Engineering linear and non-linear flow mechanics in dense suspensions of surface-anisotropic colloids

HSIAO LAB
SOFT MATTER AT RESEARCH TRIANGLE

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Introduction

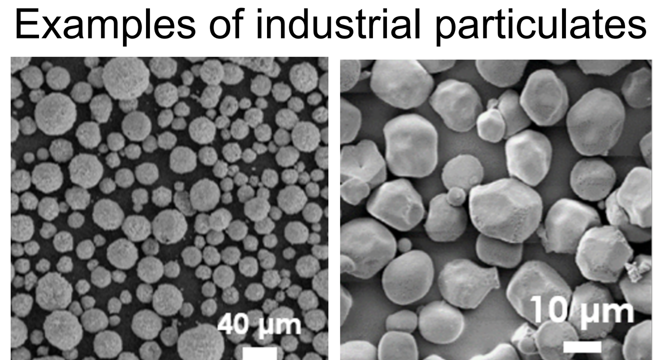
- Dense suspensions, such as colloids, foams, granular materials and gels, are found in applications ranging from consumer goods to geophysical flows.
- They are complex suspensions composed of particles with diversity in size polydispersity, surface anisotropy/roughness, interaction potential, and inherent material softness.
- In the absence of attractive interactions, as more and more particles are added to a given suspension, individual particles feel the "crowding" effect.
- The crowding dynamics along with the hydrodynamic interactions from the surrounding fluid impart the mechanical/load-bearing properties of dense suspensions.

How can we design dense suspensions with mechanical properties for desired end applications?

In most of the academic settings (textbook cases of experiments and simulations), studies at low Re flows have the following limitations:

- Constituent particles are perfectly spherical.
- Interparticle interactions are frictionless.
- Interparticle collisions are overdamped (colloids) or inelastic (granular).

Examples of industrial particulates



Ceramic particles | Cornstarch granules

Silva et al. *J. Mater Res Technology* (2019)
Liu et al. *J Eur Ceram Soc* (2018)

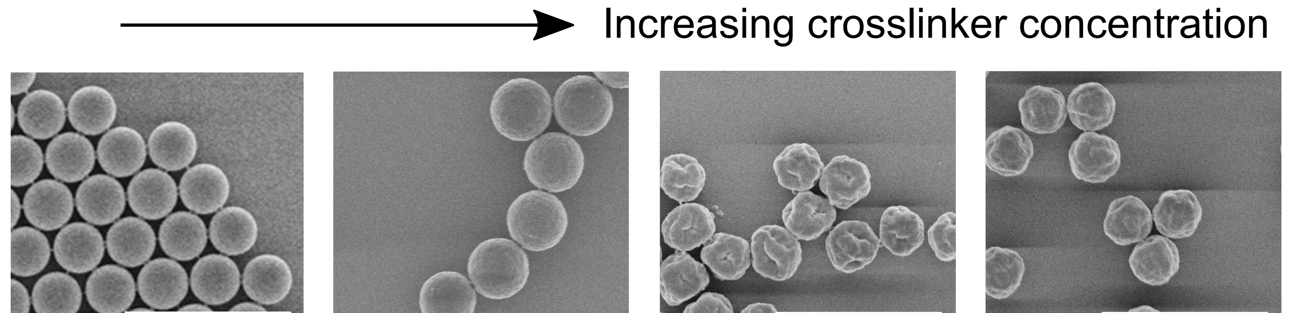
In our experiments, we focus on decoupling the effects of surface-anisotropy (particle-level surface roughness) on the linear and non-linear flow properties in dense suspensions.

Experimental Suspension System

- We use in-house synthesized poly(hydroxystearic acid)-*grafted*-poly (methylmethacrylate) (PHSA-*g*-PMMA) colloidal particles dispersed in index-matched solvent squalene for our studies: model hard-spheres.
- Surface roughness can be tuned by modulating the addition rate and amount of polymeric cross-linker ethylene glycol dimethacylate (EGDM) during the colloidal microsphere synthesis.

