Syneresis of colloidal dispersions

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Project objectives

1. Develop a numerical simulations approach to study syneresis in colloidal gels.

2. Identify the variables (microscopic and/or collective) controlling extent and rate of gel shrinkage.

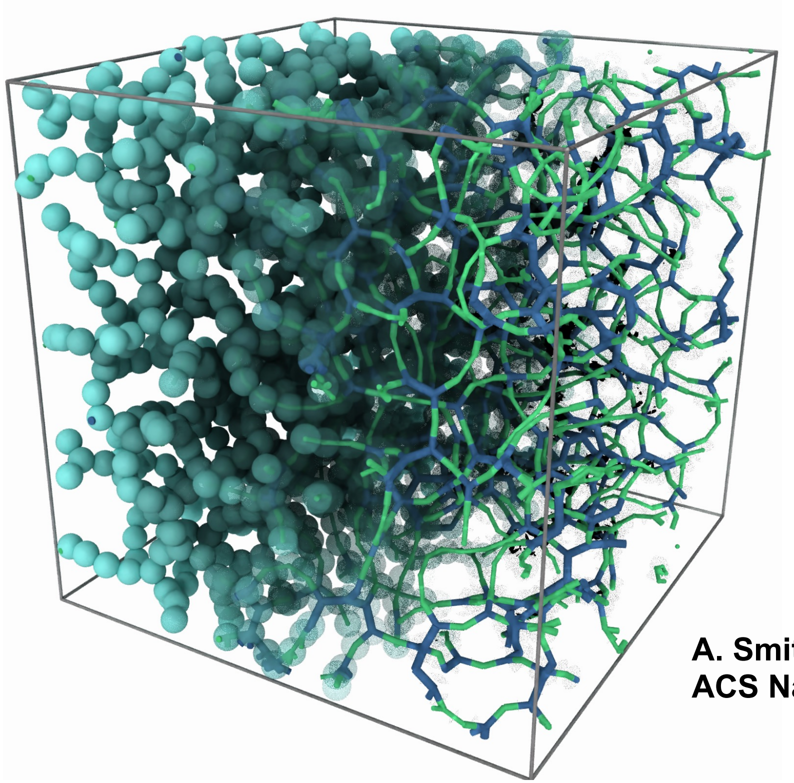
3. Use control variables to manipulate gel evolution. Devise strategies to reduce, eliminate, or enhance syneresis.

4. Investigate relationship between syneresis and delayed collapse or consolidation, to achieve a comprehensive understanding of particle gels instabilities.

Feedback with experimental and industrial partners
Experiments: Jan Vermant, Lilian Hsiao…

Motivation

- What are the variables controlling the extent and the rate of the gel shrinkage?
  - Interparticle contacts evolve and age, under different environmental conditions.
  - Key unknown: changes in the particle contacts and in the forces acting on them translate into stress redistribution triggering changes in the gel structures at larger scales.

