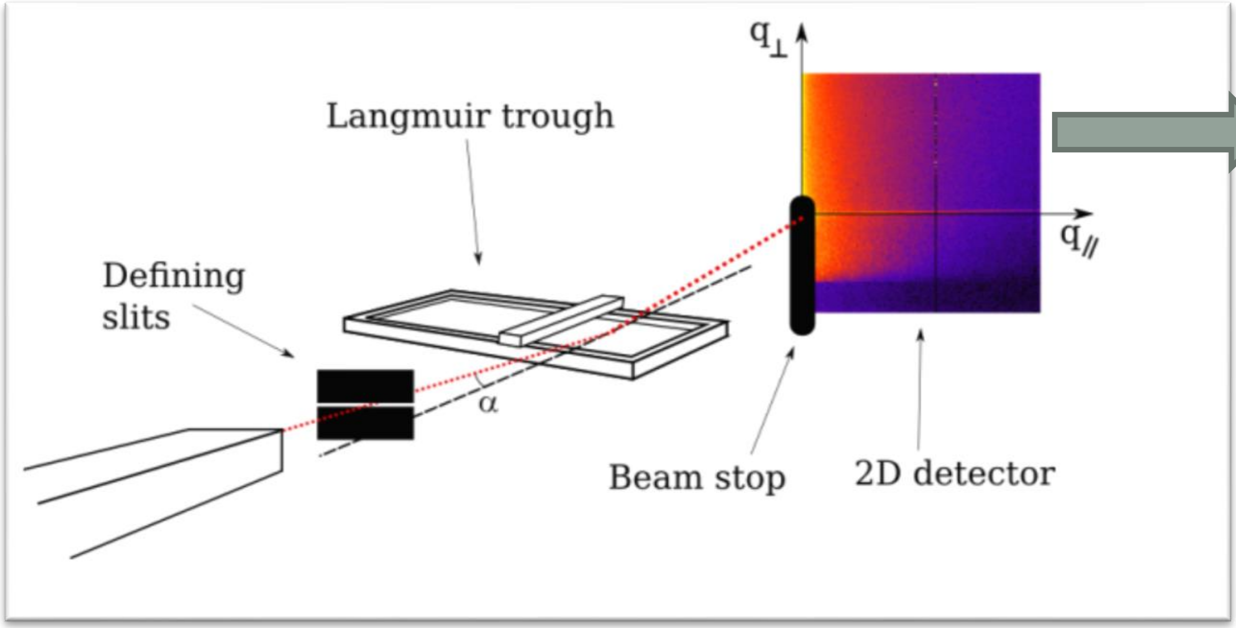
The breakage of weak links modifies the system's structure and reduces the mechanical modulus



D. Orsi, G. Baldi, P. Cicuta, and L. Cristofolini, **Colloids Surfaces A Physicochem. Eng. Asp.** 413, 71 (2012).

XPCS at the air/water interface

- 8keV coherent beam from the ID10 beamline of ESRF
- SAXS @ Grazing Incidence on water surface (α=0.1°)
- 2D detector (Medipix, 256x256 pixels) covering
  - q range 0.01 - 0.07 nm^{-1}
  - time window 0.01s - 1000s

