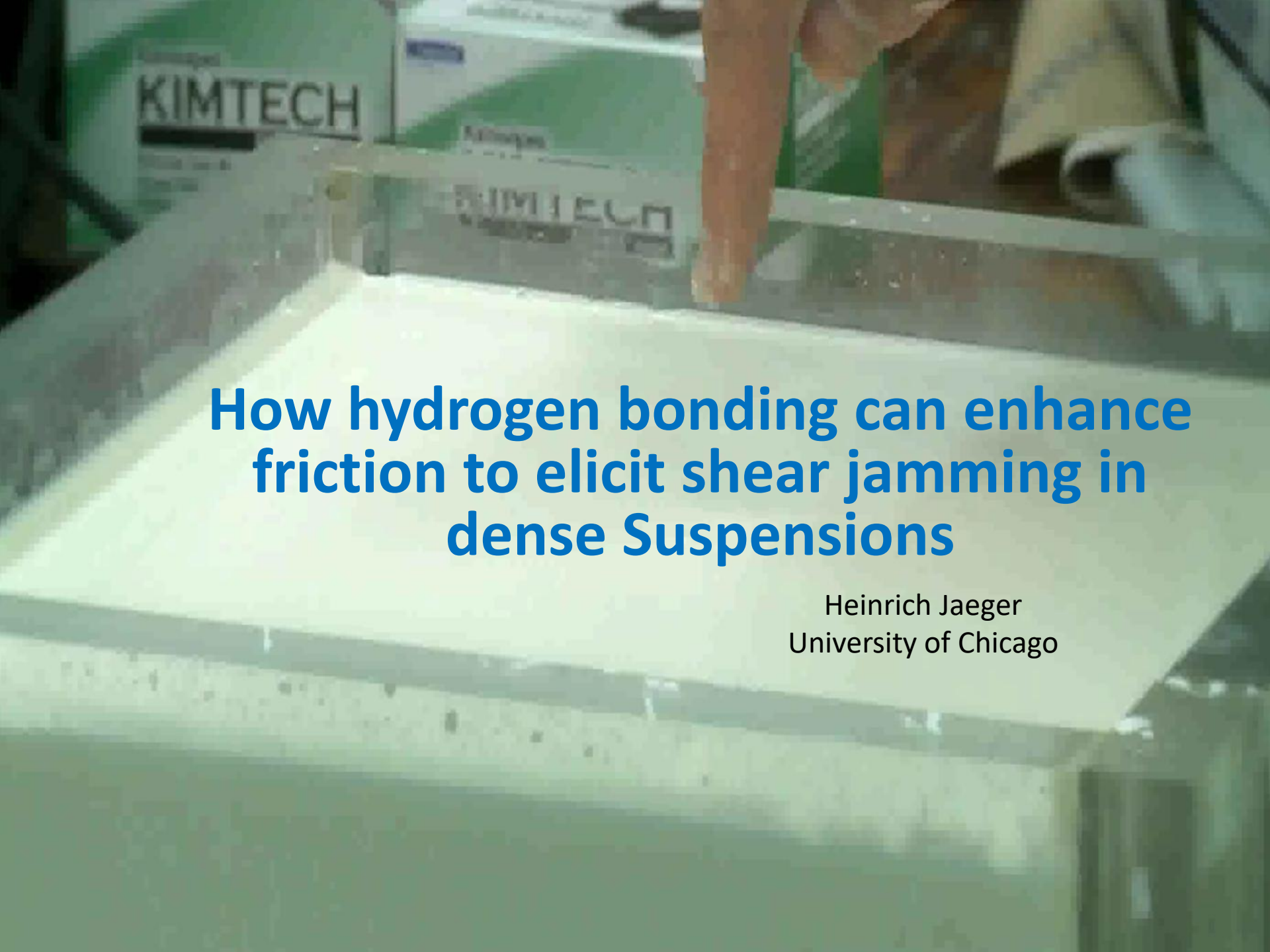
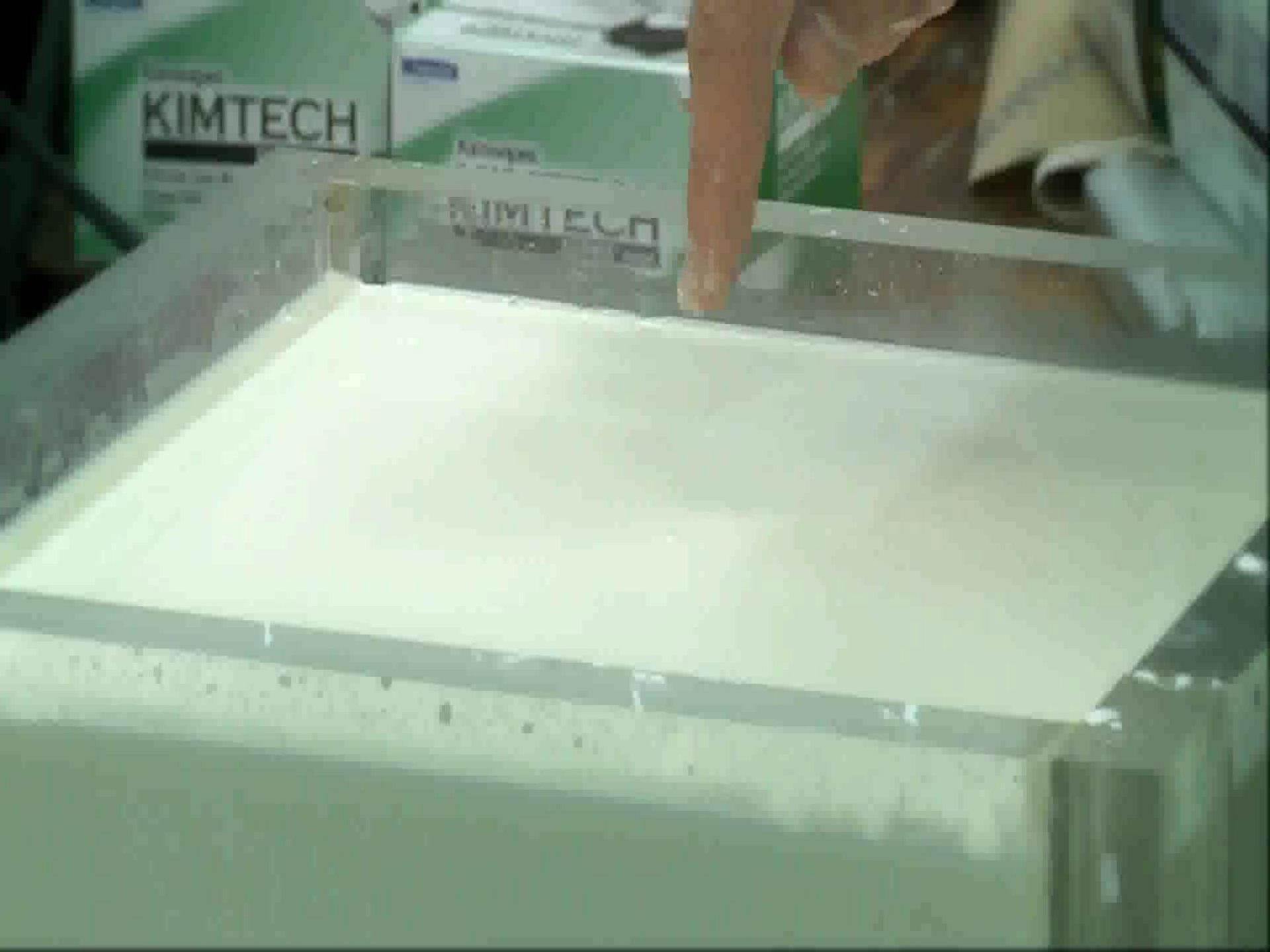
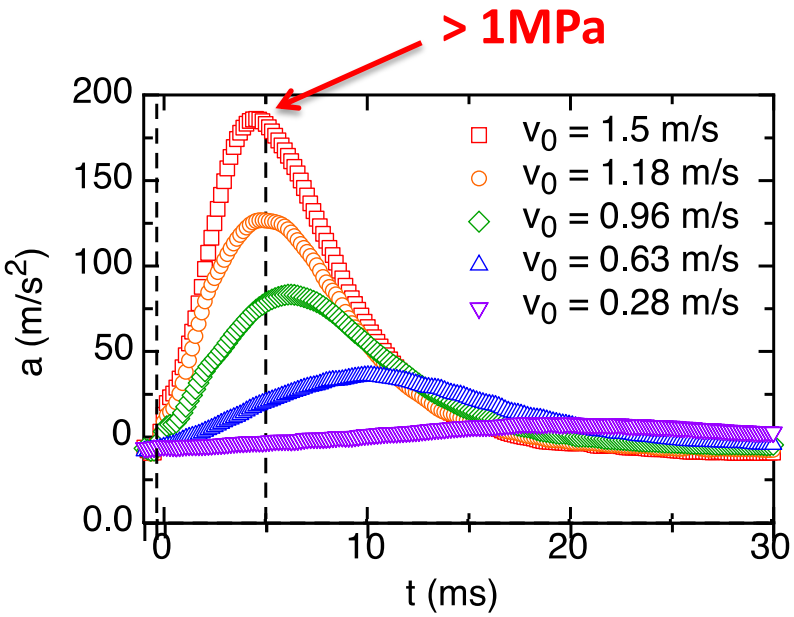


How hydrogen bonding can enhance friction to elicit shear jamming in dense Suspensions