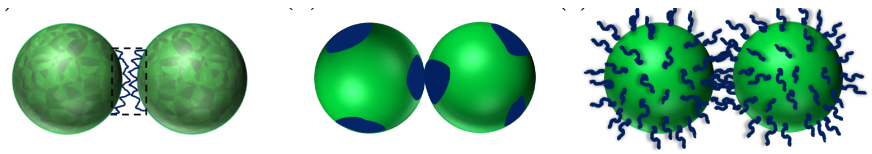


A. Smith et al., ACS Nano 2024

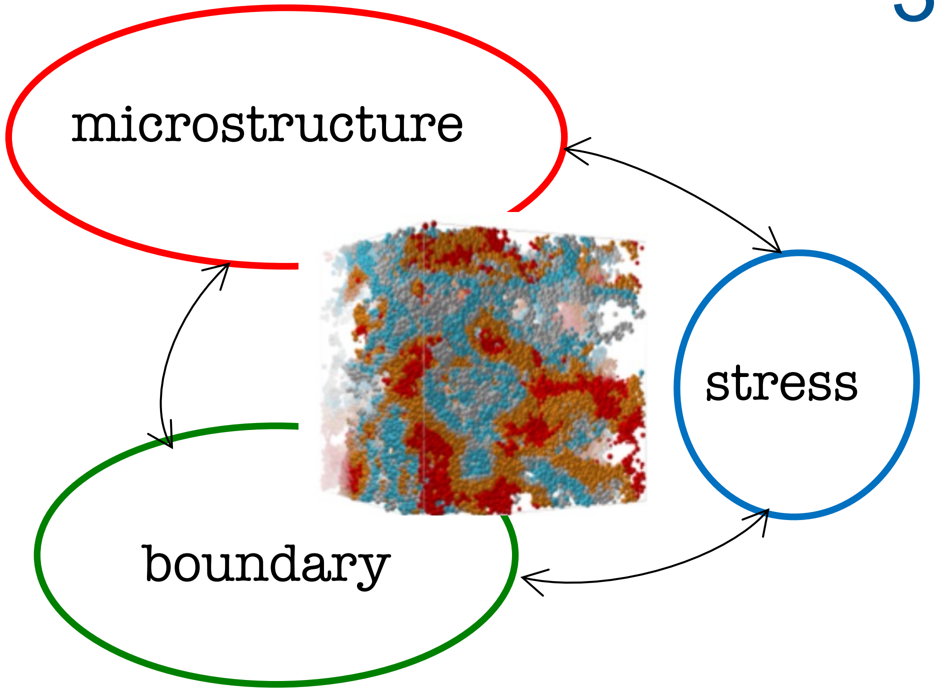
- Microscopic simulations to disentangle dynamical processes at the particle-level (single bond-breaking or forming) and large scale reorganization at level of the network structure (gel shrinkage).

General concept and workflow

- Build model gel structures representative of experimental systems. Coarse-grained models.



- Non periodic boundary conditions to introduce confinement and surface effects.



- Prepare stress structures with specific stress states and heterogeneities. Have interparticle contacts and particle-walls contacts evolve over time.
- Analyze changes in local stresses, dynamical processes, structural evolution over time. Identify underpinnings of shrinkage and contraction.

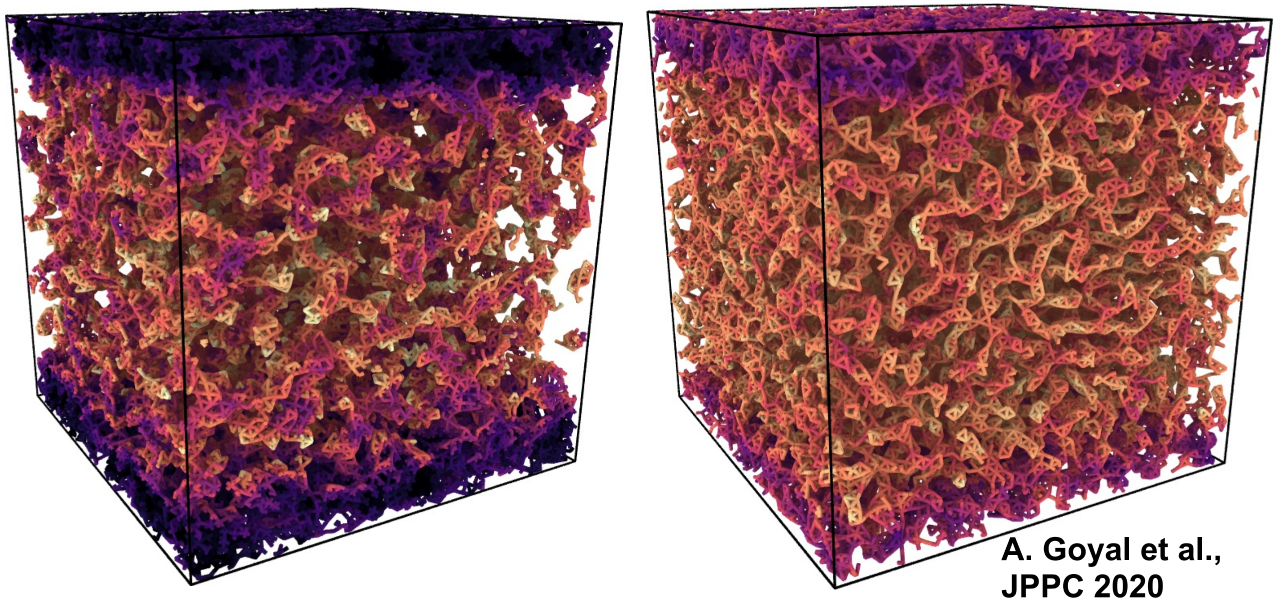
Year 1: Fall 2024 – Spring 2025

- Gel structures with smooth particles and rough particles

  Prepare stress structures with specific stress states and heterogeneities

- Introduce walls and confinement. Smooth/rough boundaries, short/long-range interactions.

