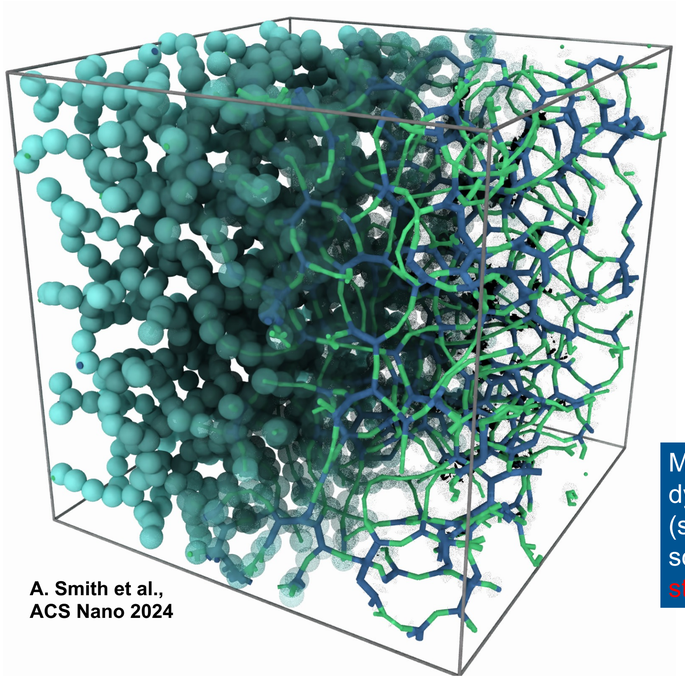
Syneresis of Colloidal Dispersions

Logan Bayer, Vinutha H. A., and Emanuela Del Gado

Department of Physics and Institute for Soft Matter Synthesis and Metrology, Georgetown University, Washington DC

The shelf-life of colloidal gel products is often limited by syneresis, where the gel structure remains largely intact but shrinks and contracts. expelling a small volume fraction of a dilute particle phase. It is clear that the nature of the interparticle contacts and their evolution, or aging, under different environmental conditions, plays a central role in this phenomenon, however there is still limited understanding of the variables controlling the extent and the rate of the gel shrinkage. A key unknown is how 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.

Yogurt – 5/16/2025



A. Smith et al., ACS Nano 2024

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.

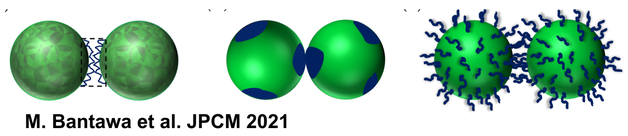
Microscopic simulations can disentangle dynamical processes at the particle-level (single bond-breaking or forming) and large scale reorganization at level of the network structure (gel shrinkage).

Objectives

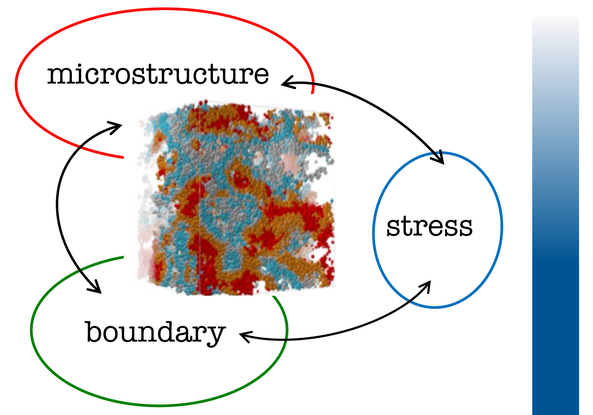
- Develop a numerical simulations approach to study syneresis in colloidal gels.
- Identify the variables (microscopic and/or collective) controlling extent and rate of gel shrinkage.
- Use control variables to manipulate gel evolution. Devise strategies to reduce, eliminate, or enhance syneresis.
- Investigate relationship between syneresis and delayed collapse or consolidation, to achieve a comprehensive understanding of particle gels instabilities.

