When gels become unstable: Yielding and syneresis in colloidal networks

Jasper van der Gucht

4TU.HTM Meeting
January 2023

WAGENINGEN UNIVERSITY & RESEARCH

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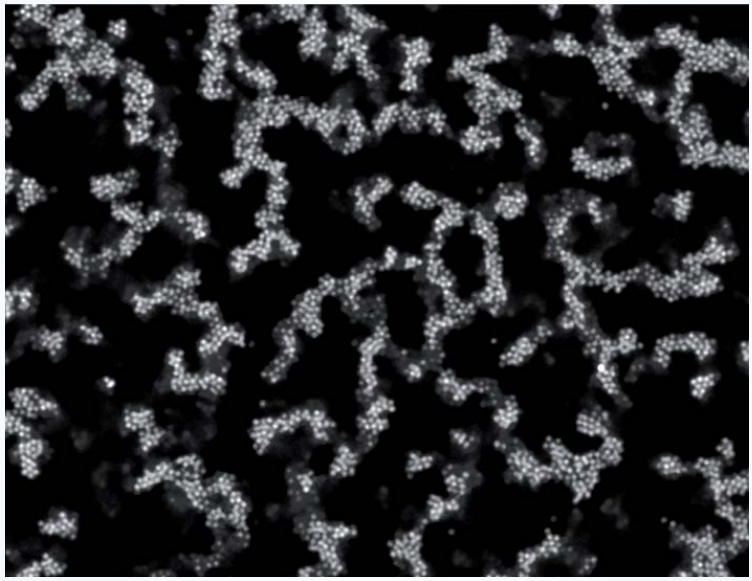
Colloidal gels



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Colloidal gels

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Challenging materials

Heterogeneous

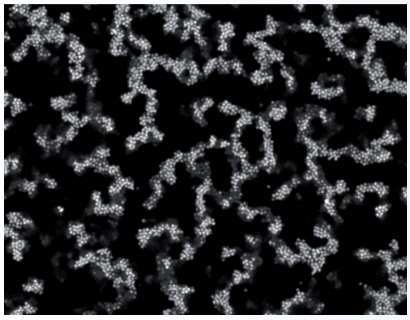
Non-equilibrium

History dependent

Ageing

Between liquid and solid

Fragile



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Outline

1. Introduction: formation of colloidal gels
2. Instability under external stress: yielding
3. Instability under internal stress: syneresis
4. Conclusion and outlook

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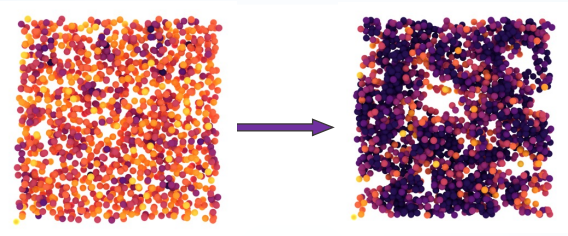
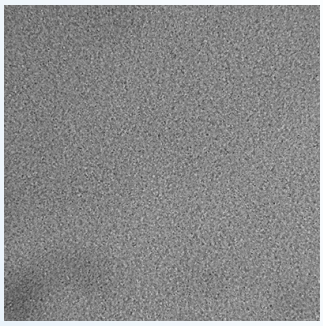
Formation of colloidal gels



Fluid-to-solid transition



Cho et al PRL 2020

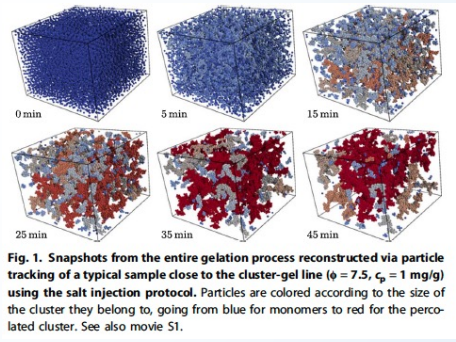


Fig. 1. Snapshots from the entire gelation process reconstructed via particle tracking of a typical sample close to the cluster-gel line ($\phi = 7.5$, $c_p = 1$ mg/g) using the salt injection protocol. Particles are colored according to the size of the cluster they belong to, going from blue for monomers to red for the percolated cluster. See also movie S1.

Tsurusawa et al Sci. Adv. 2019

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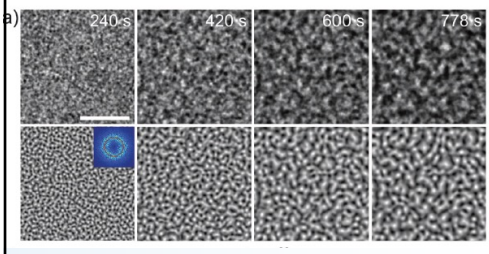
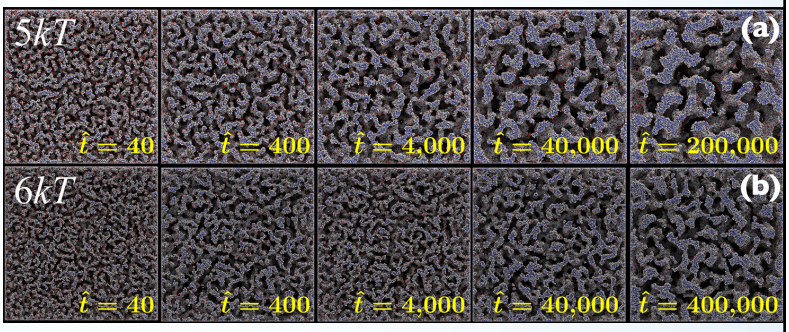
Coarsening