Increasing crosslinker concentration

Particle diameters, 1.2-1.8μm



Roughness parameter: Sphericity 2D, ψ

$\psi \approx 0.99$ | $\psi \approx 0.94$ | $\psi \approx 0.87$ | $\psi \approx 0.79$

Decreasing 2D sphericity or increasing surface roughness.

$$\psi = \frac{4A_{2D,\max}}{\left(P_{2D,\max}\right)^2}$$

maximum 2D area

perimeter corresponding to $A_{2D,max}$

Gravitational Peclet number:

$$Pe_g = \frac{4\pi a^4 \Delta\rho g}{3k_B T} \sim O(1)$$

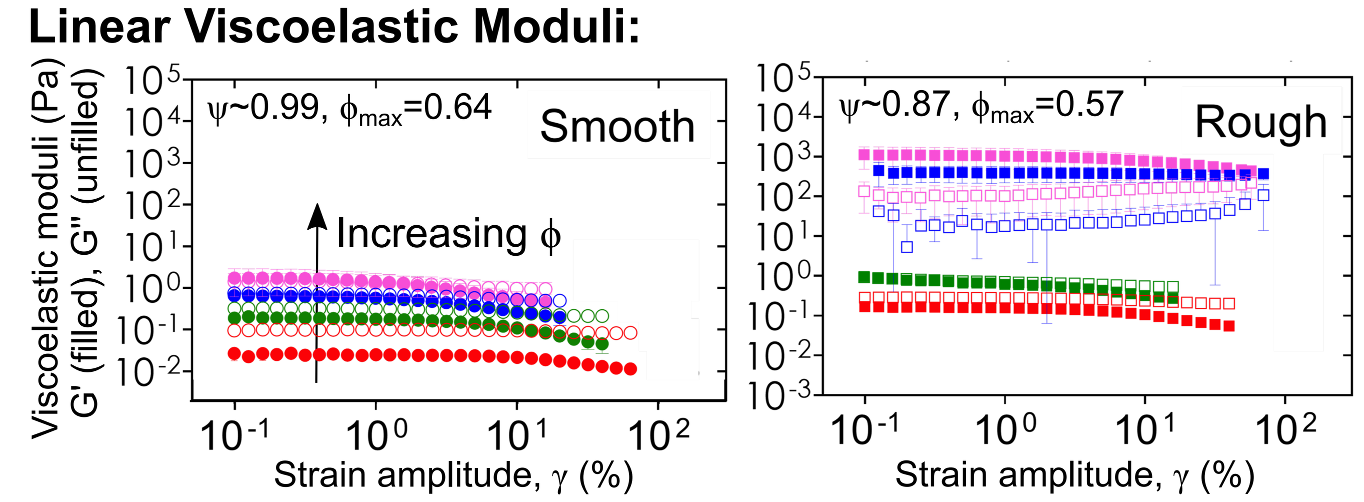
- Colloids and solvent are not density-matched.
- To produce repoducible packing, we centrifuged sample at 1500g to the maximum packing (ϕ_{max}) and diluted to the desired packing fraction (ϕ).

Linear Rheology: Viscoelasticity

- In dense colloidal suspensions, linear viscoelastic properties are a consequence of the excluded volume effects and the interplay between hydrodynamic and Brownian interactions between the particles.
- For rough colloids at high ϕ, the interparticle distance is comparable to the roughness scale and the surface asperities between nearest neighbors generate rotational constraints.

How does the surface roughness-induced geometric frustration affect the linear viscoelastic properties in dense colloidal suspensions?