Heinrich Jaeger
University of Chicago


KIMTECH

Impact at 4m/s



S. Waitukaitis & HMJ,
Nature (2012)

Discontinuous Shear Thickening

BARNES 1989

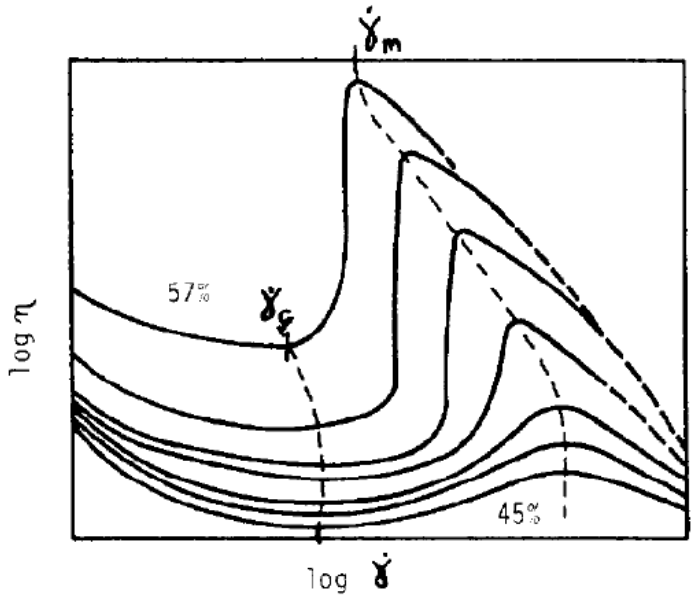
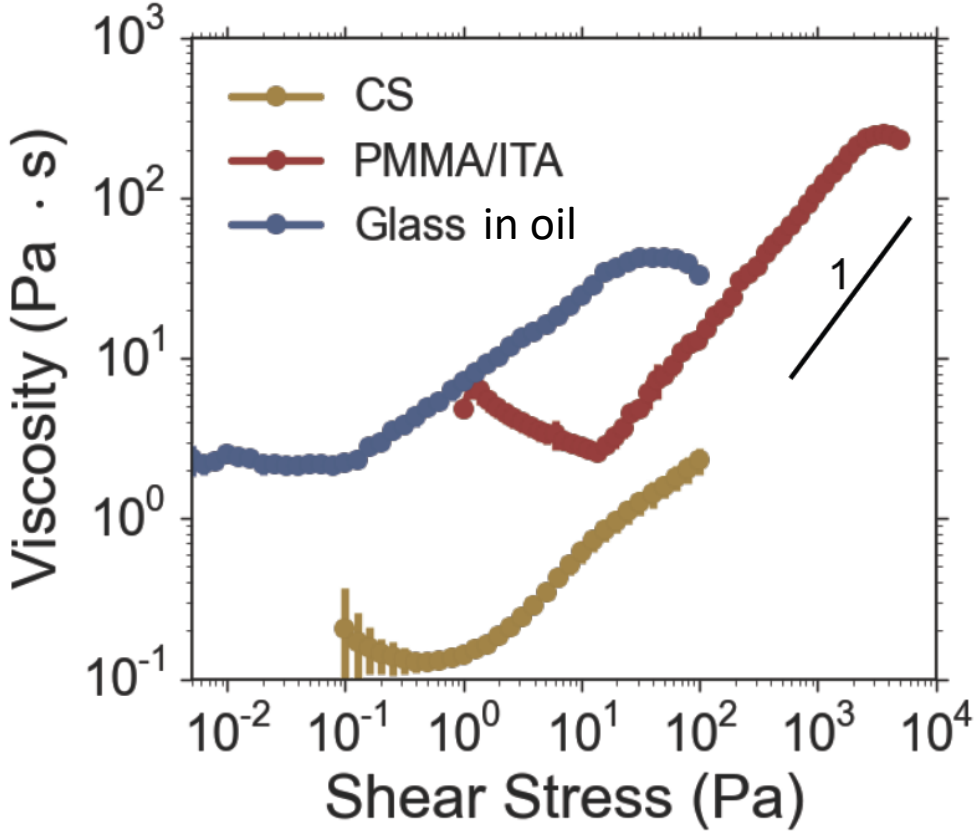


Fig. 1. Schematic representation of viscosity versus shear rate for shear-thickening systems, with approximate phase volume as parameter. Also shown are the loci of $\dot{\gamma}_c$ and $\dot{\gamma}_m$, the shear rates at the beginning and end of the shear-thickening region.

Viscosity depends on driving intensity ➔ Non-Newtonian behavior

Discontinuous shear thickening (DST) is ubiquitous for dense suspensions

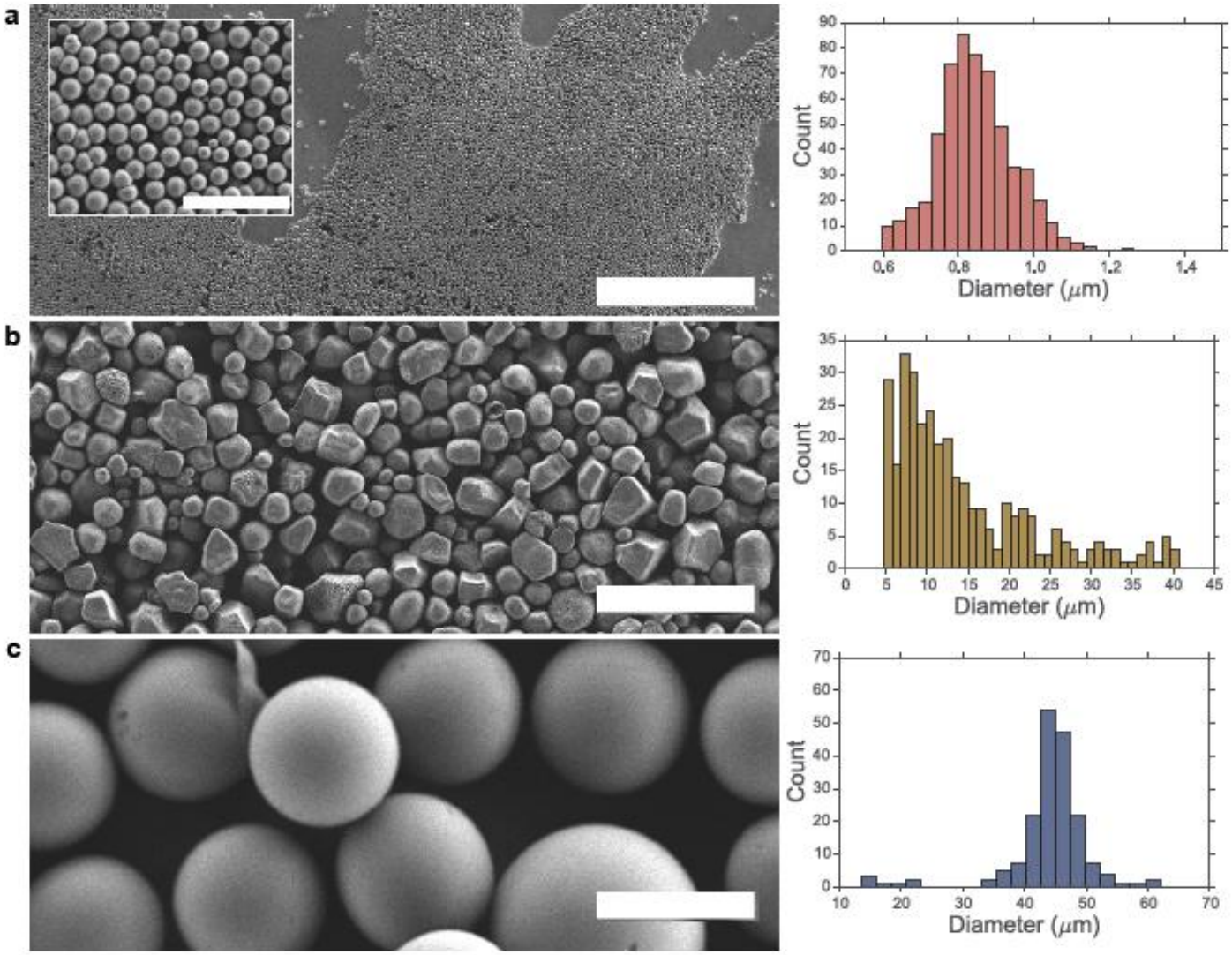


$\tau = \eta\dot{\gamma}$ Slope 1 on plot of viscosity vs stress implies DST

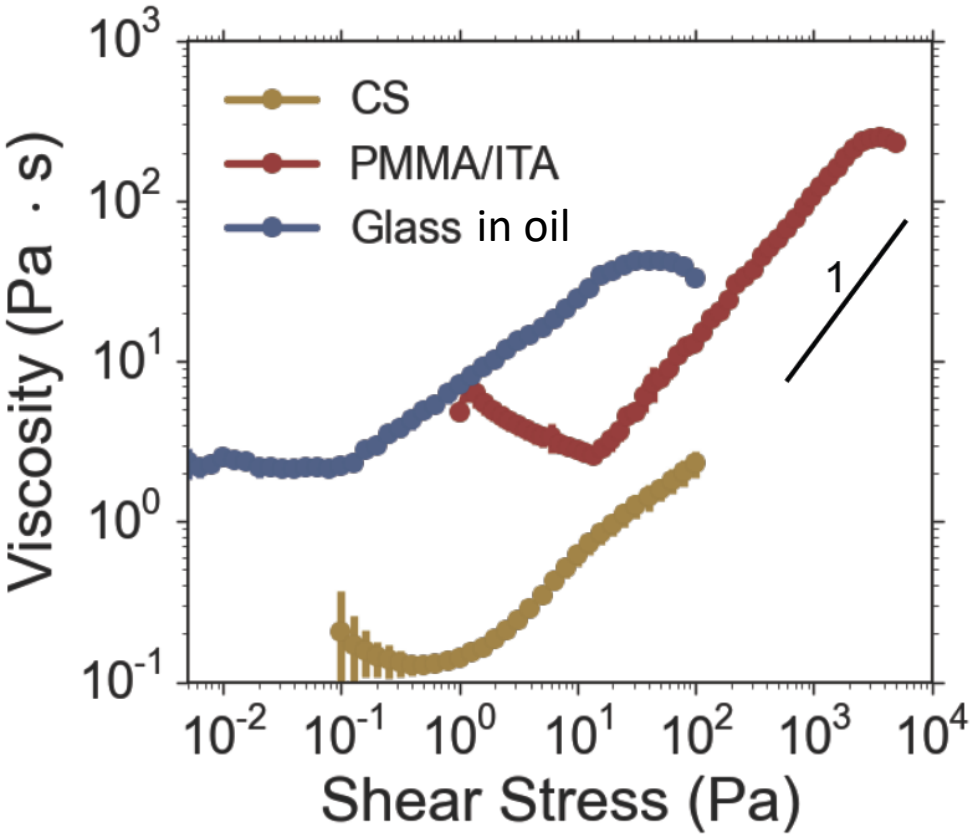
PMMA/ITA

cornstarch

glass



Do all suspensions that exhibit DST also shear jam?