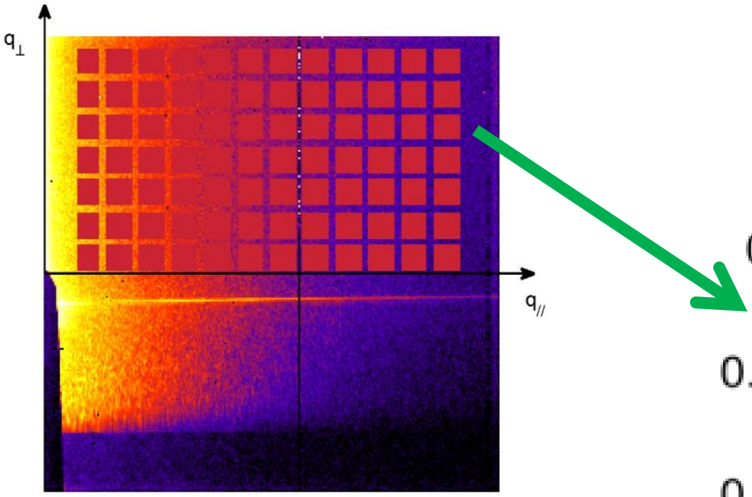


Pixels are grouped in squares identified by ($q_{||}$, $q_\perp$) coordinates

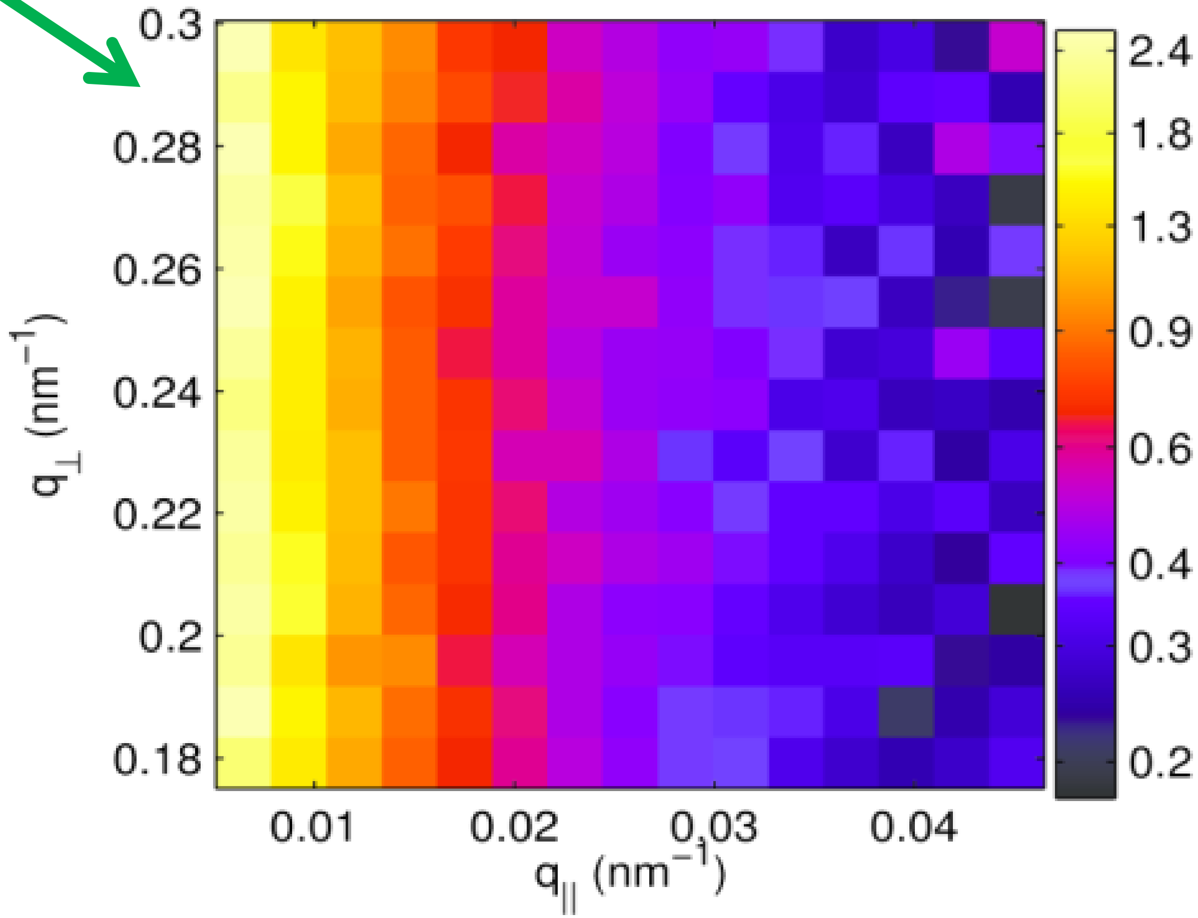
$$g^{(2)}(q,t) = \frac{\langle I(q,t_1) I(q,t_1+t)\rangle}{\langle I(q,t_1)\rangle^2}$$