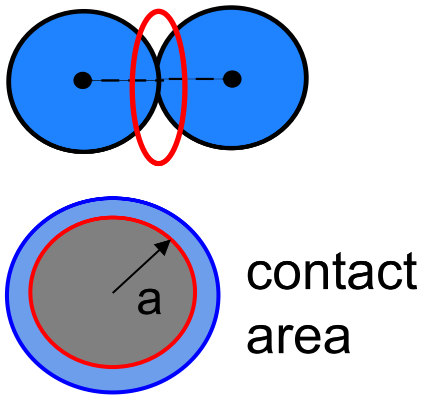
- Quantify rearrangements, changes in network topology. NAR spatial maps. Correlations with syneresis.



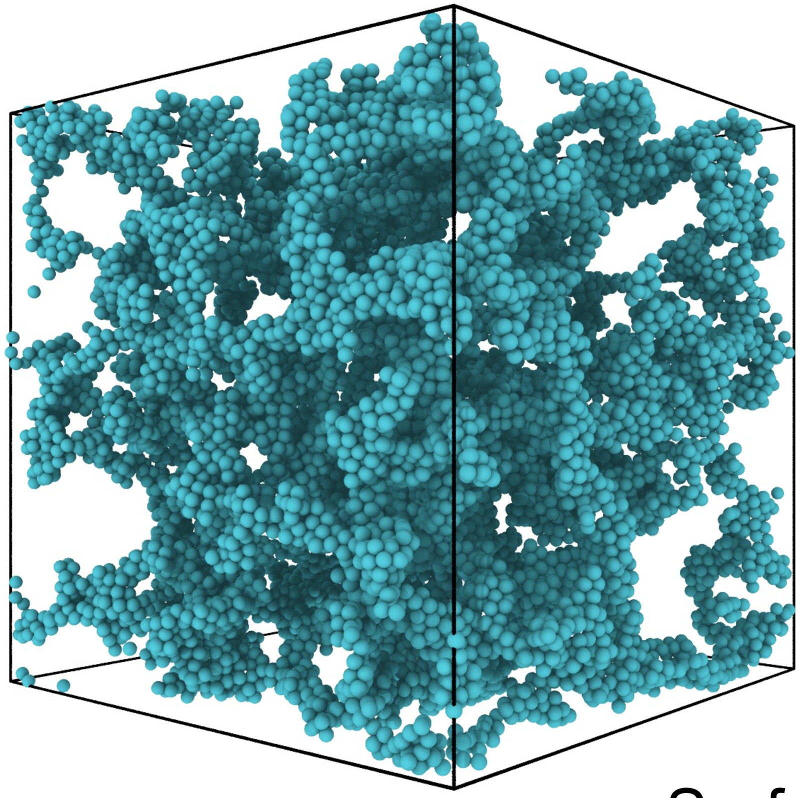
A. Goyal et al., JPPC 2020

- Connection with Hsiao and Vermant experiments.