General concept and workflow

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



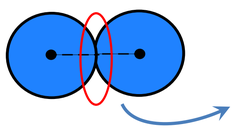
M. Bantawa et al. JPCM 2021



- 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

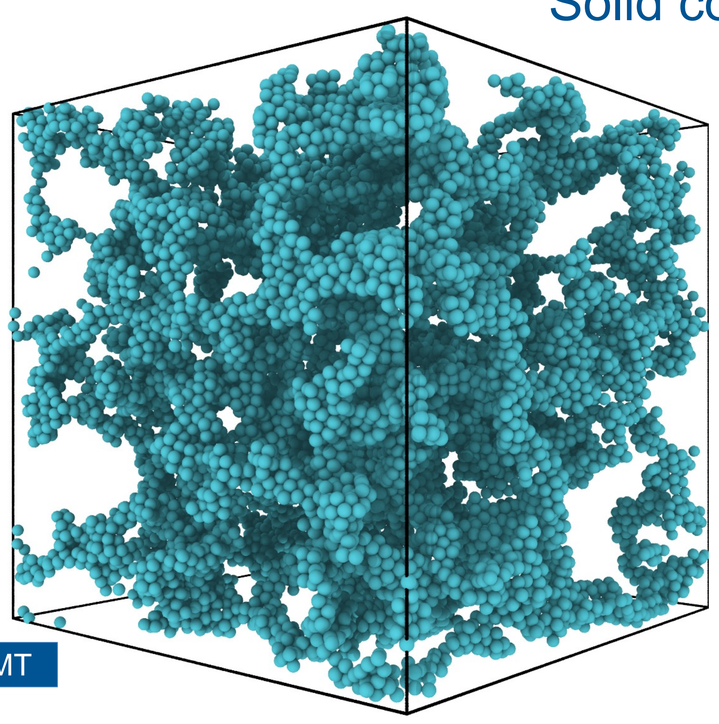
Solid contact models



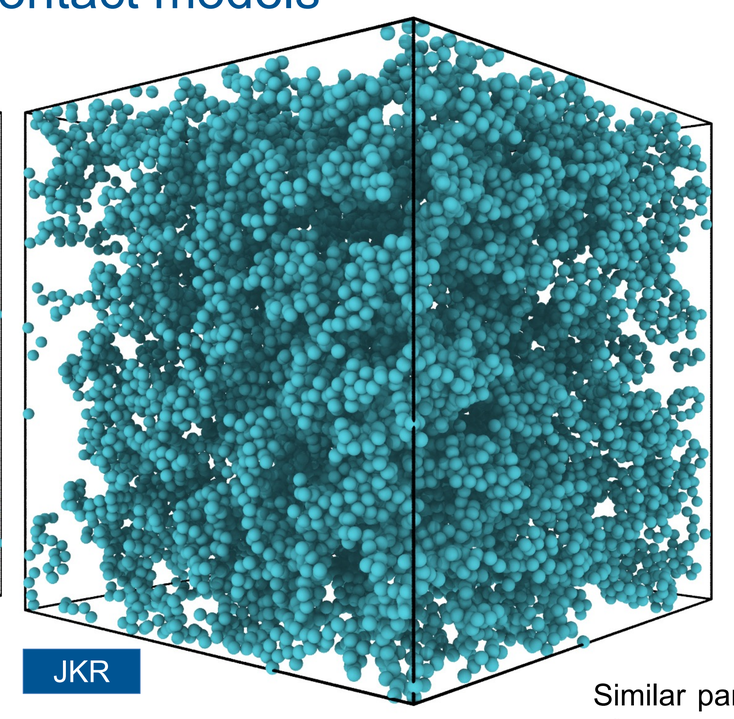
contact area

Hertz contact between particles of tunable softness (Young modulus) +

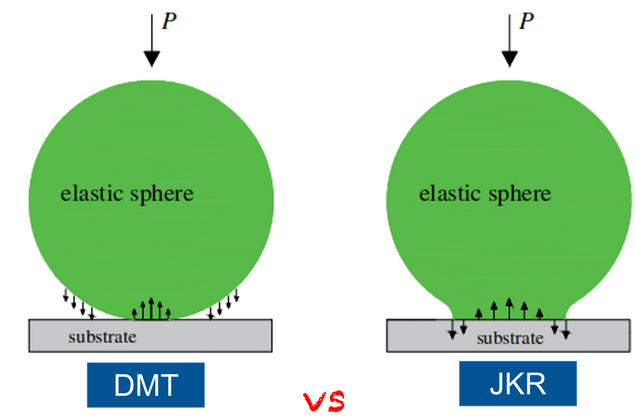
- Surface forces DMT-model for cohesive grains
- Adhesive (hysteretic contact (JKR)
- Surface roughness: sliding and rolling friction.