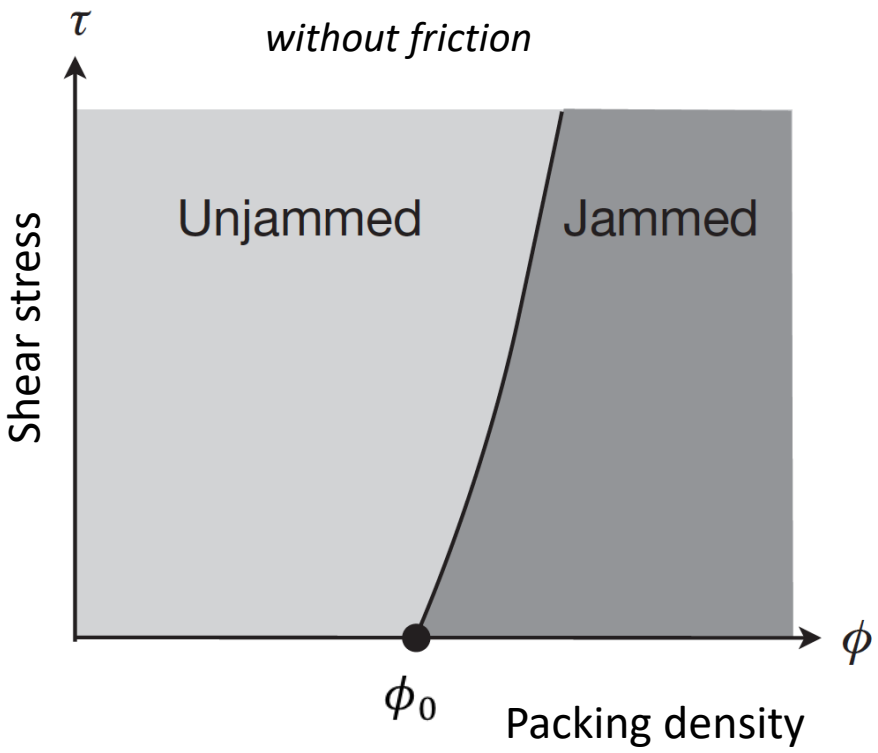
Nicole James

Jamming = onset of solid-like rigidity & non-zero yield stress

Jamming Phase Transition (for dry particles)

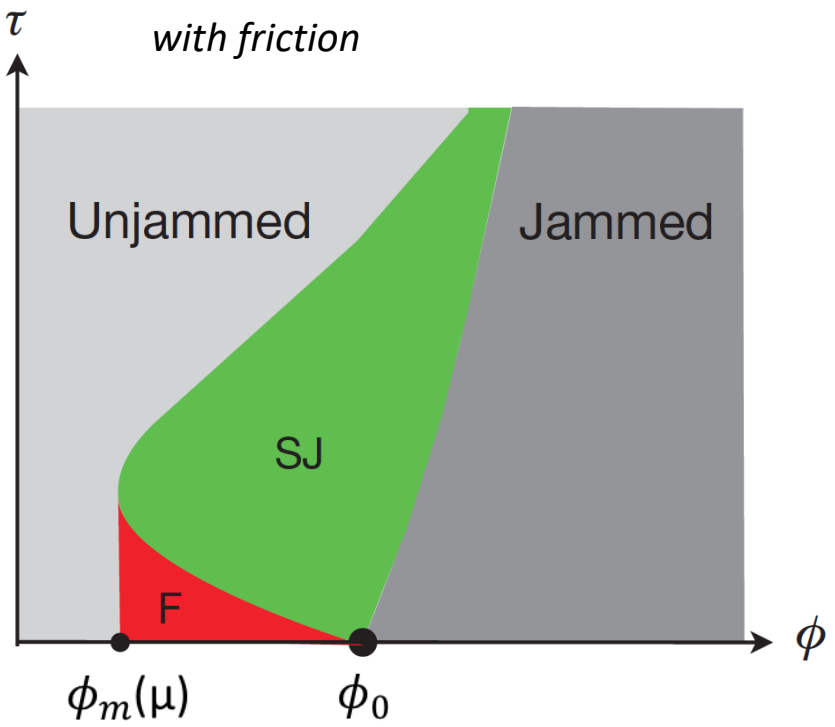
Chicago/UPenn (1998)

without friction



Duke/Brandeis (2011)

with friction



Bi et al., Nature (2011)

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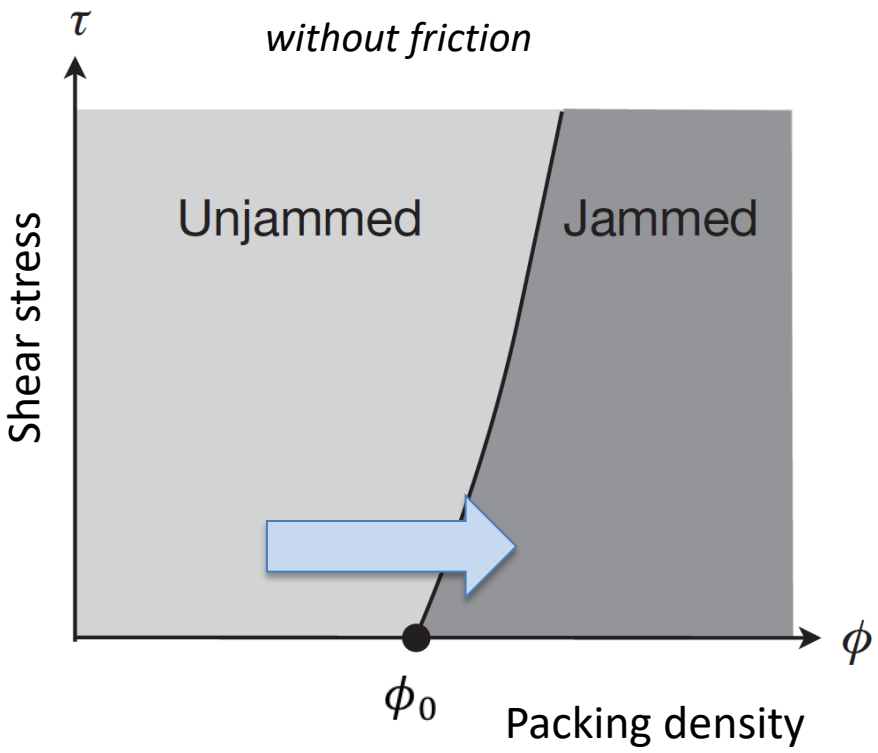

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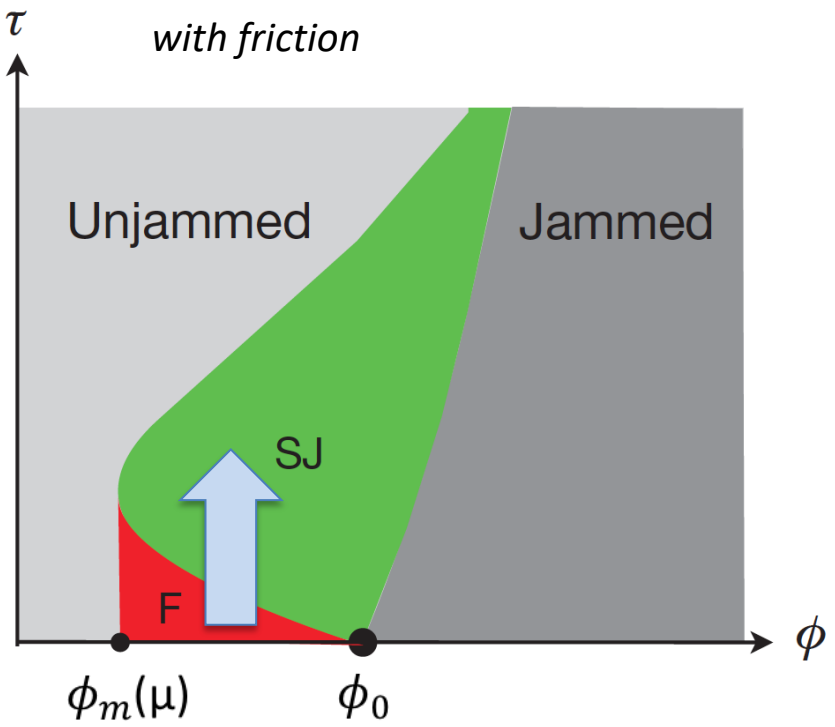
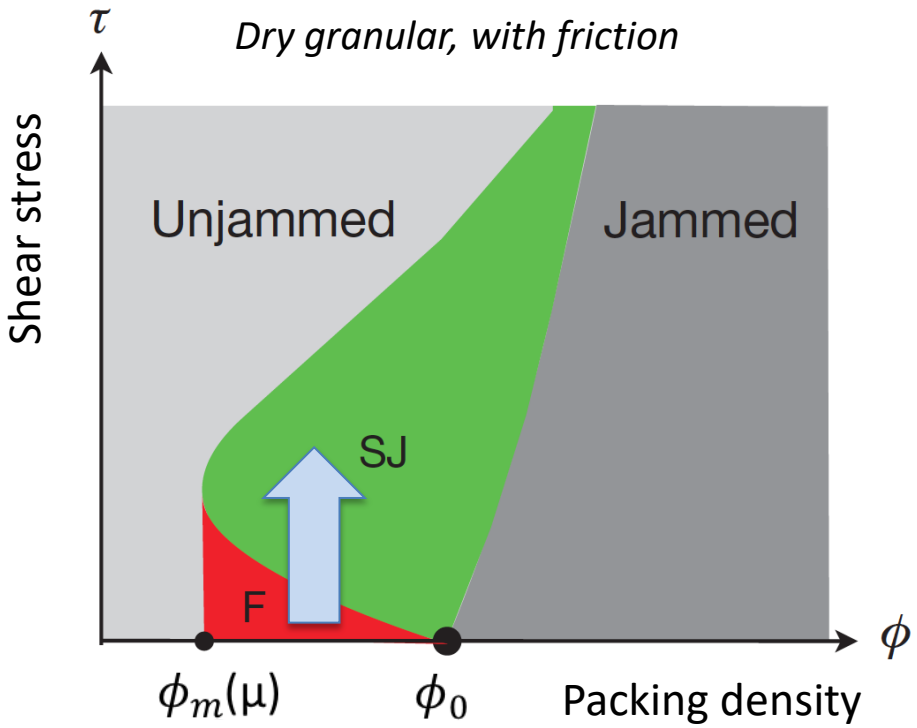