Experiments, Gao et al Soft Matter 2015



Simulations: Zia et al, J. Rheol. , 58(5), 2014

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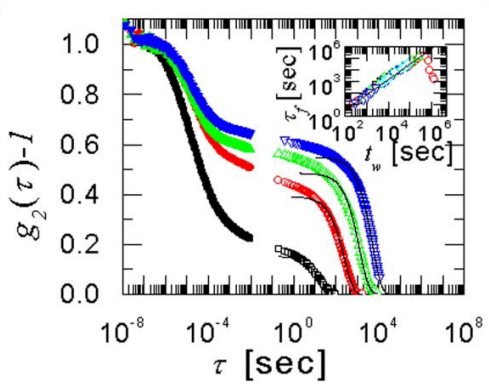
Local particle rearrangements



Ultraslow relaxations measured with DWS

Bissig et al., *PhysChemCom*., 2003.

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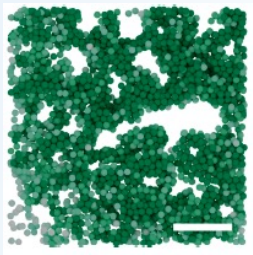
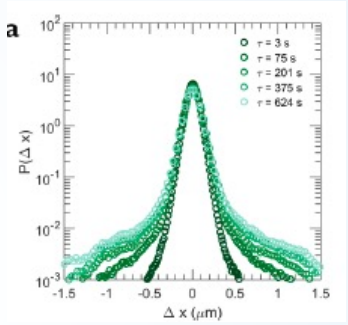
Local particle rearrangements



Particle displacements measured with confocal microscopy

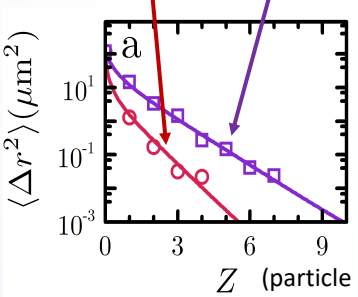
Van Doorn et al., *Phys. Rev. Lett*., 2017
Wu et al. *ACS App. Mat. Int*. 2020



Heterogeneous dynamics!
Wu et al. *ACS App. Mat. Int*. 2020

Strong attraction

Weak attraction



Van Doorn et al., *Phys. Rev. Lett*., 2017

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Mechanical failure of colloidal gels

Brittle failure in colloidal concrete (Breskens)

Ductile failure in cheese

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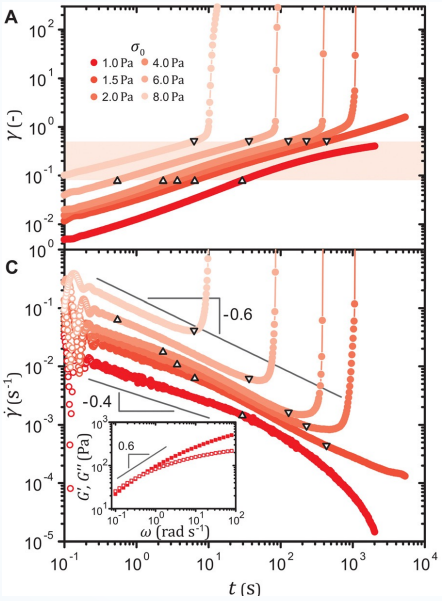
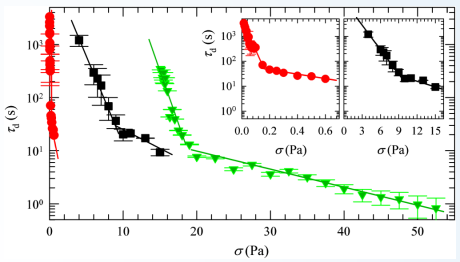
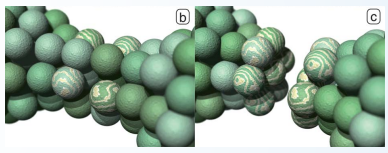
Yielding under stress

Constant stress







Sprakel et al., *PRL 2011*

Cho et al., *Soft Matter*., 2022
Grenard et al. *Soft Matter* 2014.

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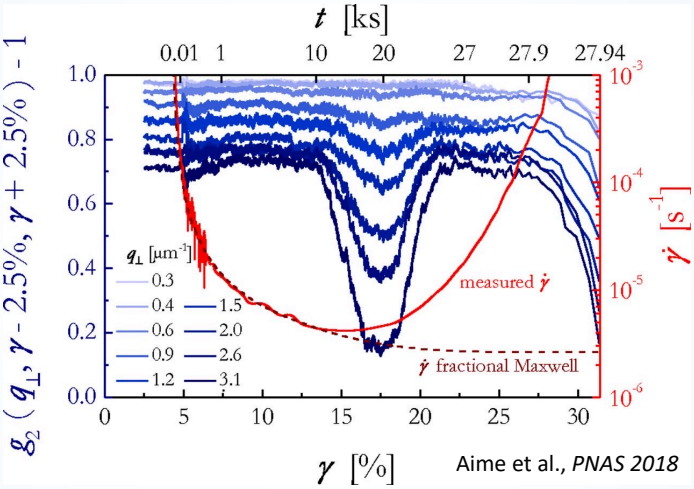
Yield precursors



Aime et al., *PNAS 2018*

What are these precursors?