$$g^{(2)}(t) = A + \beta e^{-2(t/\tau)^\gamma}$$

Dynamics confined in 2D



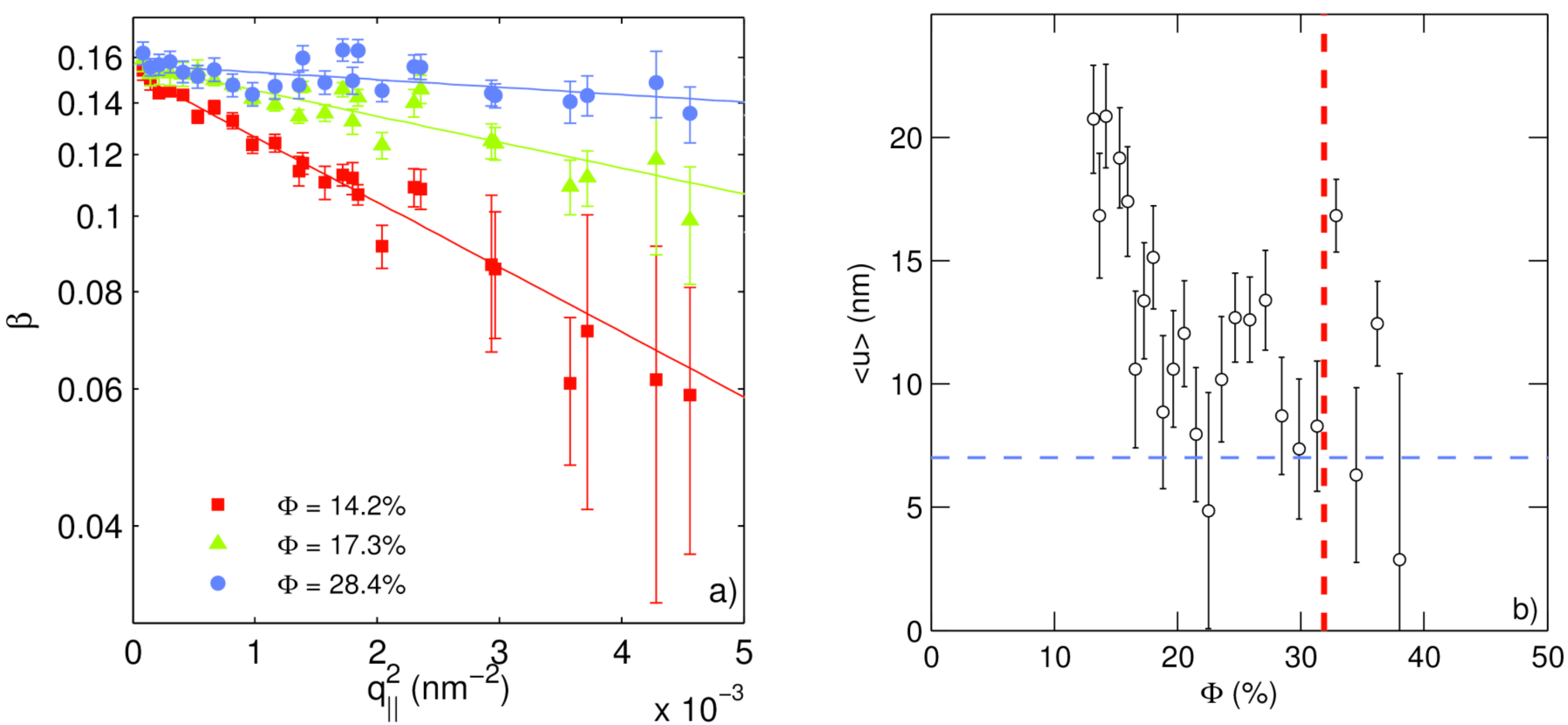
Relaxation time measured at $\Phi = 15\%$