Bi et al., Nature (2011)

Toward a state diagram for frictional suspensions

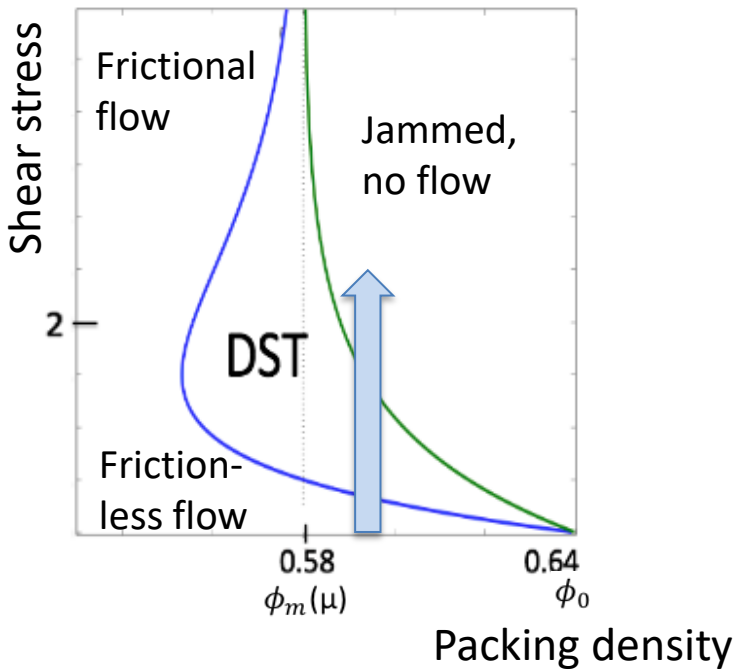
Duke/Brandeis (2011)

Dry granular, with friction



Wyart & Cates (2014)

Suspension, with friction



Key idea: strong shear stress creates frictional contacts

How do you know a suspension is shear-jammed?

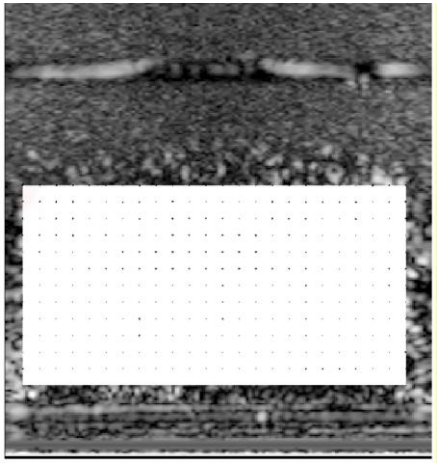
- Prepare suspension with $\phi_m < \phi < \phi_0$
- Apply shear stress (at rates below the speed of sound so the liquid doesn't compress)
- Detect the onset of solid-like rigidity

➔ Cannot use steady-state rheology!

➔ Look for propagating shear-jamming fronts

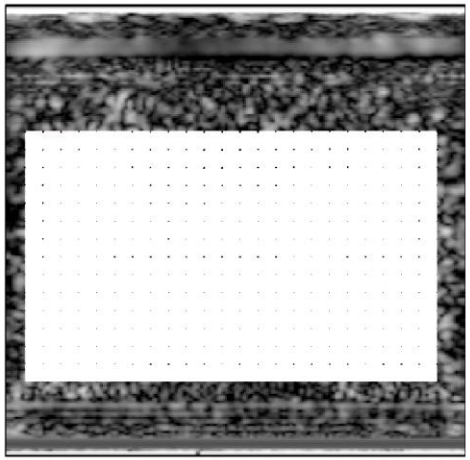
Visualizing Shear Jamming Fronts
that convert unjammed fluid into jammed solid

Majumdar *et al.*, PRE (2017)



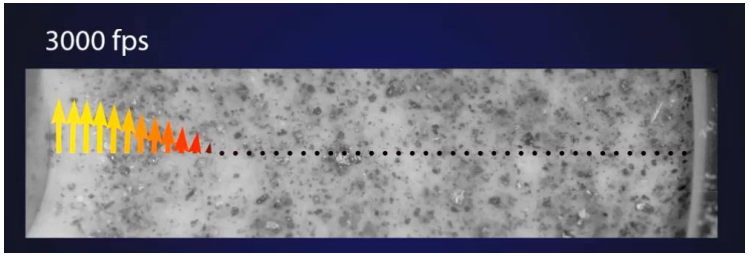
Extension (3D)

Han *et al.*, Nat. Commun. (2016)



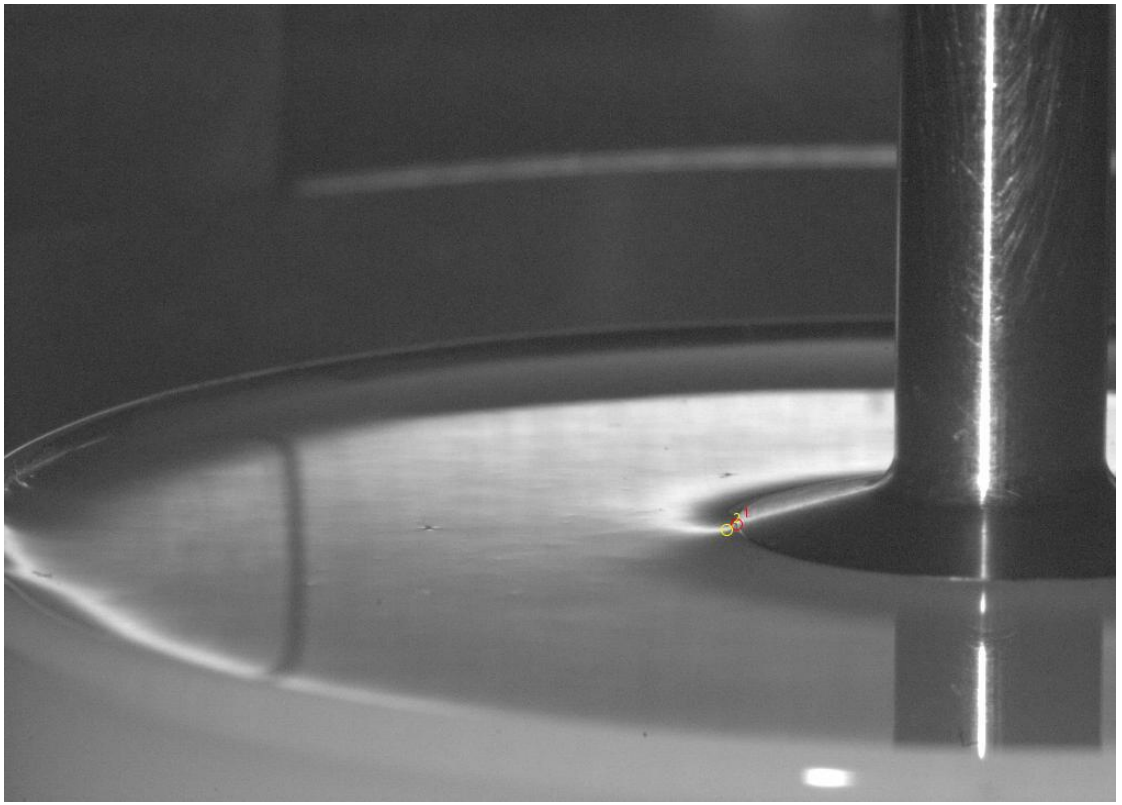
Impact (2D, 3D)

Peters *et al.*, Nature (2016)



Couette Shear (2D)