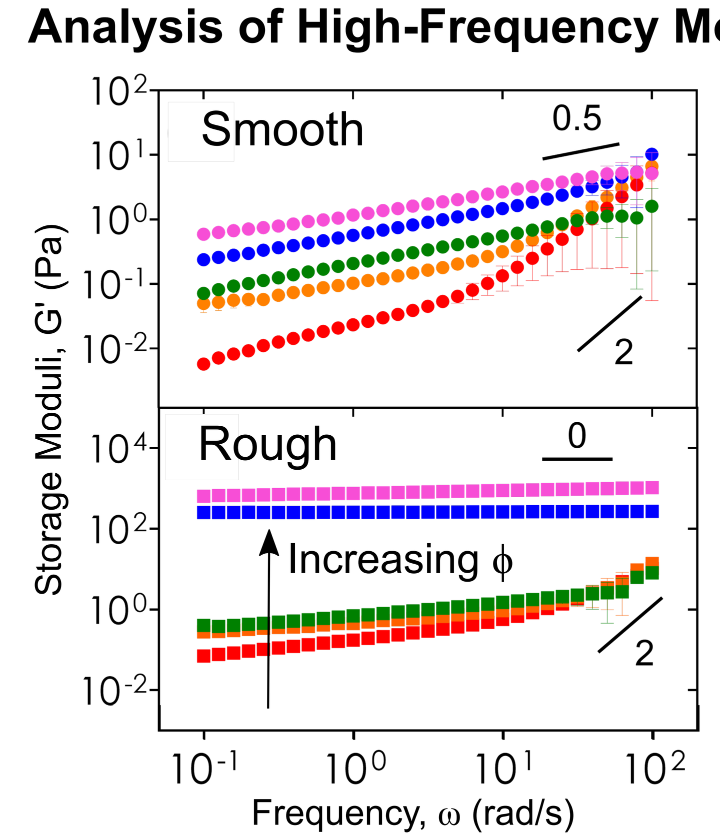
Linear Viscoelastic Moduli:



In both cases, 2a ~ 1.5μm

- The viscoelastic moduli of rough colloids above $\phi > 0.52$ is 10^3 times higher than that of rough colloids.
- Linear strain limit for small amplitude oscillatory tests, $\gamma < 10\%$

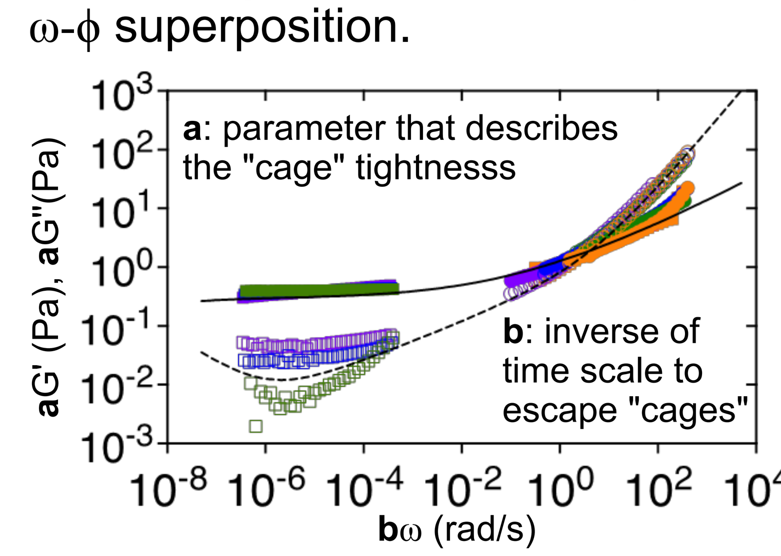
Analysis of High-Frequency Moduli:



- At high frequencies, the contributions to suspension stress become dominated by the lubrication stresses of the solvent between neighboring particles.
- For smooth suspensions at $\phi > 0.55$ and for rough suspensions at $\phi > 0.52$, the G' scales with frequency as:
  Smooth: Free-draining approximation. $G' \sim \omega^{0.5}$
  Rough: Hydrodynamic lubrication $G' \sim \omega^{0}$
- In rough suspensions, inter-asperity interactions lead to enhanced squeeze lubrication forces.

Frequency-Concentration Superposition:

The frequency sweep data for the suspensions for $\phi \geq 0.50$ collapsed onto a single master curve by ω-ϕ superposition.