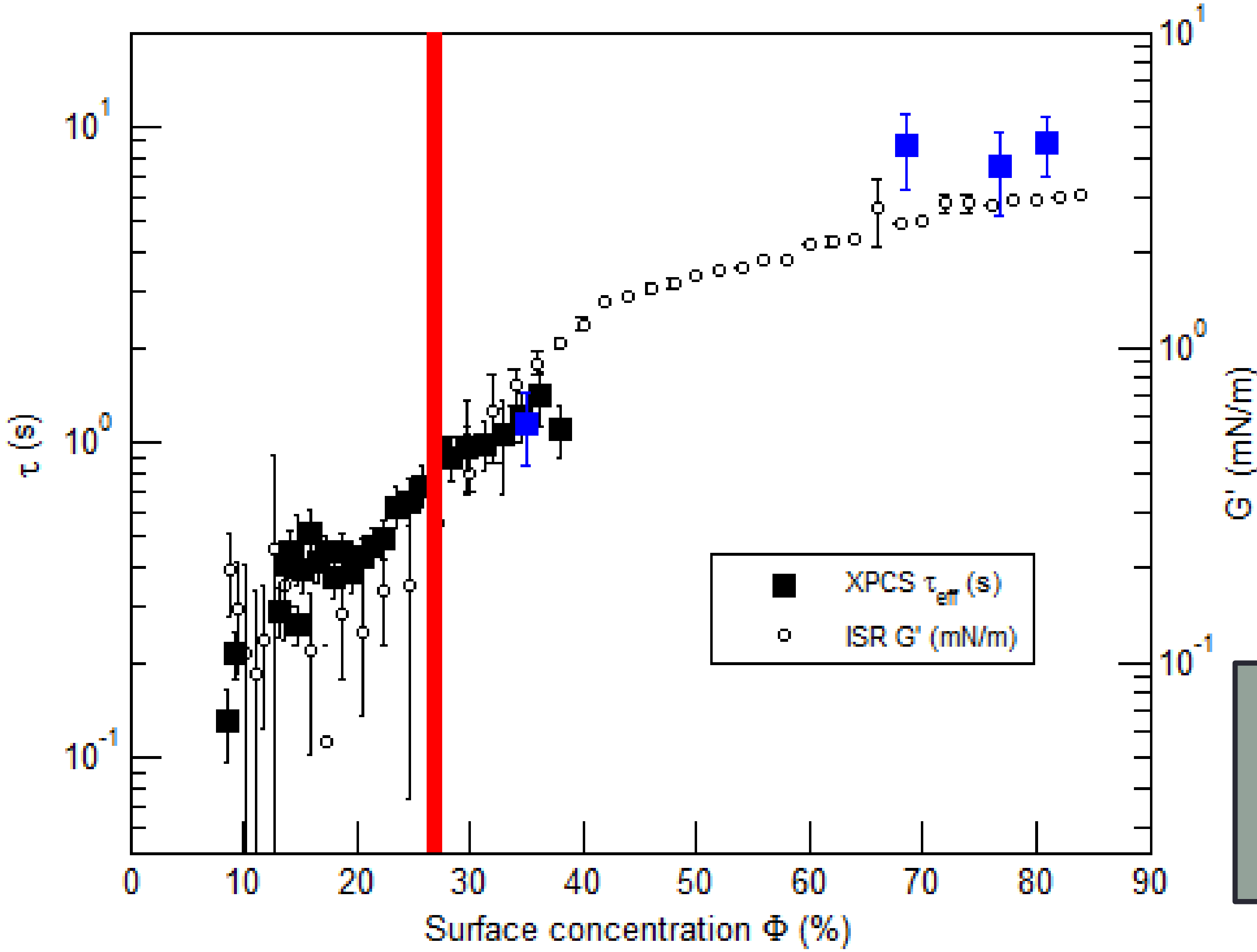
Faster dynamics is present

The presence of dynamics faster that the exposure time is revealed by the Debye-Waller decrease of the contrast

$$\beta = \beta_0 \, exp\left(-\frac{{q_{\parallel}}^2 \langle u^2 \rangle}{3}\right)$$



Relaxation time τ ⟷ shear modulus G’



This is predicted by models ascribing XPCS dynamics to stress-relaxation (e.g. Bouchaud – Pitard)