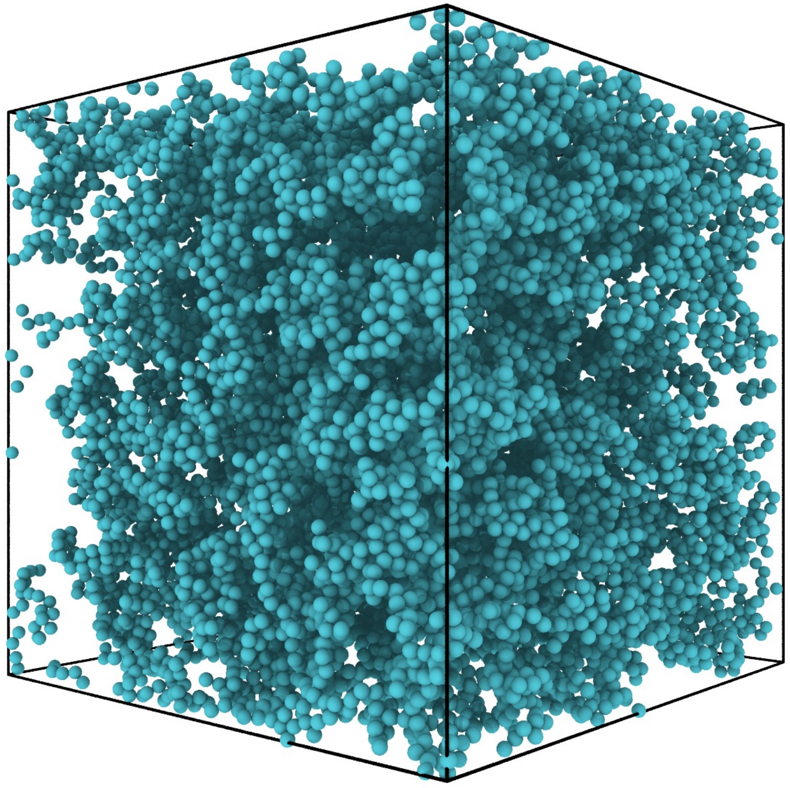
Year 1 – Solid contact models



Hertz contact + surface forces DMT-model for cohesive grains



Hertzian contact + adhesion (JKR)