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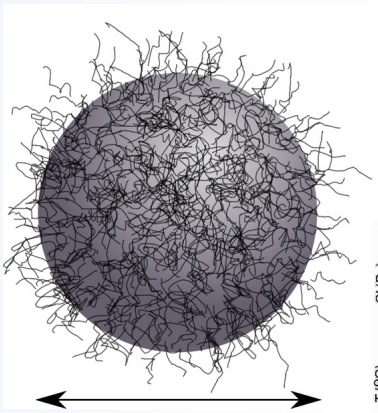
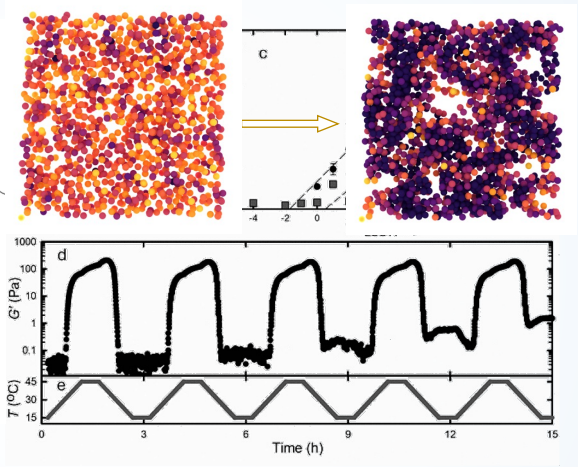
Model colloidal gels



$d \approx 90nm$



Kodger, T. E., & Sprakel, J. (2013).. *Advanced Functional Materials*, *23*(4), 475-482.

Thermoresponsive surfactant:
$U > 50\ kT$ at high T

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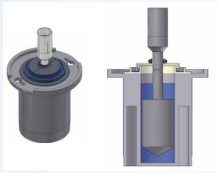
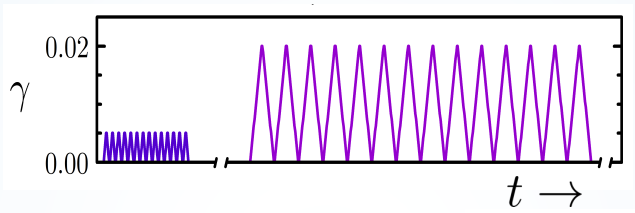
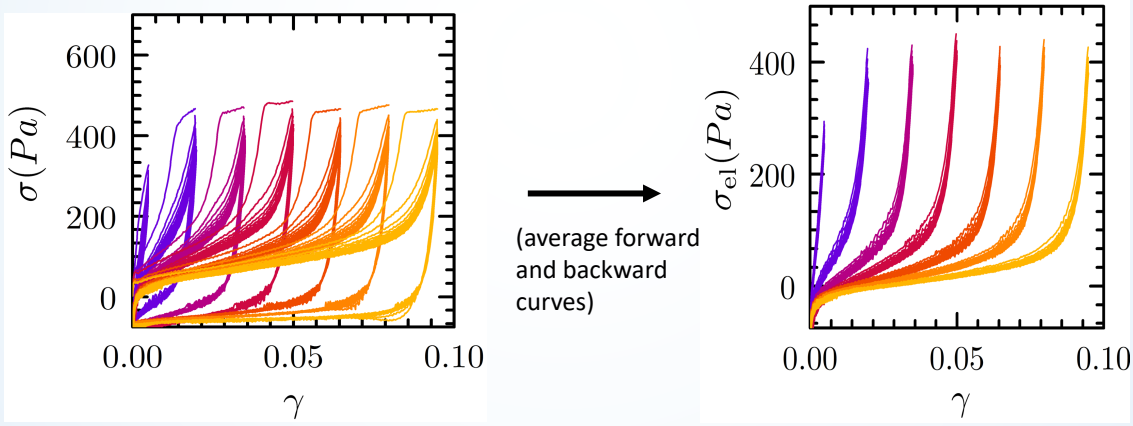
Cyclic deformations







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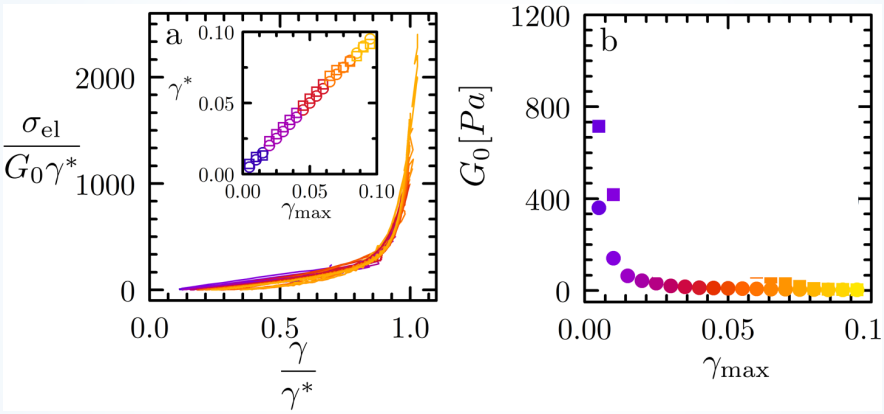
Data collapse