Example of Fluctuation-Mechanical Response Relation

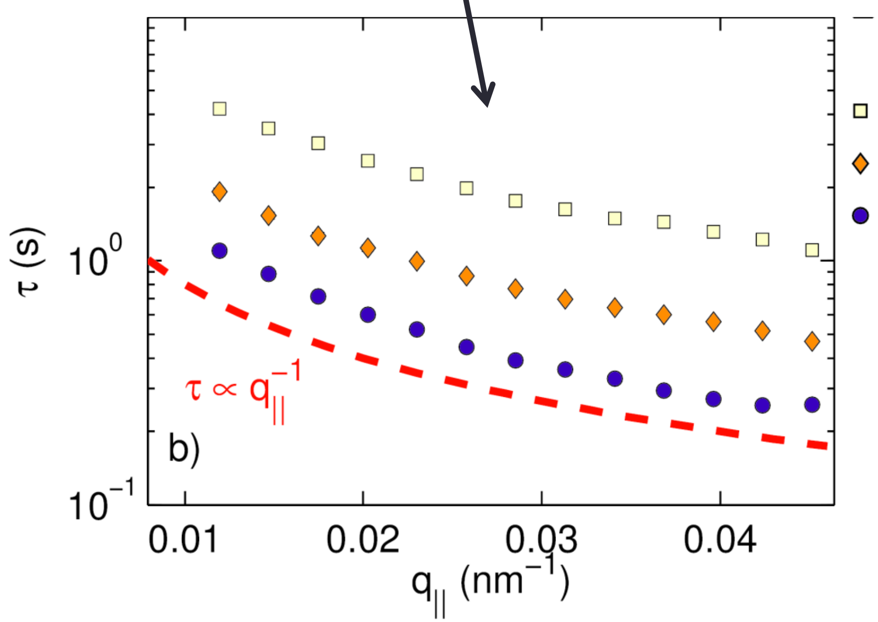
τ and G’ increase in the same way below and above the percolation threshold

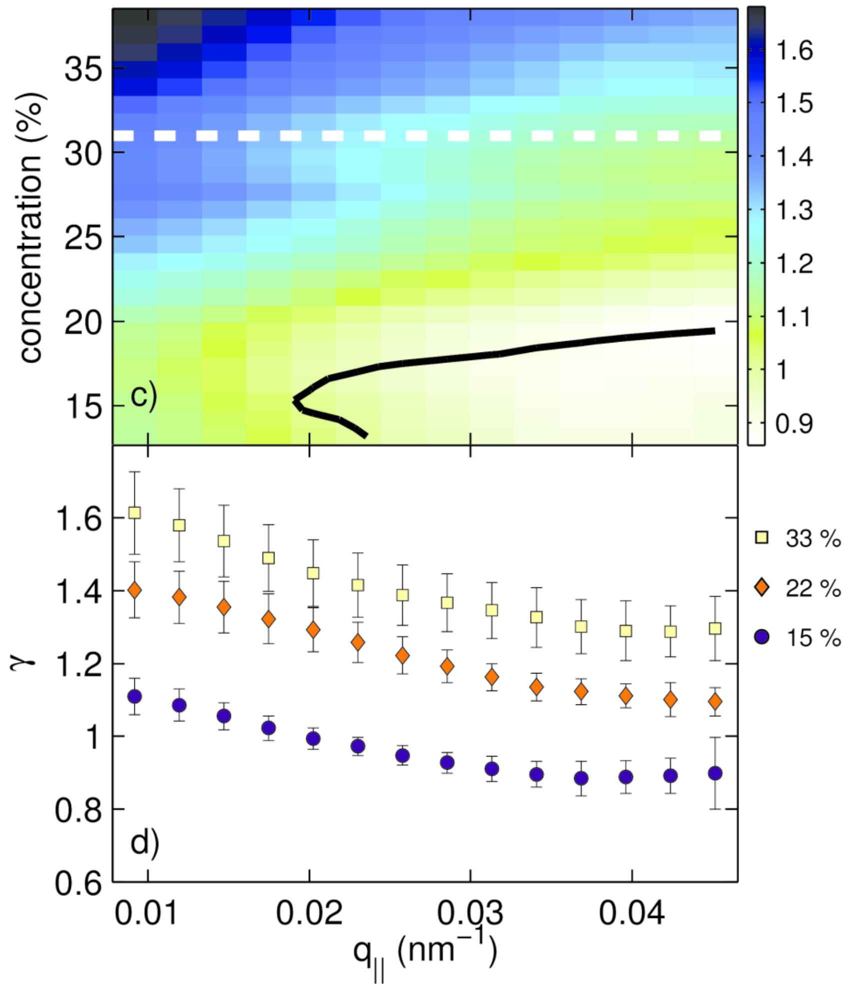
Non-brownian dynamics

Several models have been proposed to explain this behaviour $\gamma \neq 1$

Our data seems to be well described, in particular, by a model proposed bt Duri and Cipelletti: $\tau \propto q_{||}^{-1}$