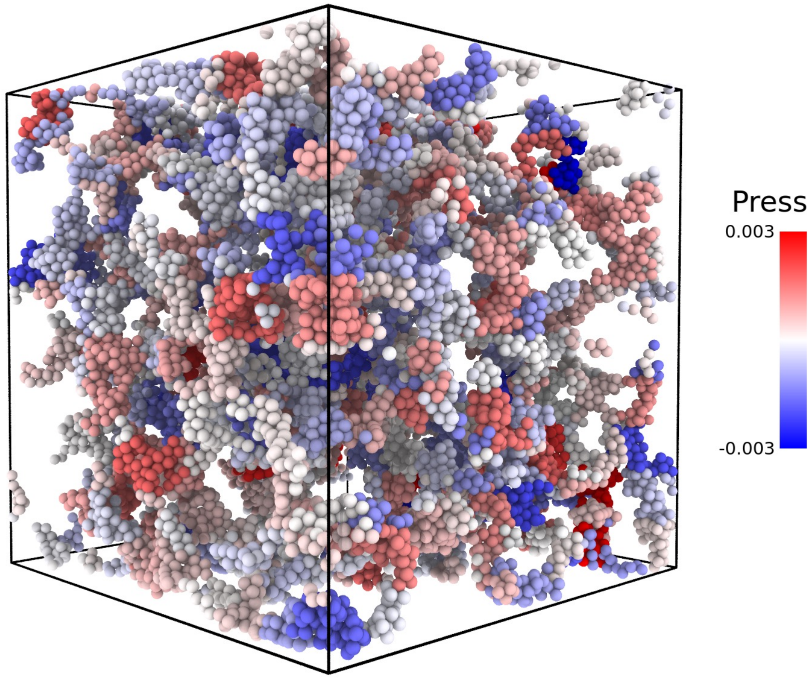


Surface roughness: sliding and rolling friction

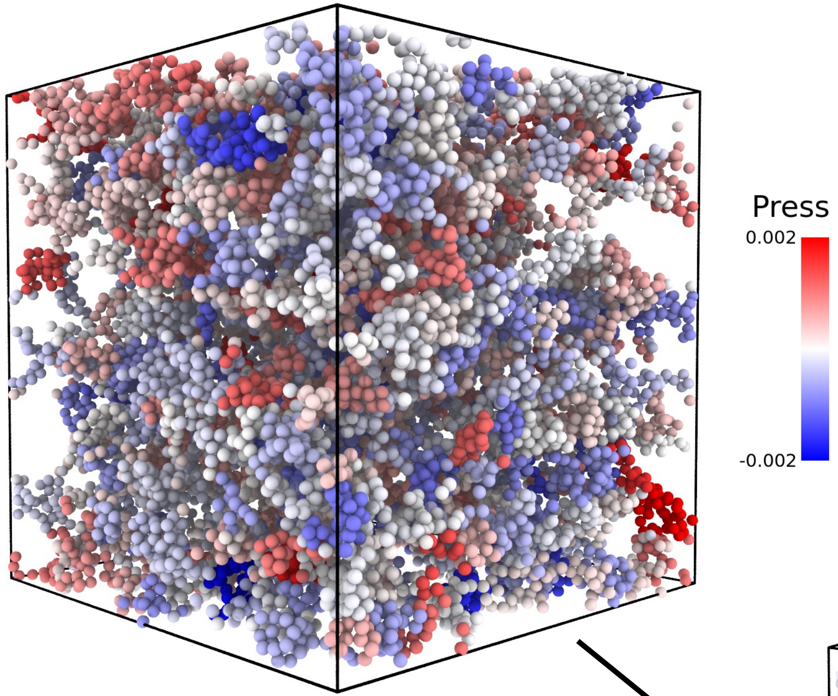
Volume fractions 10-30%, varying adhesion strength, varying gelation kinetics.
Characterization of stress distributions, with different model interactions.

Derjaguin, Muller, Toporov, J. Colloidal and Interface Sci. **53** (1975)
Johnson, Kendall, Roberts, Proc. R. Soc. Lond A. **324** (1971)