Plastic rearrangements lead to softening

van Doorn et al., Phys. Rev. Lett, 2018

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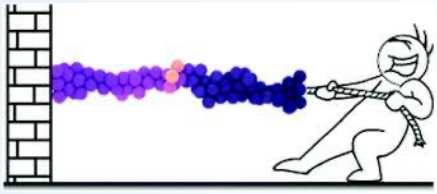
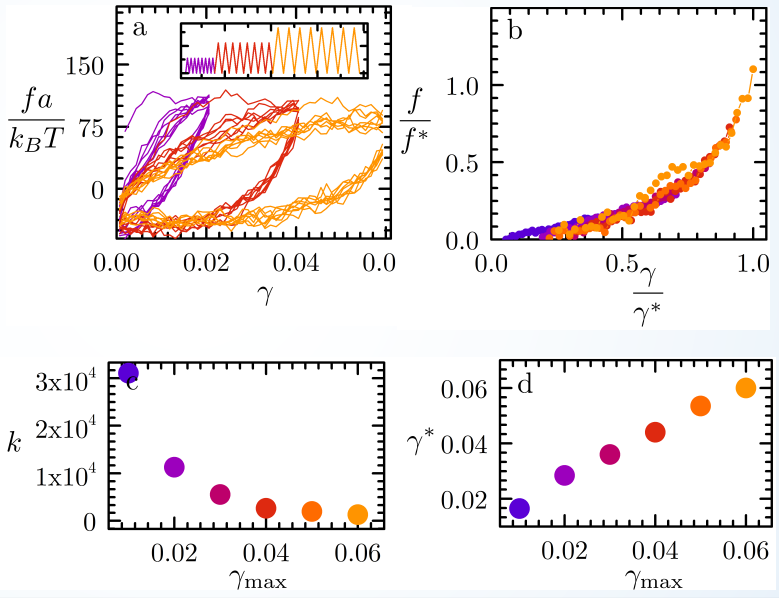
Single gel strand





van Doorn et al., *Phys. Rev. Lett*, 2018
Verweij et al. *Soft Matter* 2019

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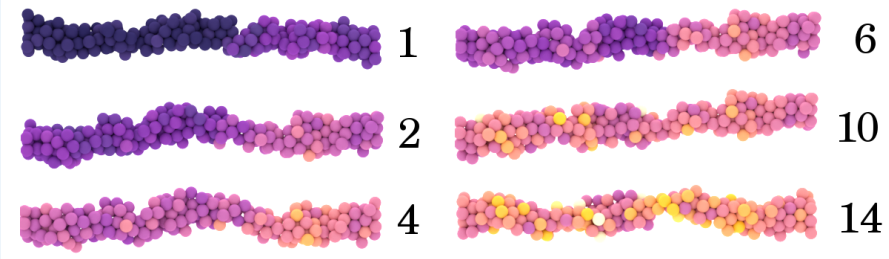
Single strand plasticity

Cumulative Plastic Deformation



increasing plasticity

Necking eventually leads to rupture

van Doorn et al., *Phys. Rev. Lett*, 2018
Verweij et al. *Soft Matter* 2019

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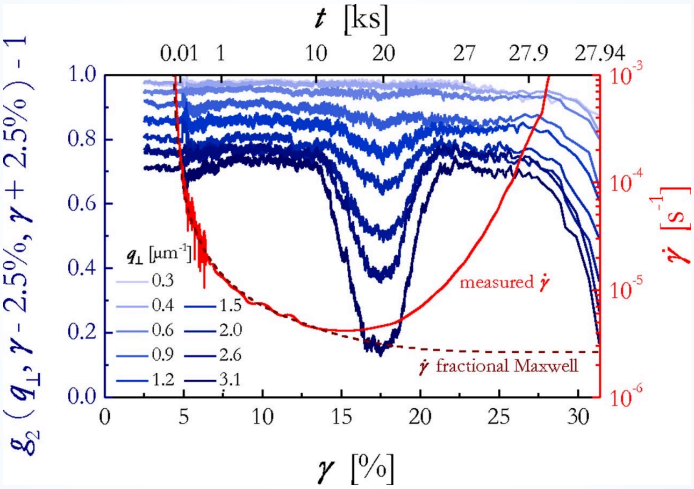
Plastic rearrangemnets precede yielding



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Syneresis

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Syneresis in low fat mayonnaise

Soft Matter

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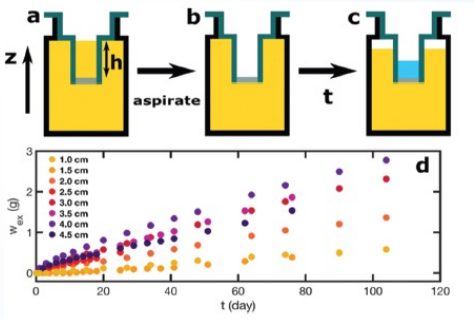
Cite this: *Soft Matter*, 2019, **15**, 9474

Gravity-driven syneresis in model low-fat mayonnaise†

Qimeng Wu,[a] Melle T. J. J. M. Punter,[b] Thomas E. Kodger,[a] Luben Arnaudov,[c] Bela M. Mulder,[b] Simeon Stoyanov[ac] and Jasper van der Gucht*[a]