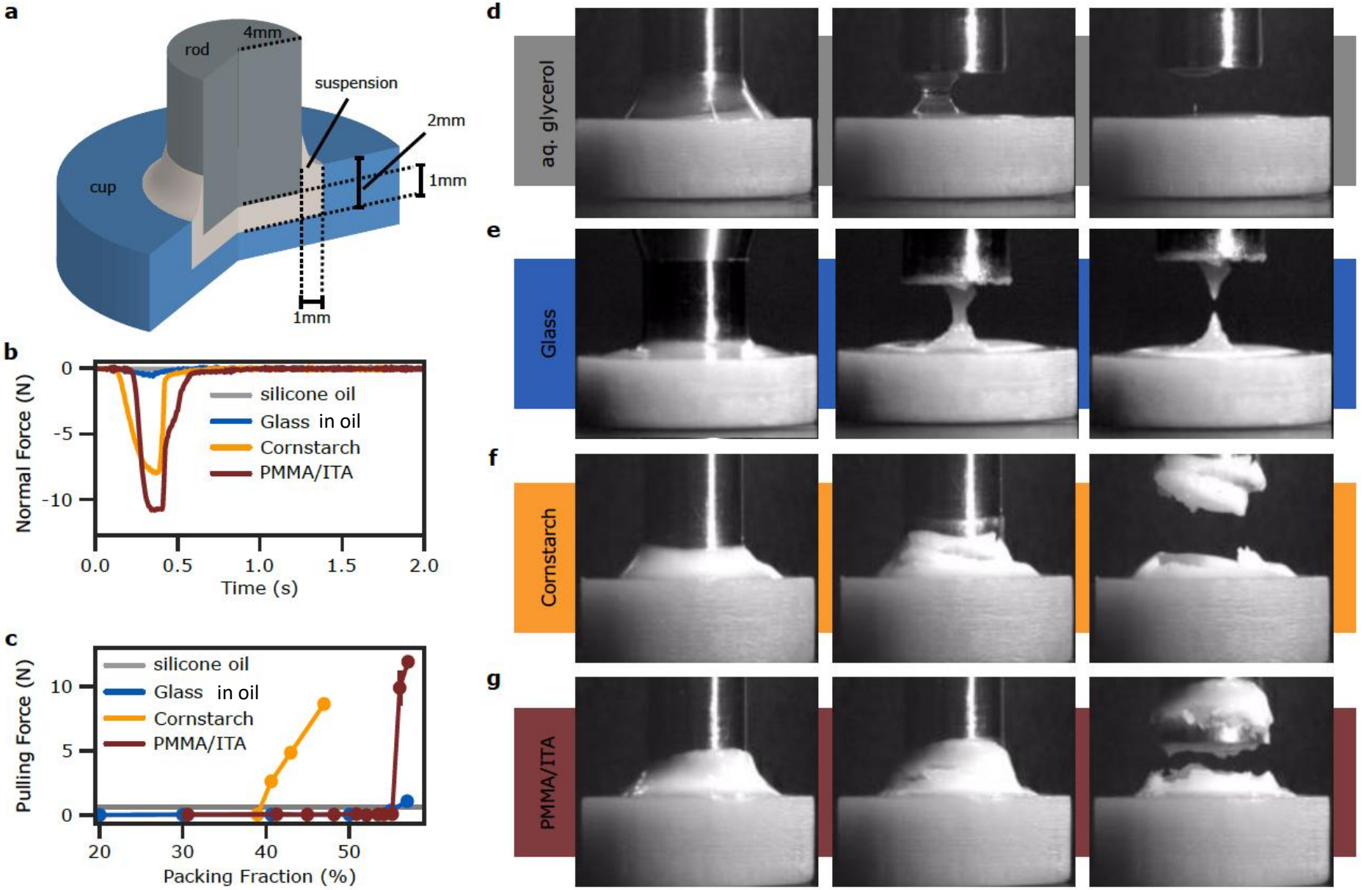
Even easier test for SJ: Pull on the suspension surface



Sayantan Majumdar

- Tensile loading creates jammed, solid-like state
- Jamming front appears during tensile loading
- Tensile force shoots up when front reaches boundaries

Pull test for shear jamming



So why do some dense suspension exhibit DST but not shear jamming (SJ) behavior?

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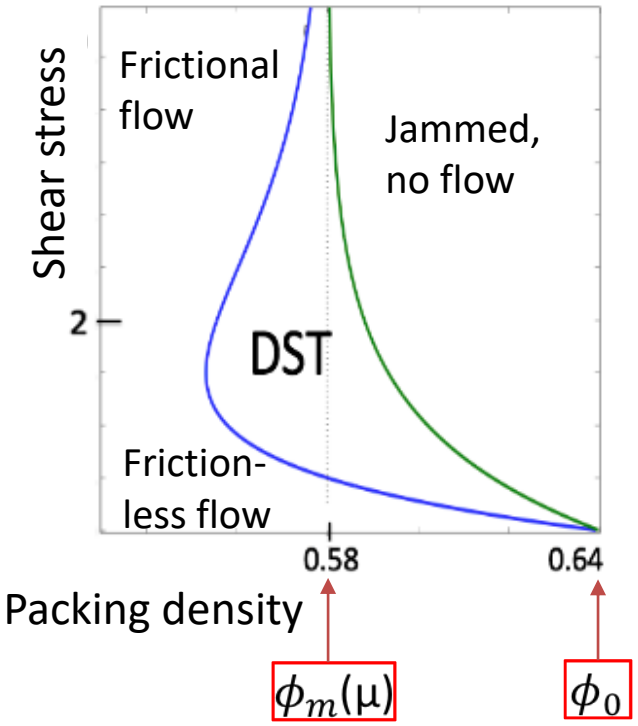
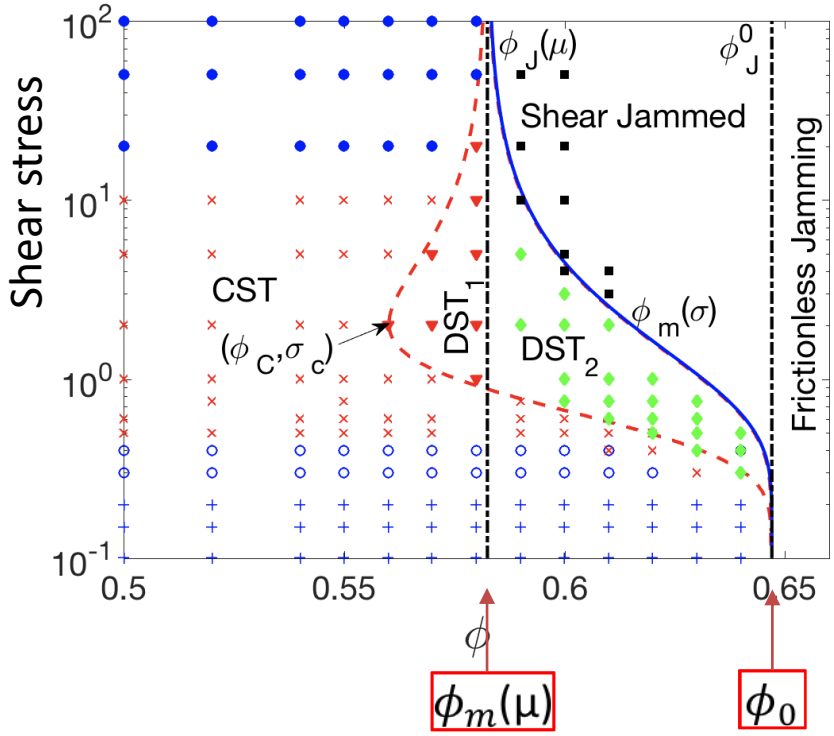
Wyart & Cates (2014)



Singh, Mari, Denn, Morris (in press)



Scenario:

- Particles interact via lubrication ($\mu = 0$) if stress is low
- Particles interact via friction ($\mu > 0$) if stress > threshold stress

- Onset of jamming depends on friction:

$$\phi_{onset} = \phi_0 \qquad \mu = 0$$
$$\phi_{onset} = \phi_m(\mu) < \phi_0 \qquad \mu > 0$$

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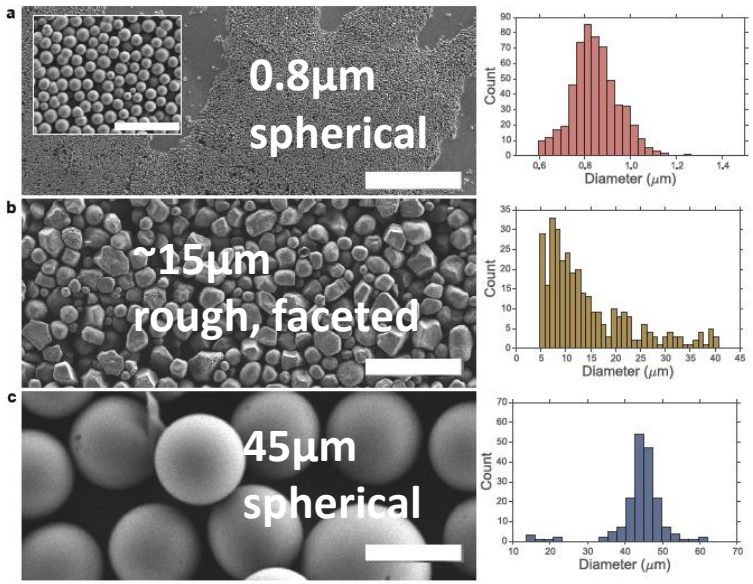
What controls the inter-particle friction?