Year 1 – Structures and stress heterogeneities



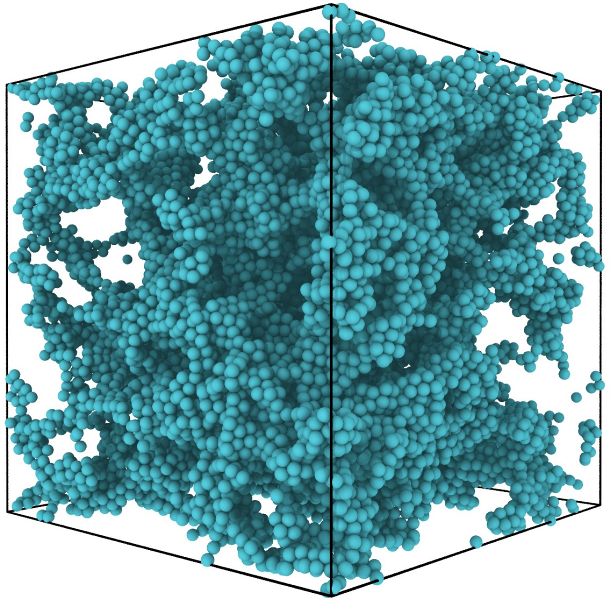
DMT



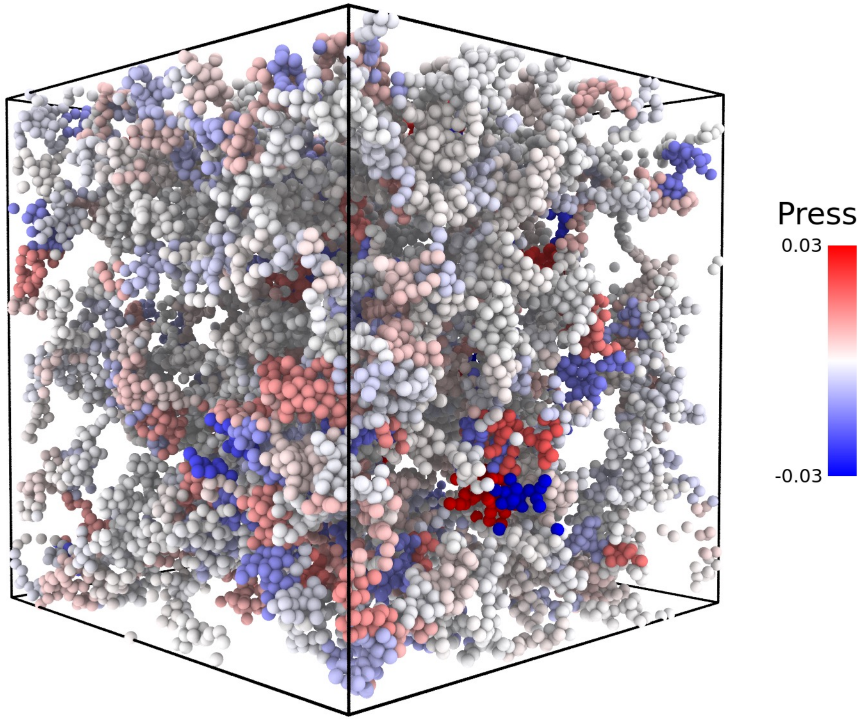
JKR

Similar parameter choices, different coexistence of compressive and tensile stresses.

Increasing volume fraction

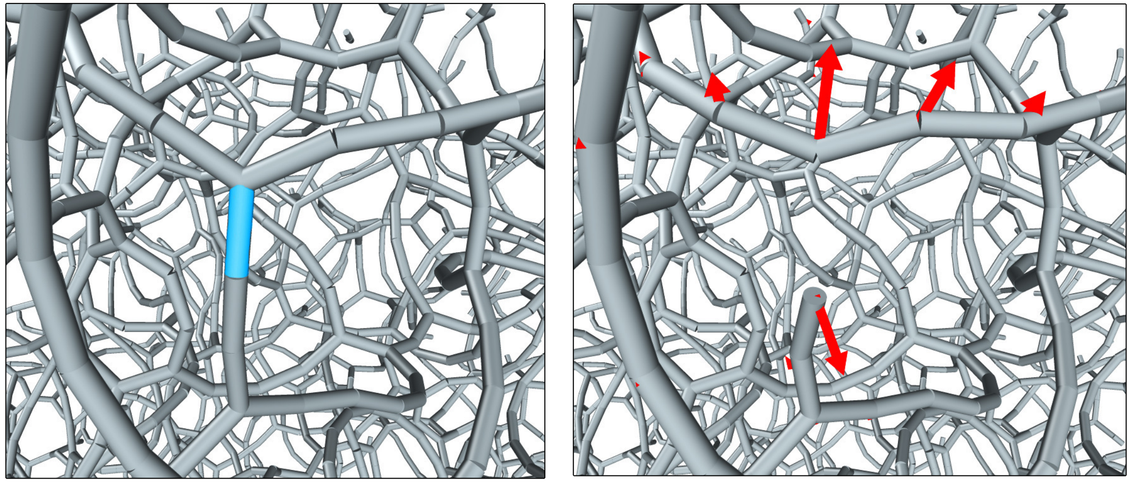


Increasing adhesion strength



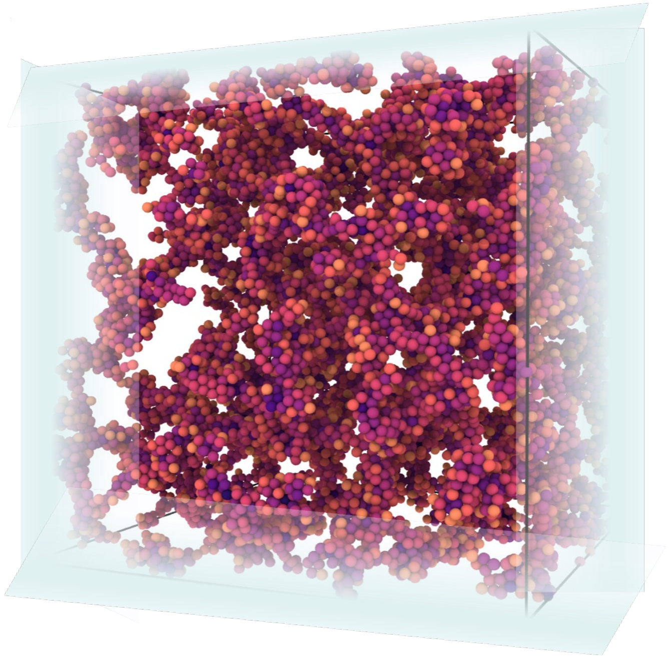
Year 1 – Work in progress

Bouzid et al., Nature Comm. 2017



Design of tests to establish tendency to syneresis:

- Scan internal stresses and remove bonds where stresses are higher: does this trigger syneresis?
- Release the fixed volume constraint: does the gel shrink?