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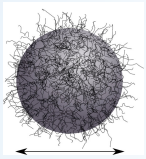
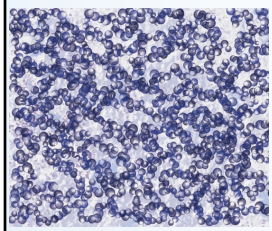
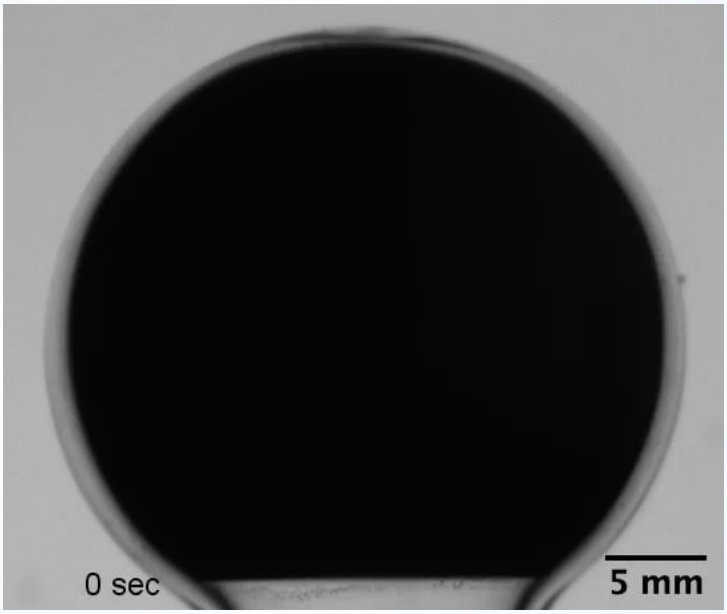
Spontaneous syneresis of a model colloidal gel



Density matched, coated with thermoresponsive surfactant





Wu et al., *PRL*, 2020

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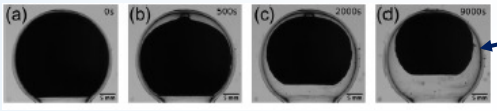
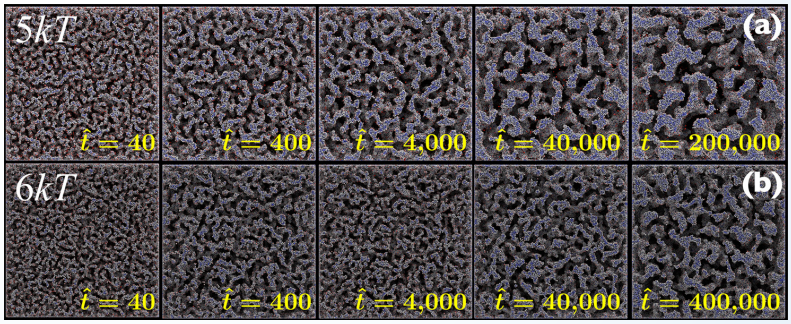
Syneresis is driven by internal stresses



Container wall coated with polyelectrolyte multilayer (weaken adhesion)



Coarsening (Zia et al 2014)

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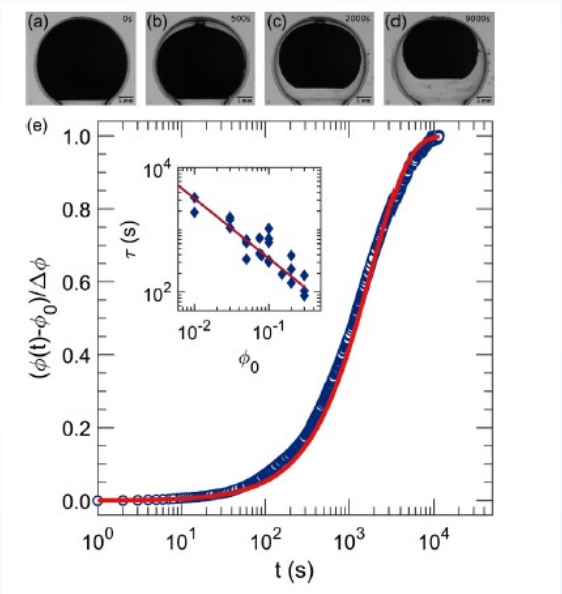
Compaction dynamics



$$\frac{\phi(t)-\phi_0}{\Delta\phi} = 1-\exp(-t/\tau)$$

$$\tau \sim \phi_0^{-1}$$

Wu et al., *PRL*, 2020

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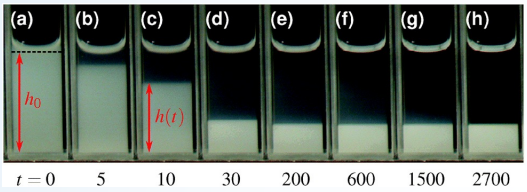
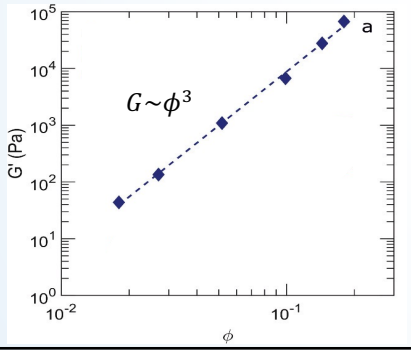
Collapse under gravity



(Harich et al. 2016)



From Manley et al. PRL 2005:

Poro-elastic process: stress is balanced by Darcy pressure and network elasticity

$$h_0 - h(t) = \Delta h(1 - e^{-t/\tau})$$

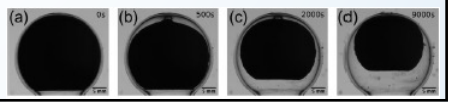
$$\tau = \frac{4\eta(1-\phi)h_0^2}{\pi^2 k_0 E}$$