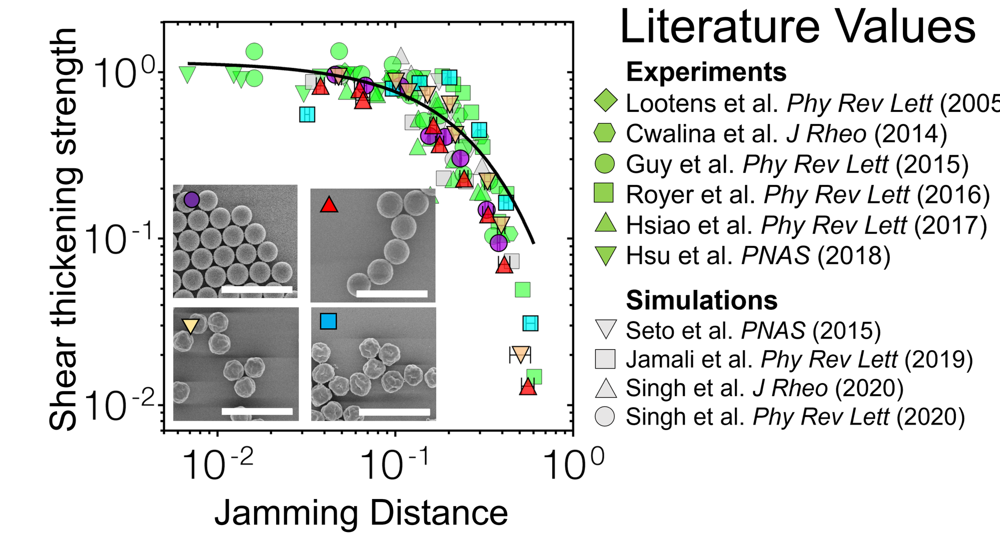


- The horizontal factor **b** > 1 for smooth suspension indicate rapid relaxation - for rough suspensions **b** is six orders smaller indicating long relaxation time scales.
- Vertical factor **a** is a microstructural parameter ~ stresse scale required to overcome the near-equilibrium microstructure - how tight the "cage" is?
  a: qualitative cage volumes
  a<<1 for rough - small "cages"
  a>1 for smooth - large "cages"

Non-Linear Rheology: Shear Thickening

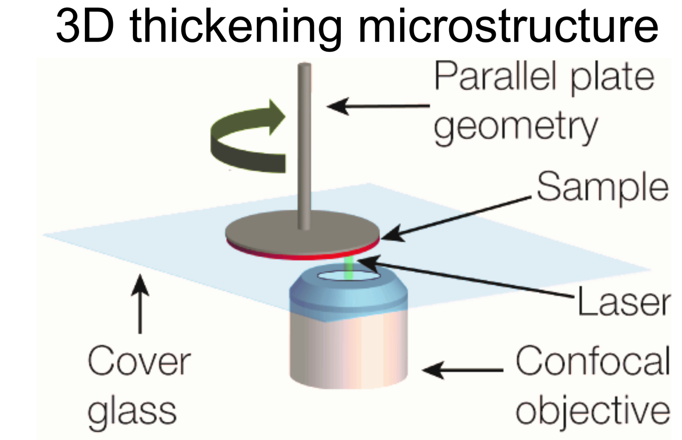
- At high deformation rates, the viscosity of colloidal suspensions increases with increasing shear causing shear thickening.
- Shear thickening shares similarities to jamming in that the particles in a flowing suspension become impeded by the nearest neighbors and therefore require more stress to continue flowing.