Introduce walls and confinement:

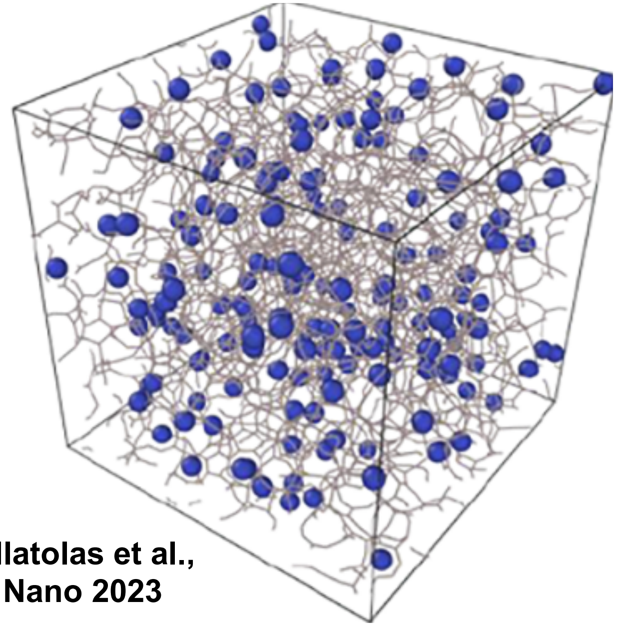
- Stress structures with specific stress states and heterogeneities, with confinement and different particle-wall interactions: what is the impact on syneresis tendency?
- Interparticle contacts and particle-walls contacts evolve over time.

Year 2

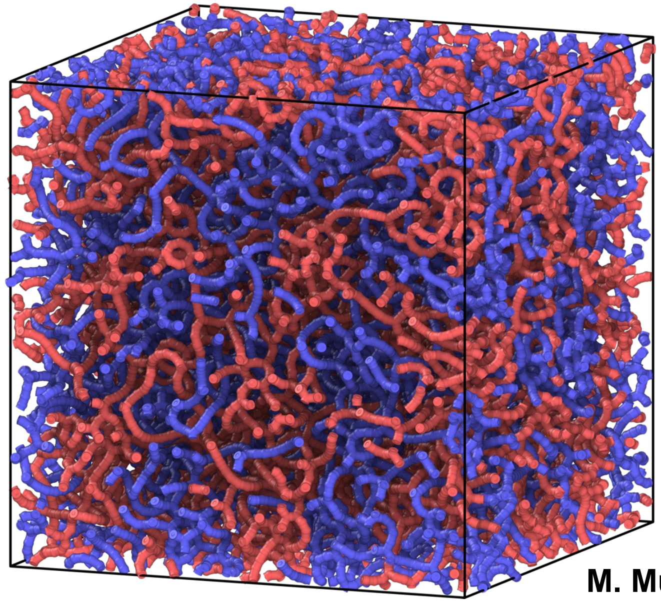
Syneresis reduction strategies:

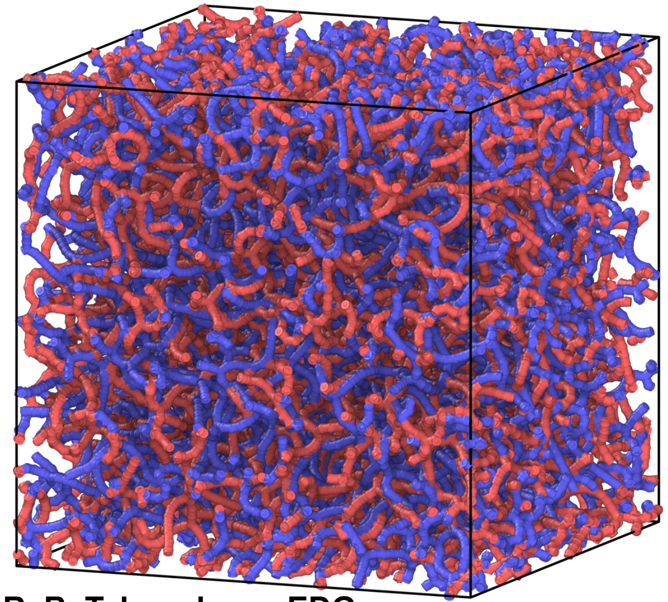
- Relax internal stresses and reduce stress heterogeneities through cyclic deformation. Create more mechanically stable configurations. Mimic ultrasound (Hsiao).