$k_0 \sim \frac{a^2}{\phi^{2/(3-d_f)}}$ permeablity of the gel

$d_f \approx 1.9$: fractal dimension

Assume compression modulus $E \sim G \sim \phi^3$

$\longrightarrow$ $\tau \sim \phi^{-1.1}$



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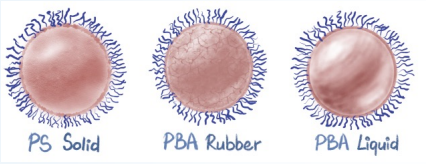
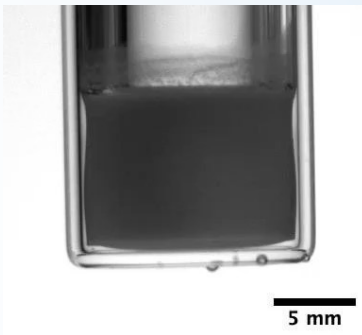
Droplet versus particle gels



Hard solid Soft solid Liquid

Same interparticle potential!

Solid



Liquid

Wu et al., *PRL*, 2020

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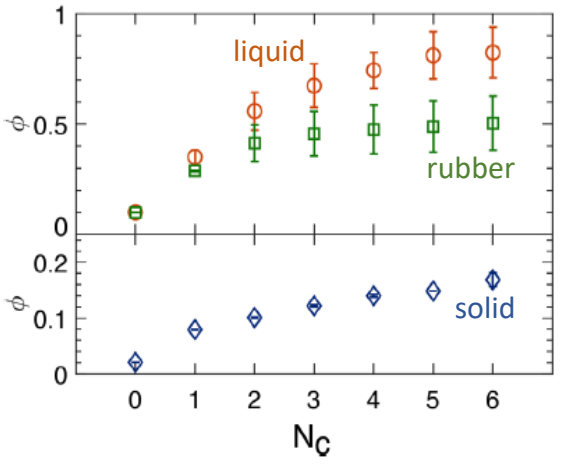
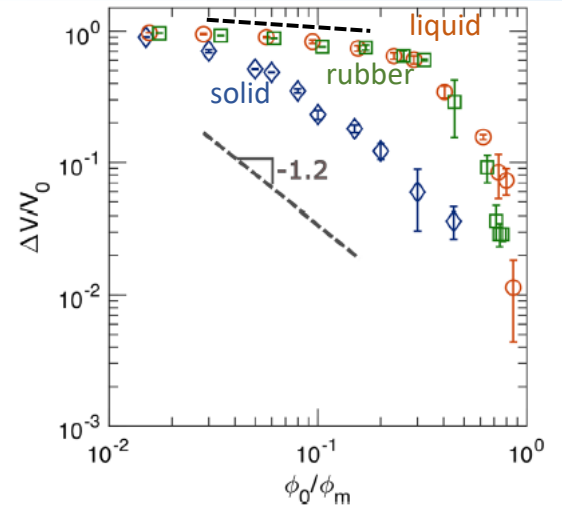
Final extent of syneresis



Repeated cooling-heating cycles



Wu et al., *PRL*, 2020

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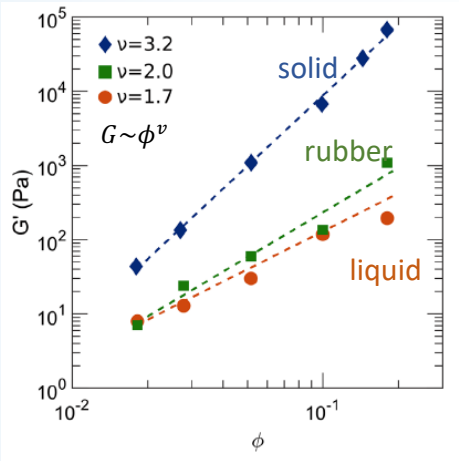
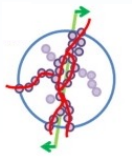
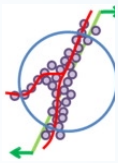
Relation to different modes of supporting stress



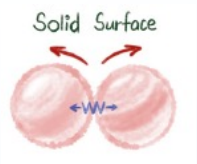


Strand bending:
$\nu \approx 3.2 - 3.8$

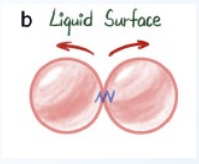


Strand stretching:
$\nu \approx 1.6 - 2.1$

Sahimi et al., *PRB*, 1998
Oliveira Reis *JCIS* 2018



Solid surfaces give
bending resistance



Slippery surfaces give
no bending resistance

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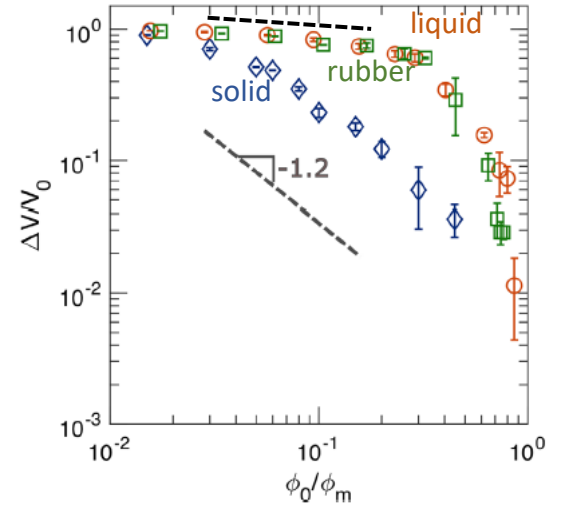
Relation to different modes of supporting stress