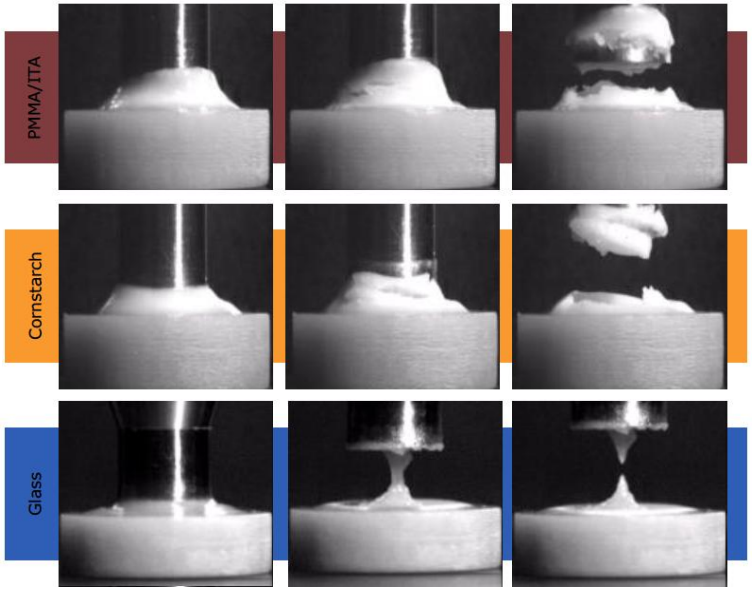
Particle size or geometry are not the deciding factors

PMMA/ITA

cornstarch

glass





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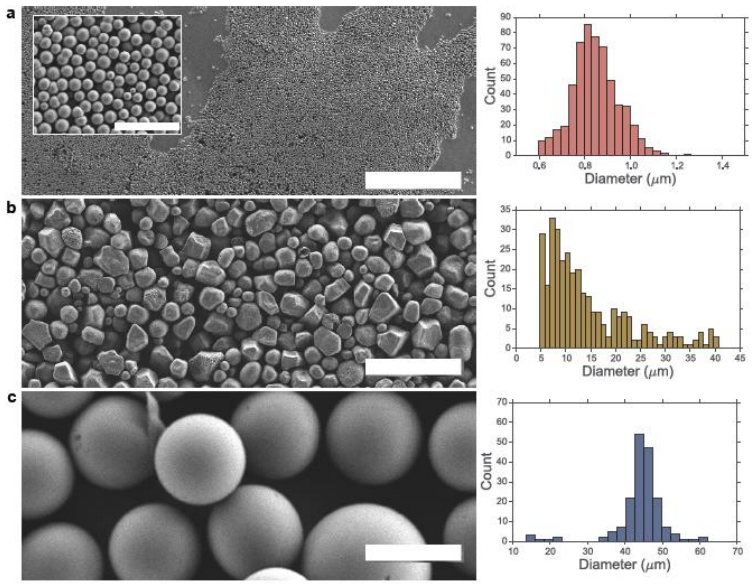
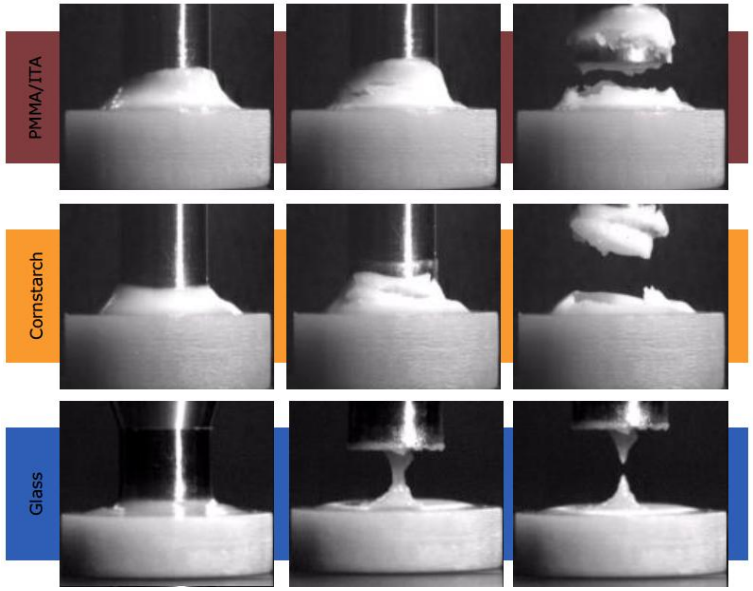


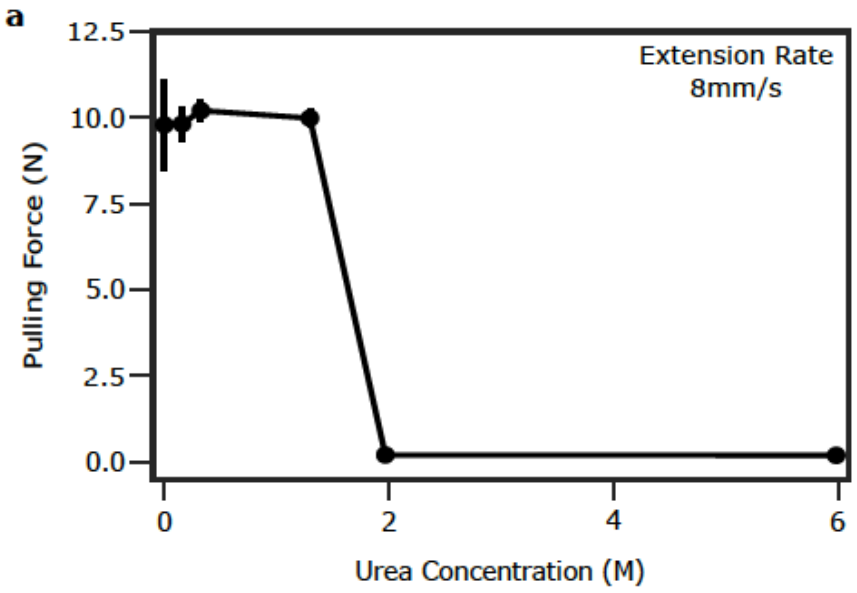


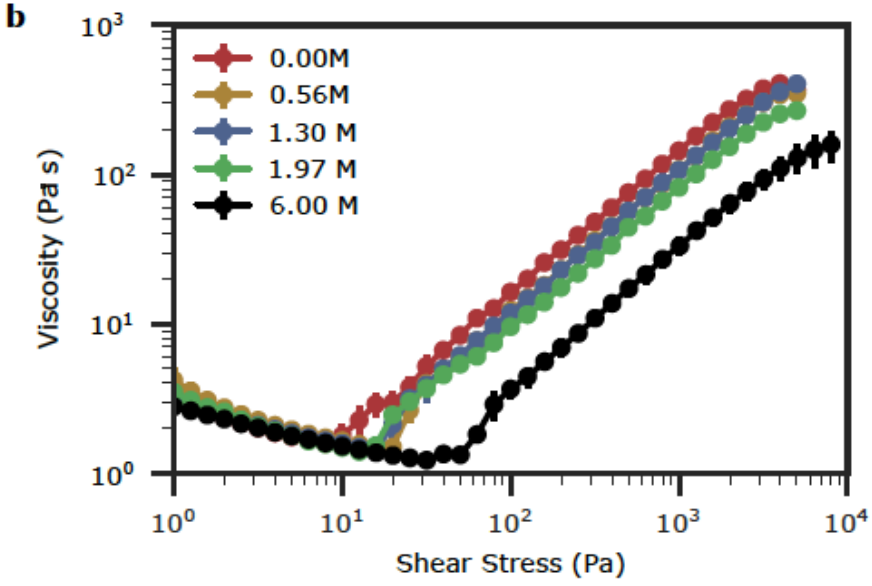
Nicole

What about surface chemistry?

Adding a chaotrope kills shear jamming…

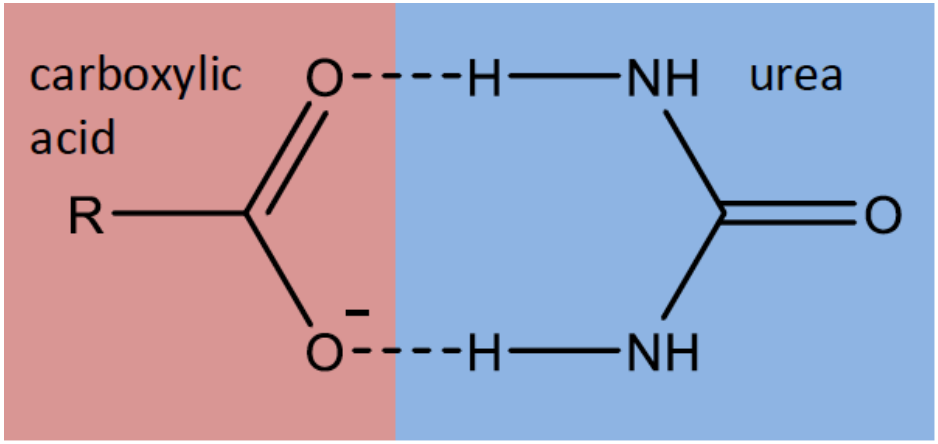
…but not DST!