the compressed shape is due to rare, intermittent rearrangements

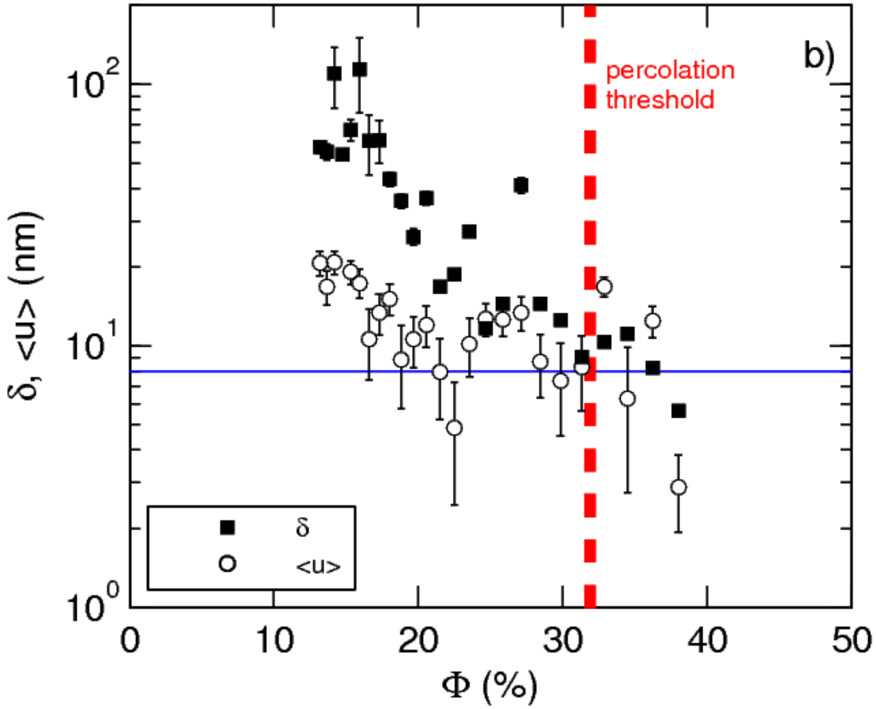




Also found in ageing laponite suspension - R. Angelini et al. **Soft Matter** 9, 10955 (2013)
metallic glasses - B. Ruta et al. **Phys. Rev. Lett.** 109, 165701 (2012)

Intermittent rearranging events

- Slow dinamics ➔ istantaneous, random discrete rearrangements = long range elastic deformation of the gel under the action of dipolar stresses.
- The model predicts $\tau \propto q^{-1}$ and a q-dependent γ: this holds at all concentrations. From the model we extract the characteristic length scale of the random rearrangements δ (building a master curve).