Assume compresive pressure $P \sim B_2\phi^2$ $(B_2 < 0)$

Leads to compression $\Delta V/V_0 \approx -P/E$

With bulk modulus $E \sim G$

Solid: $G \sim \phi^{3.2}$ $\rightarrow \Delta V/V_0 \sim \phi^{-1.2}$

Liquid: $G \sim \phi^2$ $\rightarrow \Delta V/V_0 \sim \phi^0$

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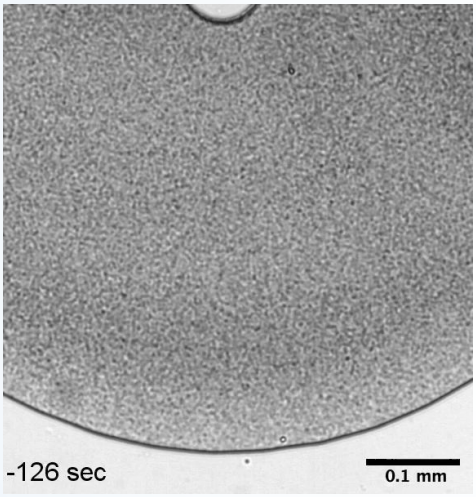
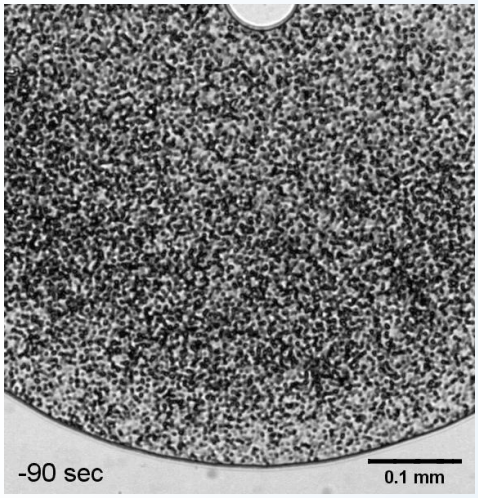
Microscopic picture



Solid



Liquid

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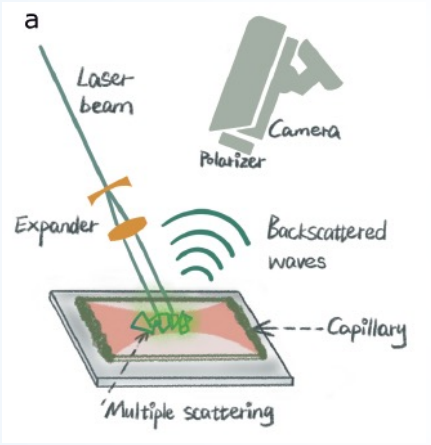
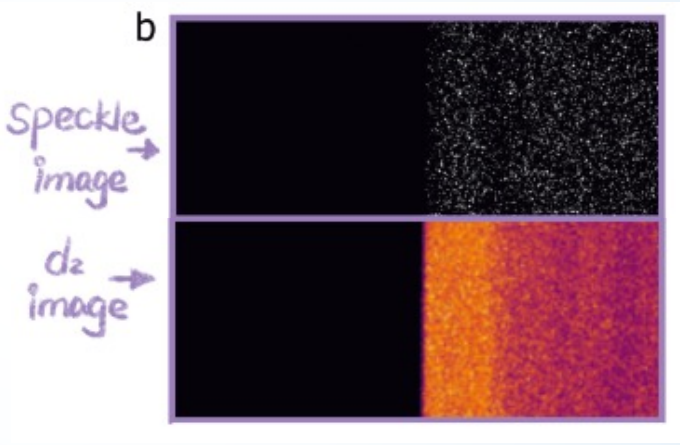
Laser speckle imaging of syneresis





$$d_2(t,x,y,\tau) = \frac{\langle [I(t,x,y) - I(t+\tau,x,y)]^2 \rangle}{\langle I(t,x,y) \rangle \langle I(t+\tau,x,y) \rangle}$$

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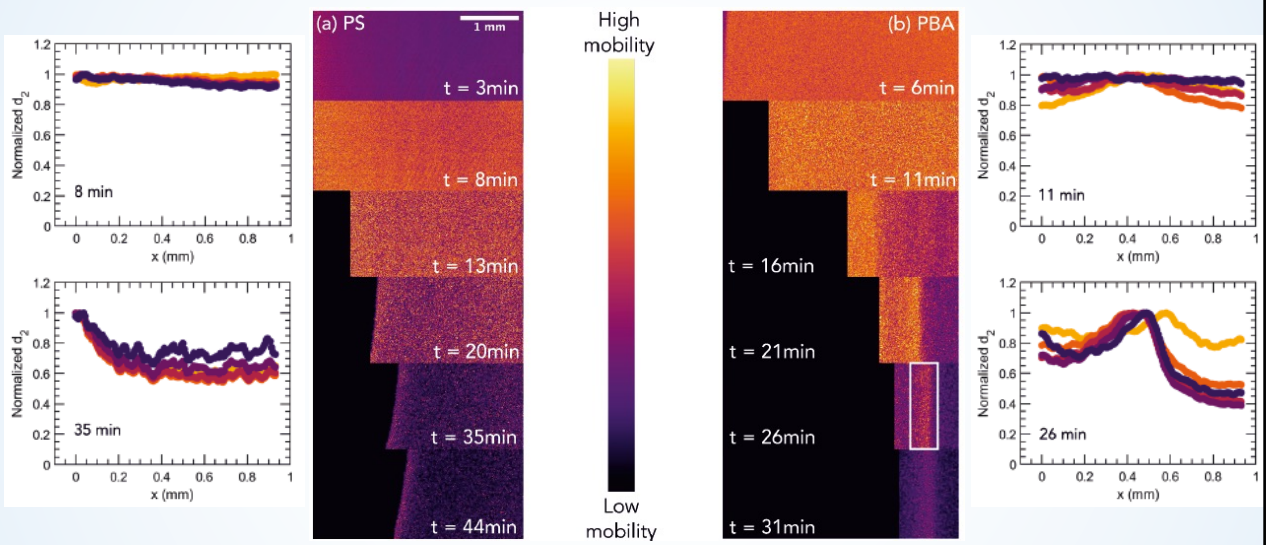
Laser speckle imaging of syneresis