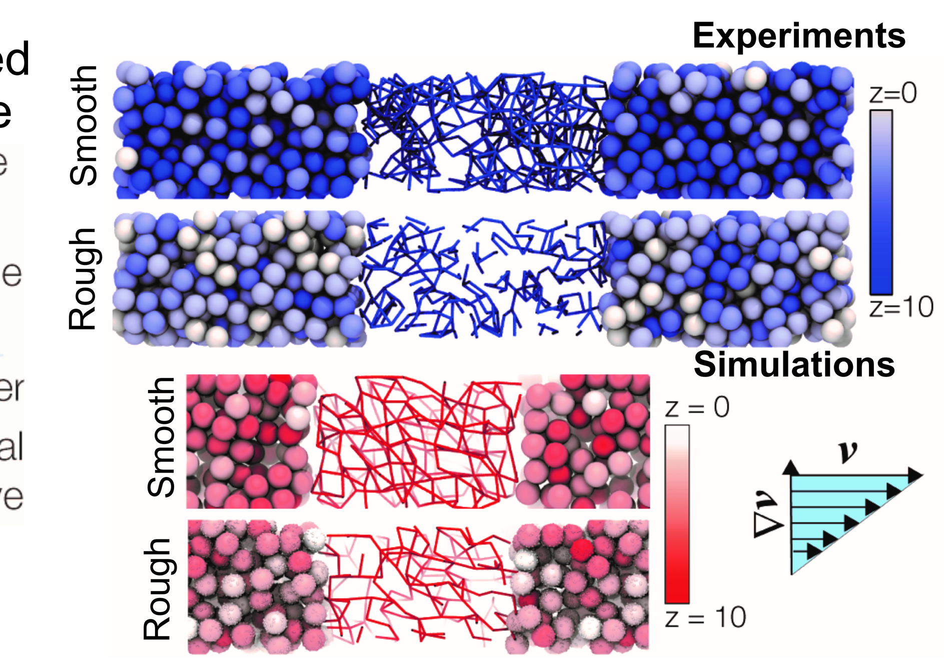
How to we engineer shear thickening in dense suspensions?



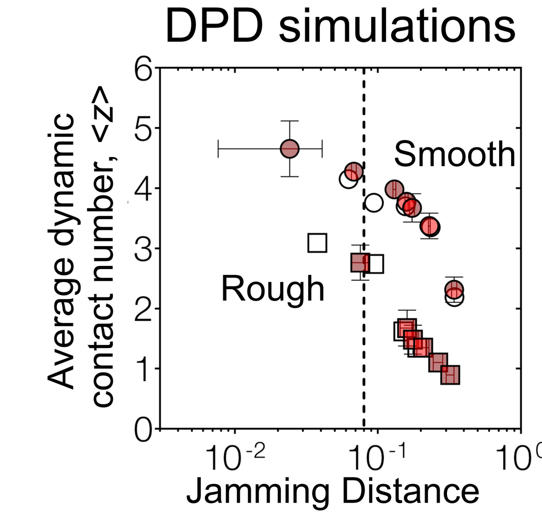
- Shear thickening strength is the rate of increase of viscosity with applied stress.
- Shear thickening strength scales universally with jamming distance between various colloidal suspensions.

Confocal rheoscope captured 3D thickening microstructure





Experiments and DPD simulations



- The smooth colloids, on average, require 1.5-2 additional contacts to maintain the same shear thickening strength as compared to the rough colloids.
- The free volume available to rearrange under shear is greater for smooth colloids than the rough colloids, because smooth colloids can rotate freely with no hydrodynamic resistance.

Scaled jamming distance is a strong predictor for the shear thickening behavior of a broad class of colloidal suspensions.

Summary

- Colloidal particle roughness can be tuned to acheive desired flow properties in dense suspensions.
- In the linear regime, increased roughness imparted enhanced lubrication interactions between the particles, resulting in stronger stress-bearing structures and higher elastic properties for rough suspensions.
- In non-linear (high shear) regime, the suspension thickening properties can be unified on the basis of "jamming distance".

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Journal Publications:
Shravan Pradeep, Alan Wessel, Lilian Hsiao, "Hydrodynamic origins for the suspension viscoelasticity of rough colloids", *Journal of Rheology* (2022): Editor's Highlighted Article.
Shravan Pradeep, Mohammad Nabizadeh, Alan Jacob, Safa Jamali, Lilian Hsiao, "Jamming distance dictate colloidal shear thickening", *Physical Review Letters* (2021).
Shravan Pradeep, Lilian Hsiao, "Contact criterion in dense suspensions of smooth and rough colloids", *Soft Matter* (2020).

For more details, scan the QR code to check out my website!