DMT



JKR

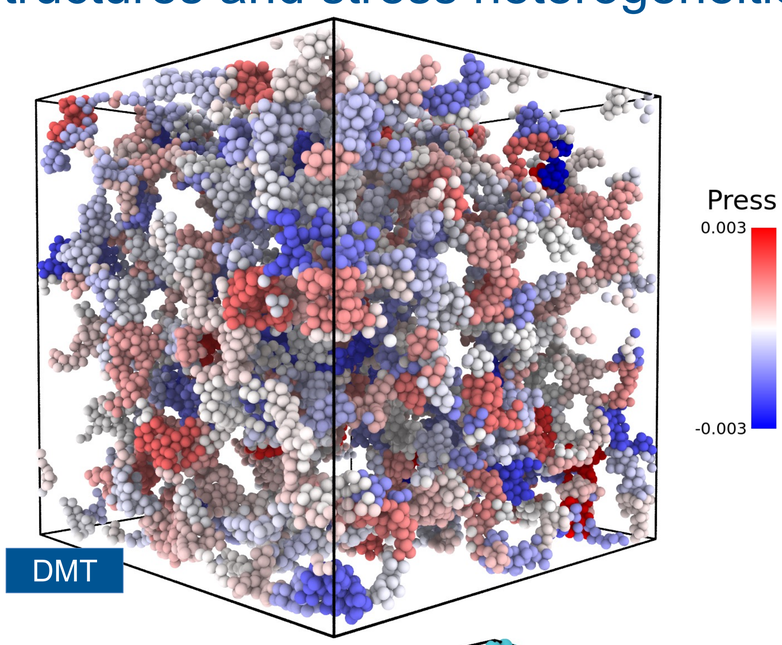


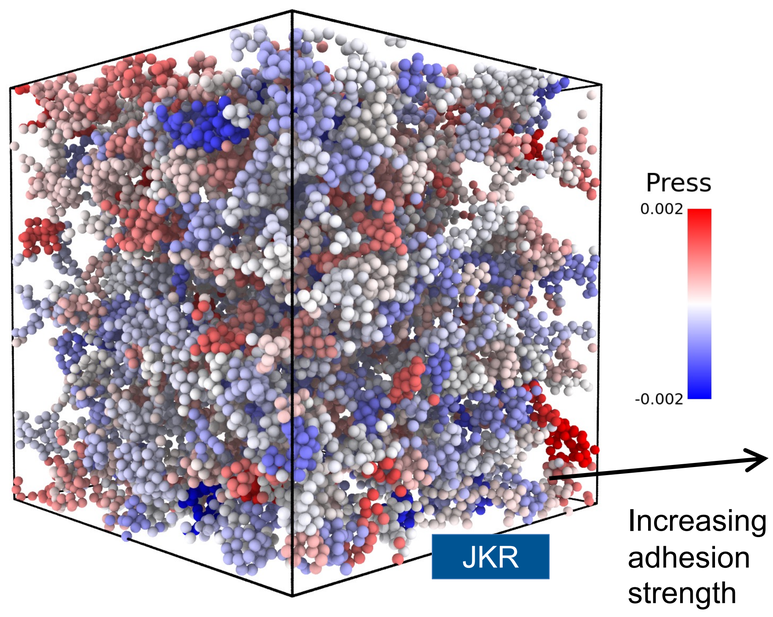
Ciavarella et al., *J. R. Soc. Interface*, R. Soc. (2019)