Solid — Homogenous contraction

Liquid — Dynamic ‘band’

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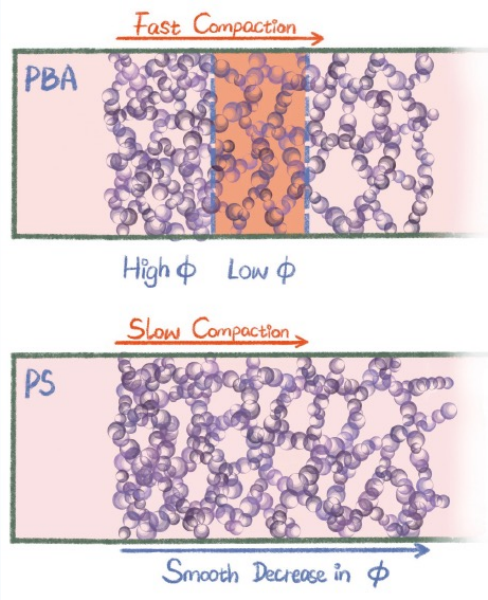
Laser speckle imaging of syneresis



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Ongoing work

Article | Open Access | Published: 13 July 2021

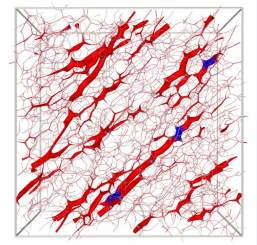
Life and death of colloidal bonds control the rate-dependent rheology of gels

Mohammad Nabizadeh & Safa Jamali

Nature Communications **12**, Article number: 4274 (2021) | Cite this article

Can we identify which bonds are breaking / forming and how this affects network topology?

How does the topology relate to stress distributions?



Colombo, Degado et al. PRL (2014)

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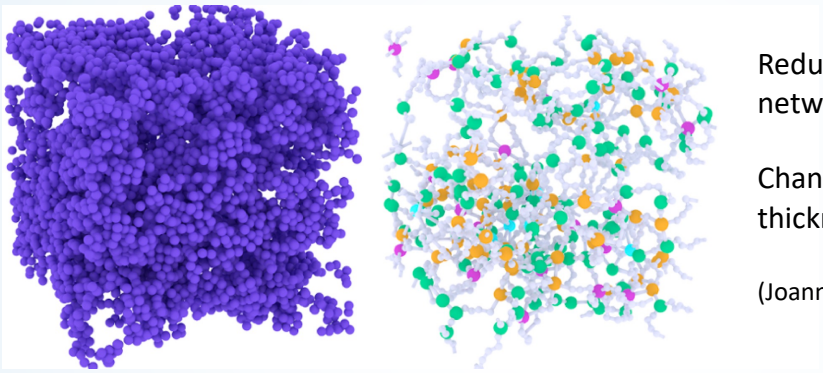
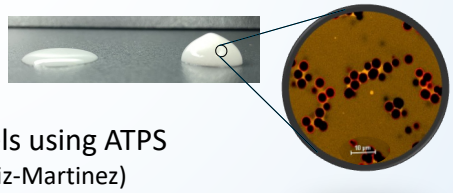
Ongoing work: network topology



Reduction alogorithm to obtain network topology

Changes in toplogy, strand thickness, length, number, etc

(Joanne Verweij, Berend van der Meer)



Capillary gels using ATPS
(Leonardo Ruiz-Martinez)

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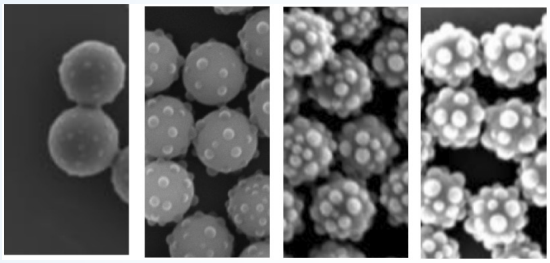
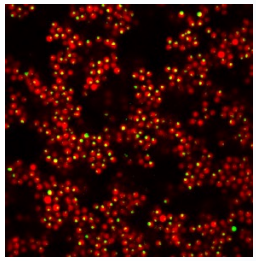
Ongoing work: rough particles





Berend van der Meer with Roel Dullens (Nijmegen)

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Conclusions

- Colloidal gels are marginally stable soft solids
- Yielding (solid-to-fluid transition) is preceded by large plastic rearrangements that soften the gel
- Internal stresses can lead to collapse, called syneresis
- The particle surface matters: solid particles give more stable gels than rubbery particles or liquid droplets

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