PMMA/ITA in aq. glycerol

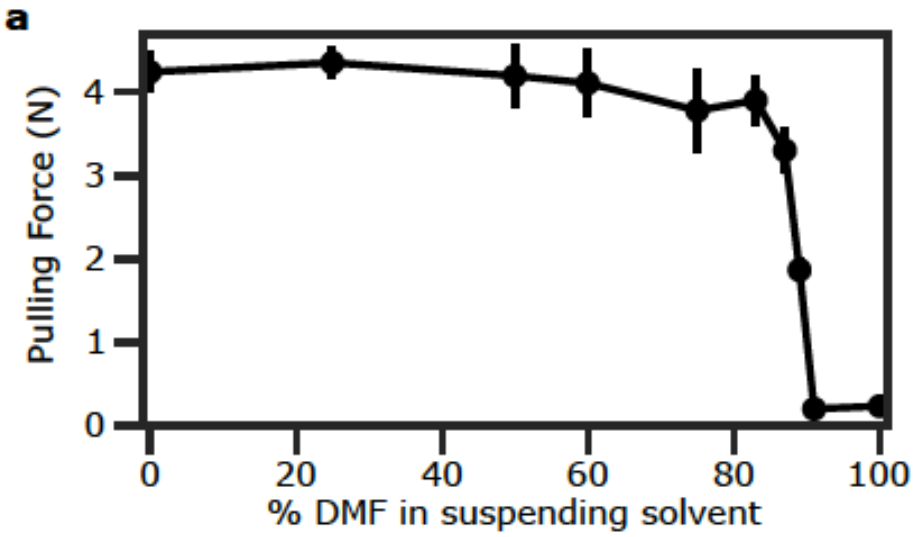
PMMA/ITA particles specifically designed to have surface terminated with COOH groups

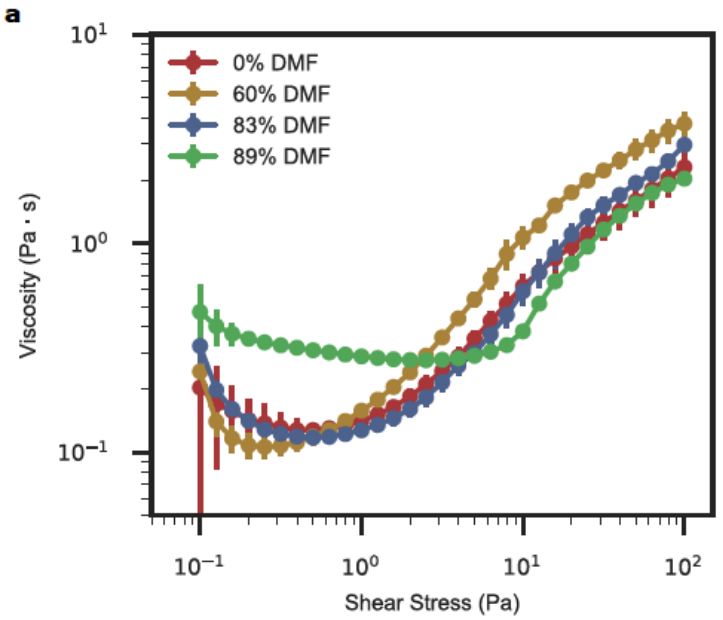


Urea couples to COOH ➔ interferes with hydrogen bonding capacity

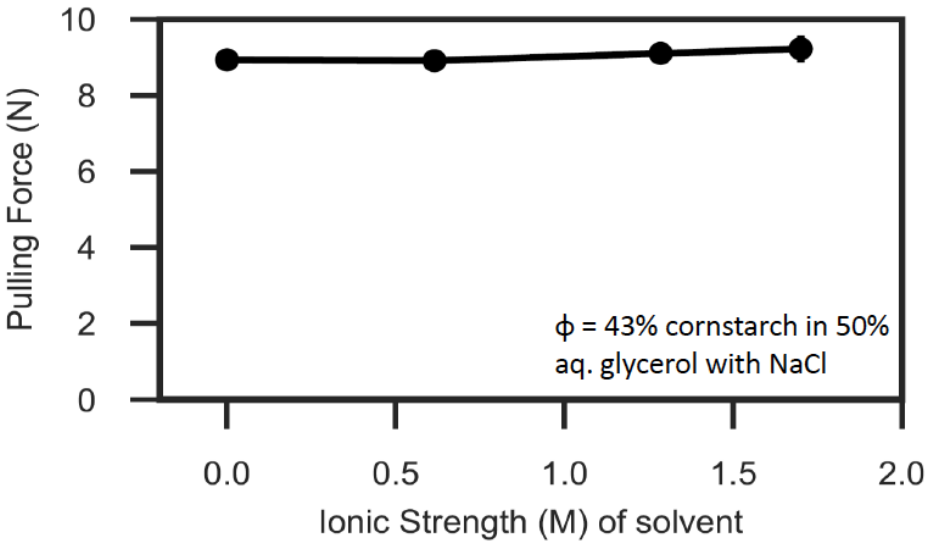
Deplete hydrogen bonding capacity in cornstarch suspensions

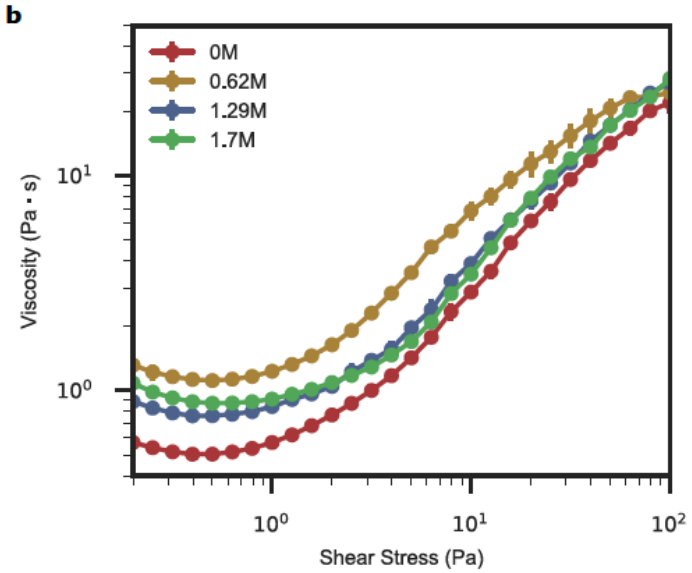
➔ *SJ no longer observed…but DST alive & well*





Is this really linked to particle “contacts”?