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

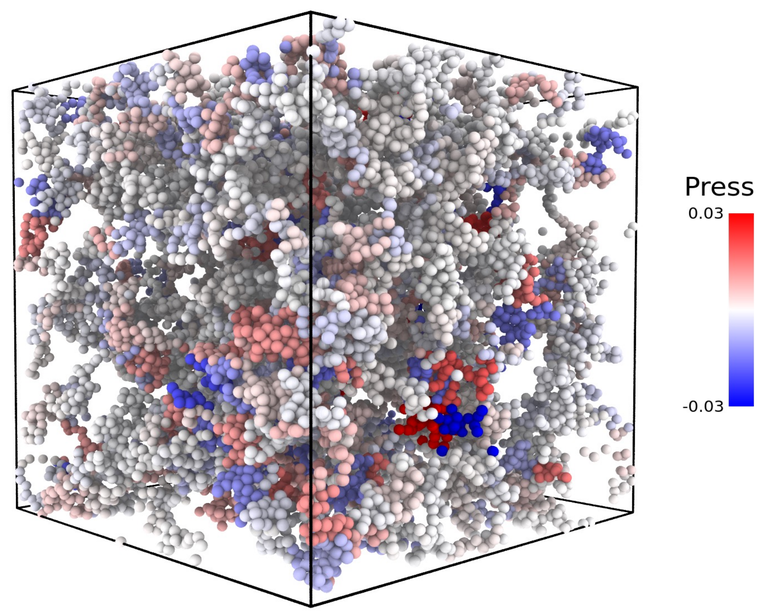
Structures and stress heterogeneities

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

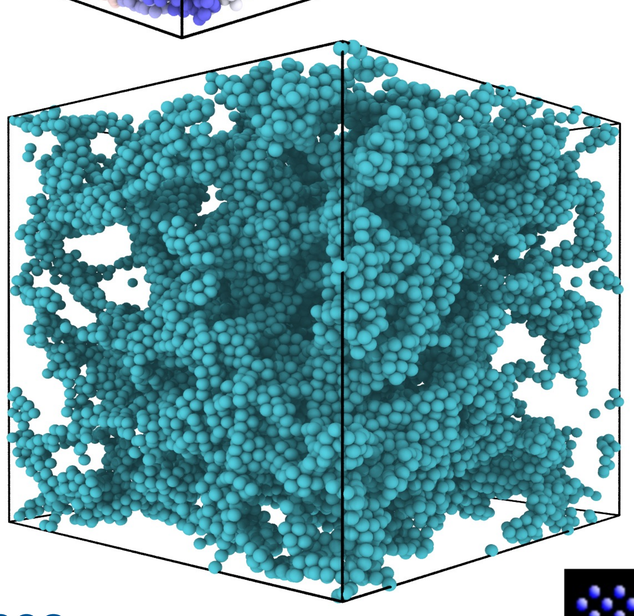




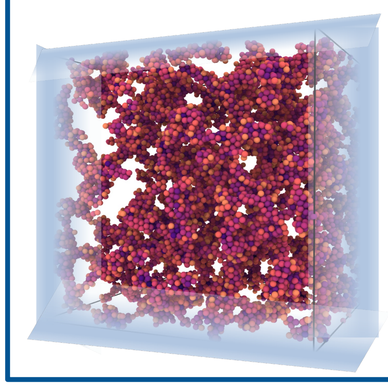
Increasing adhesion strength



Increasing volume fraction



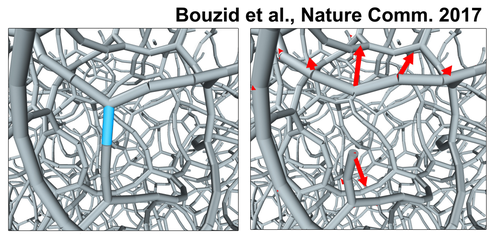
Next Steps



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?

Bouzid et al., Nature Comm. 2017



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.

Work in progress

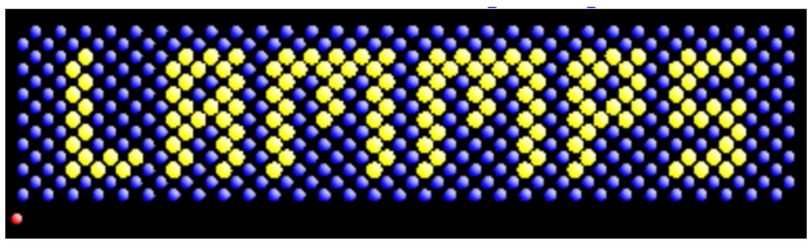
References

Derjaguin, Muller, Toporov, J. Colloidal and Interface Sci. **53** (1975)

Johnson, Kendall, Roberts, Proc. R. Soc. Lond A. **324** (1971)

Mindlin and Deresiewicz, J. Appl. Mech. (1953);

Luding, Granular Matter **10** (2008)



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