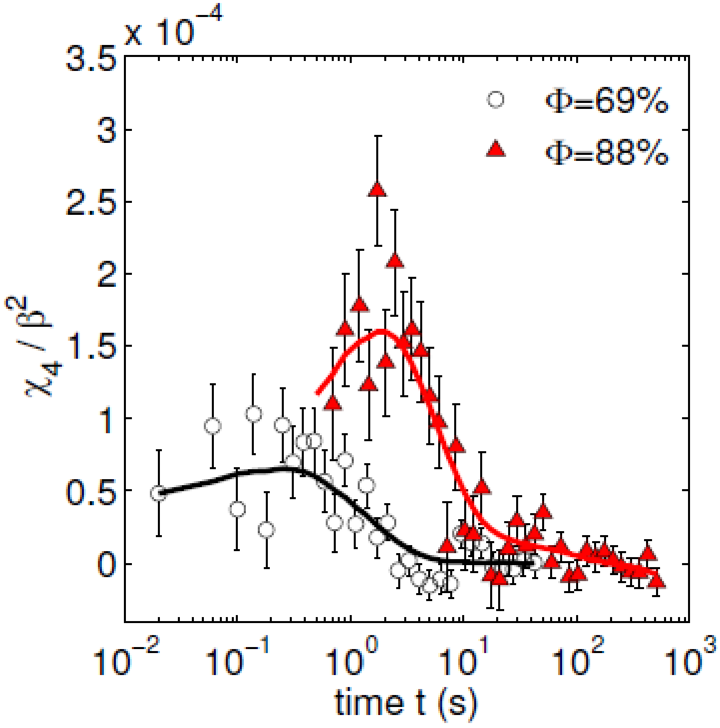


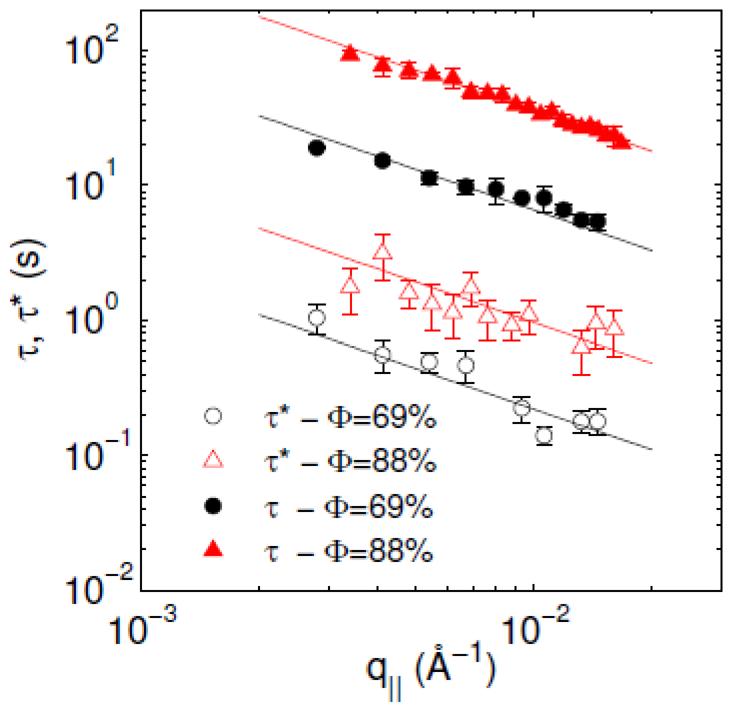
Two different regimes exist, above and below the percolation threshold: below it, the length scales $\langle u \rangle$ and δ of the fast and slow dynamics decouple, while above it they **become equal** within experimental accuracy, and also comparable to the size of the single nanoparticle.

D. Orsi, B. Ruta, Y. Chushkin, A. Pucci, G. Ruggeri, G. Baldi, T. Rimoldi and L. Cristofolini, **submitted to Physical Review E**

Dynamical heterogeneities

Accessed by means of fourth order correlation functions:





At higher Φ:

- Increase in peak - larger Cooperative Rearranging regions
- Slower dynamics

- $\tau^* \propto q^{-1}$
- Faster dynamics than τ

D. Orsi, L. Cristofolini, G. Baldi, and A. Madsen, **Physical Review Letters** 108, 105701 (2012)

Conclusions

We were able to characterize the formation of a two-dimensional gel from different, complementary perspectives:

- Structural
  - – finding analogies with **2D percolation theory**
- Rheological
  - – measuring the **elastic response** commonly found in gels, **even at low concentration**
  - – finding interesting analogies in the concentration dependence of the shear modulus, compared to the one of the internal dynamics
- Dynamical
  - – observing **non-brownian** dynamics taking place on two different spatial scales, that converge as the percolation threshold is reached
  - – characterizing the **dynamical heterogeneities** of the sample

Thank you!

- **Structure of the gel network**
  - D. Orsi, A. Vezzani, R. Burioni, A. Pucci, G. Ruggeri, and L. Cristofolini, **Colloids Surfaces A Physicochem. Eng. Asp.** 441, 912 (2014)

- **Mechanical response**
  - D. Orsi, G. Baldi, P. Cicuta, and L. Cristofolini, **Colloids Surfaces A Physicochem. Eng. Asp.** 413, 71 (2012).