- Introduce fillers and produce interpenetrated networks.



I. Dellatolas et al., ACS Nano 2023





M. Mugnai, R. B. Tchuenkam , EDG PNAS 2025

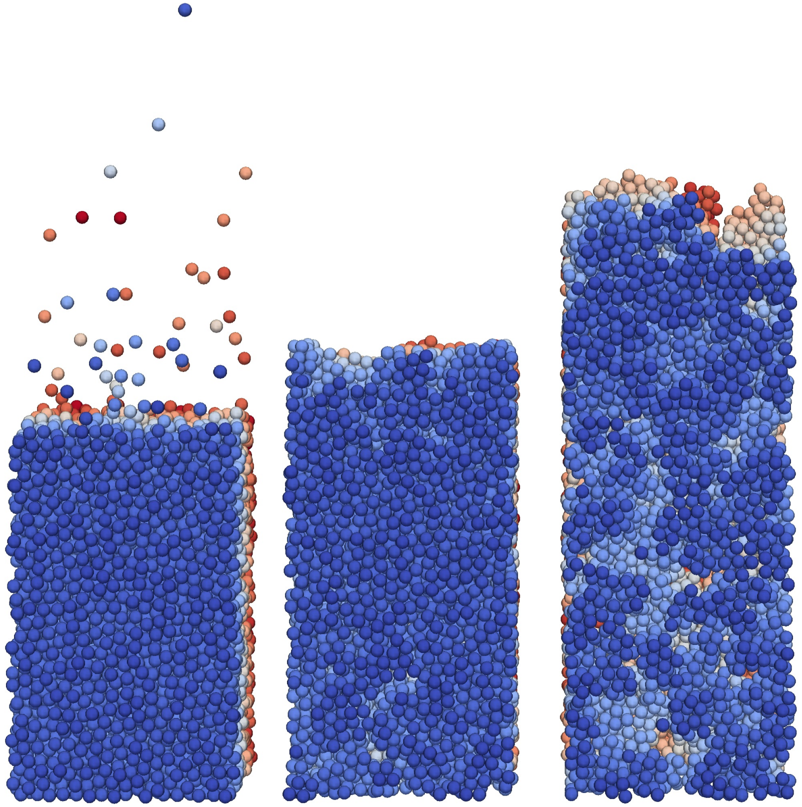
Year 3

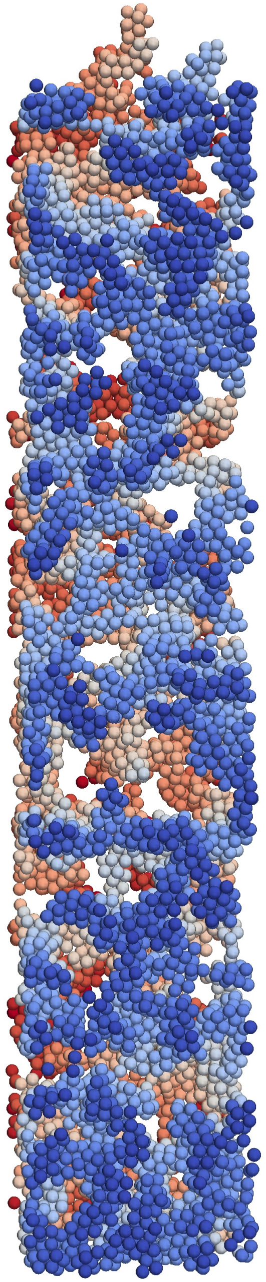
Syneresis, delayed collapse, and consolidation

- Initiate syneresis, collapse, and consolidation in the same structures by changing interactions in the bulk and at the walls.

- Compare control variables, microscopic changes, precursors, and dynamics.

- Implications for macroscopic behavior, rheology to propose rheological diagnostics.





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