- **Internal dynamics**
  - D. Orsi, L. Cristofolini, G. Baldi, and A. Madsen, **Physical Review Letters** 108, 105701 (2012).
  - D. Orsi, B. Ruta, Y. Chushkin, A. Pucci, G. Ruggeri, G. Baldi, T. Rimoldi and L. Cristofolini, **submitted to Physical Review E**

Intermittent rearranging events

$$g_2(\tau, q) - 1 = \sum_{n=0}^{\infty} P_\tau(n) h(n, q)$$

- Slow dinamics ➔ istantaneous discrete events occurring with Poissonian statistics
- The degree of correlation related to n events at a given q is given by the Fourier transform of the probability distribution function (PDF) of the particle displacements, assuming long range elastic deformation of the gel under the action of dipolar stresses $h(n,q) = \exp[-(qn\delta)^{1.5}]$

Since $PDF \propto \Delta R^{-(1.5+1)}$ for dipolar stresses randomly scattered in space

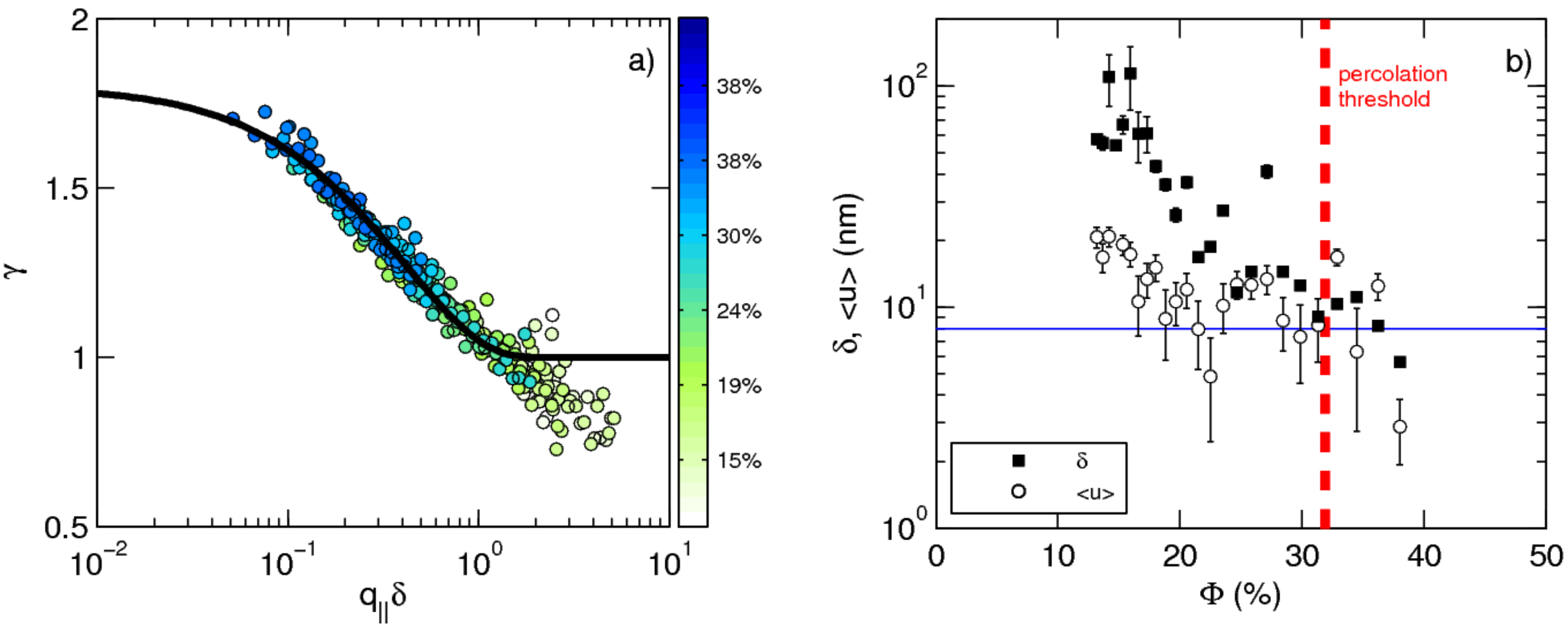
The resulting correlation functions are fitted with stretched exponentials to retrieve the q dependence of the parameters

$q\delta \to 0\colon \gamma = 1.5$ $\qquad$ $q\delta \gg 1\colon \gamma = 1$

[A. Duri and L. Cipelletti, Europhys. Lett. 76, 972 (2006)]

Intermittent rearranging events

The dynamics measured above and below the percolation threshold can be described within the same framework! Therefore, we build a mastercurve.



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