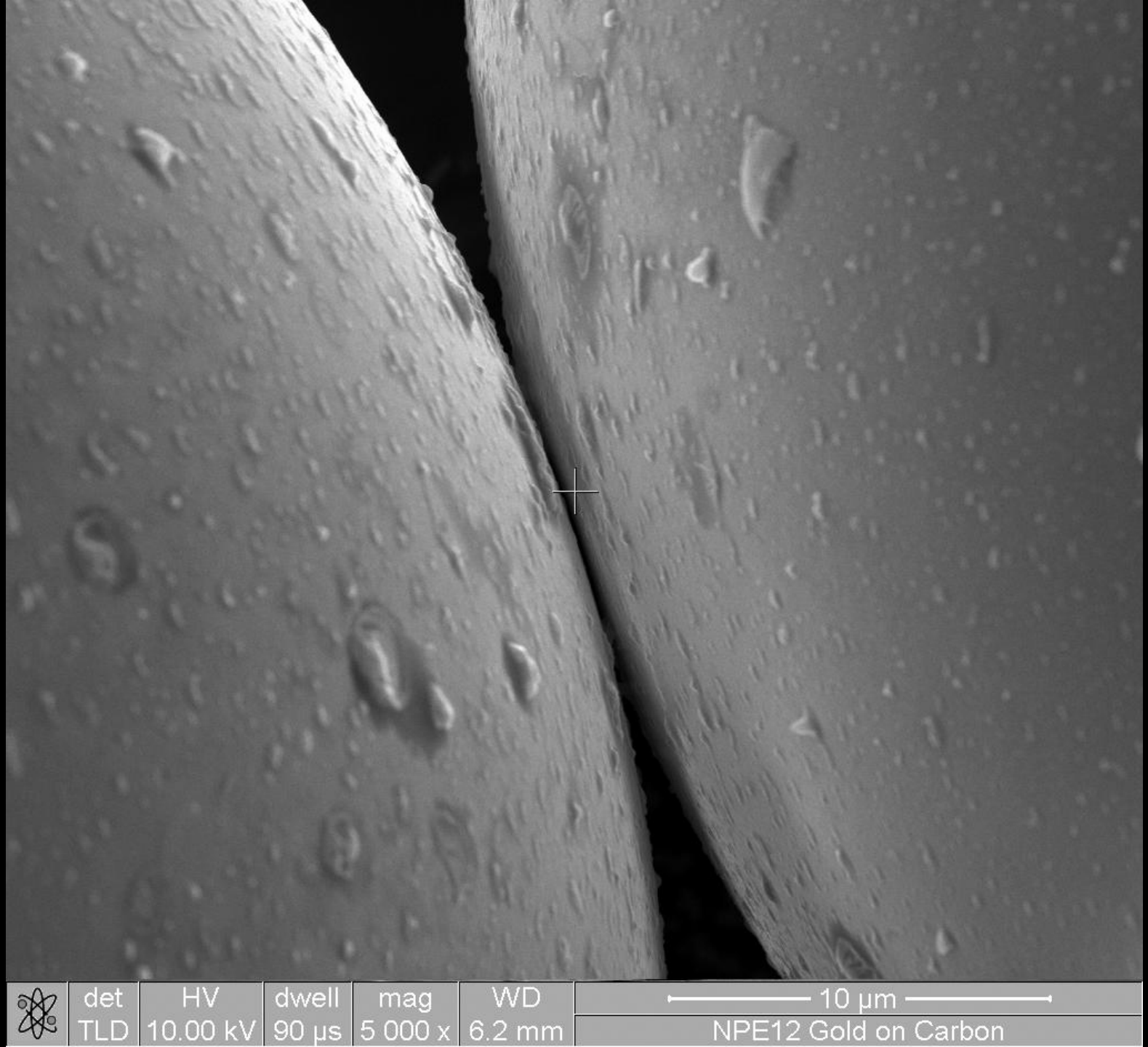


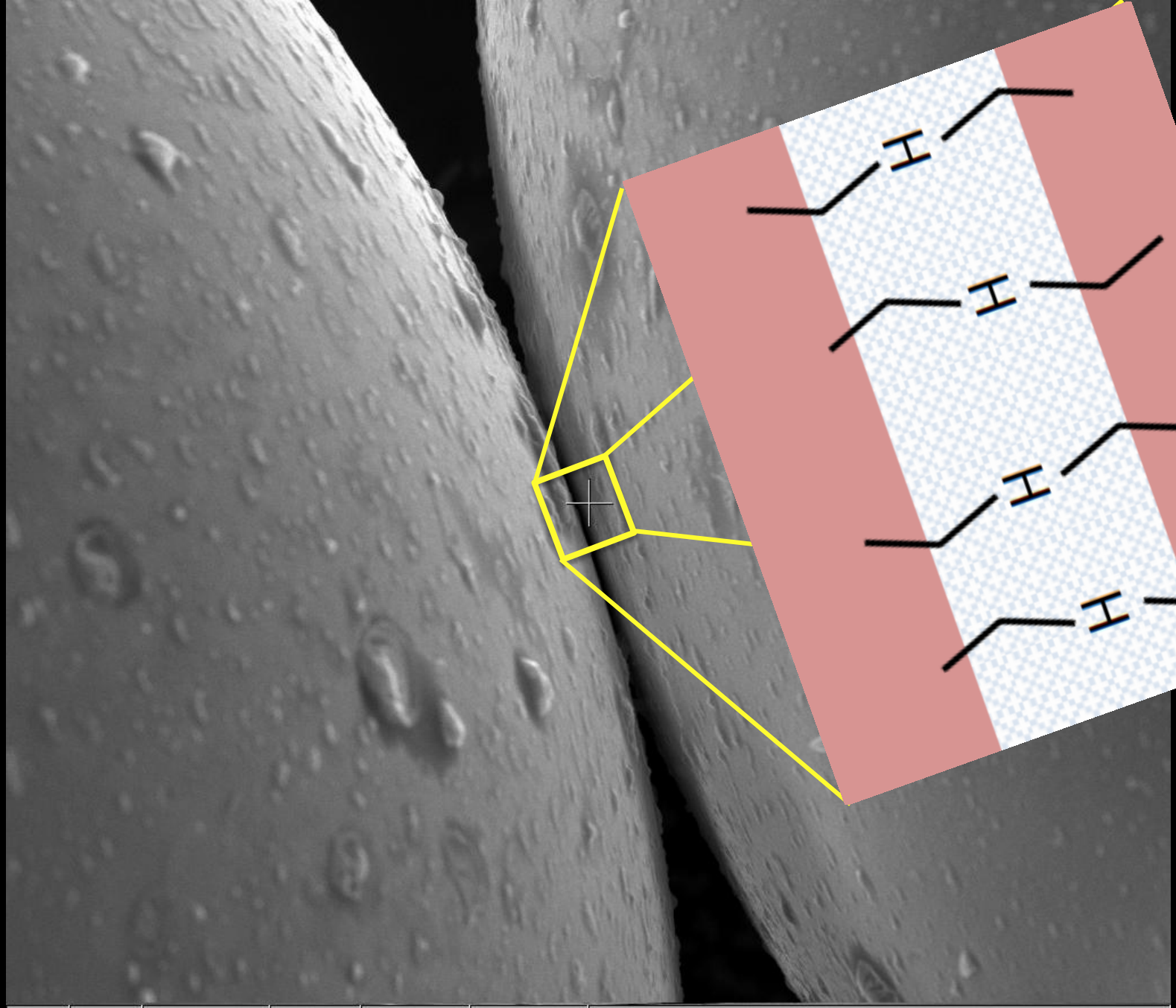
$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}}$$ (Debye length)

$$\kappa^{-1}(1.7M\ \mathrm{NaCl}) \approx 2\text{Å}$$

➔ Extremely close range effect

➔ likely not solvation, but direct contact


det
TLD
HV
10.00 kV
dwell
90 µs
mag
5 000 x
WD
6.2 mm
10 µm
NPE12 Gold on Carbon


det
TLD
HV
10.00 kV
dwell
90 µs
mag
5 000 x
WD
6.2 mm
10 µm
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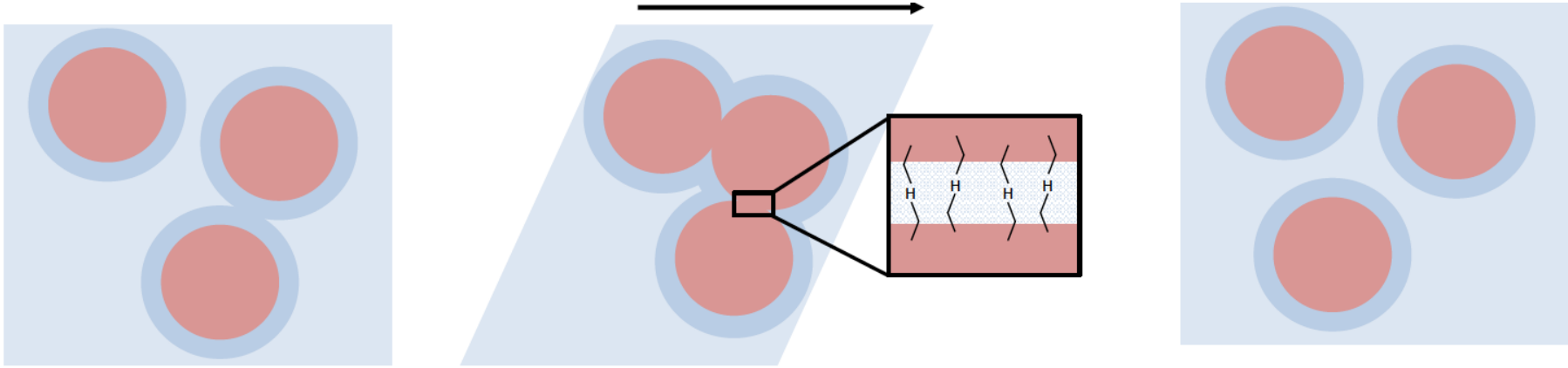
Proposed scenario



Lubricated contacts
low stresses or rates
ϕ_0 is key

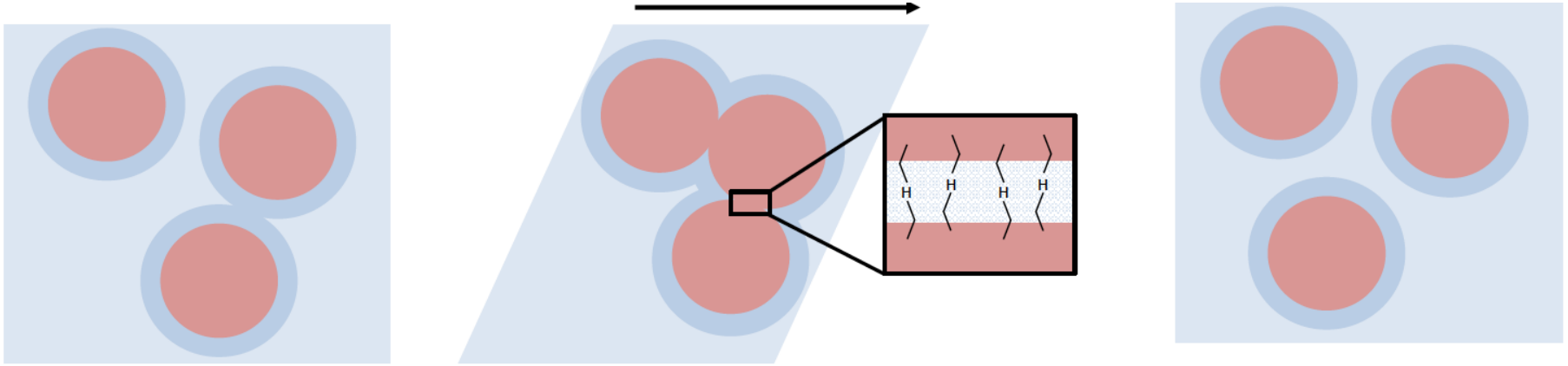
Frictional contact
Lubrication layer is broken
ϕ_m is key

H-bonding
enhances friction between particles

Relaxation
Stress is removed; particle-particle H-bonds may be replaced by solvent-particle bonds

Important: H-bonding is reversible in protic solvents like water

Proposed scenario



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Relaxation
Stress is removed; particle-particle H-bonds may be replaced by solvent-particle bonds

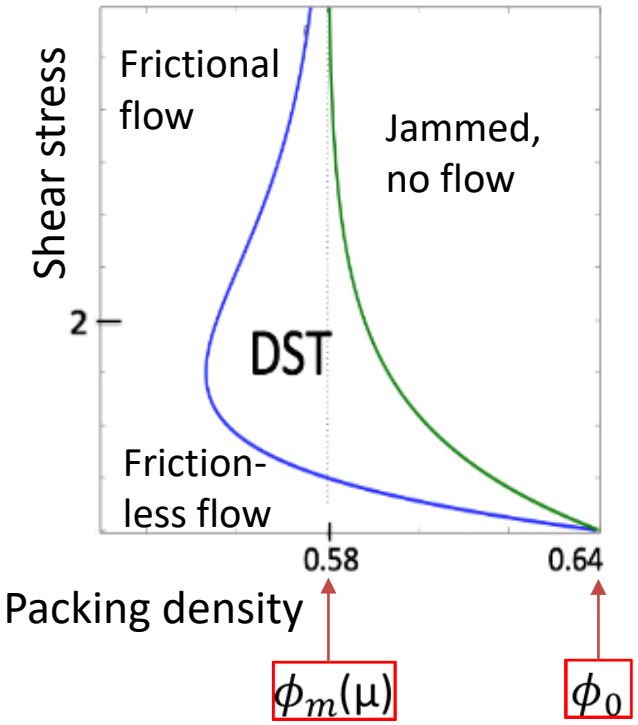
- Inter-particle hydrogen bonding enhances contact friction
- This decreases $\phi_m(\mu)$ & enlarges SJ regime

Conversely:
Reduced hydrogen bonding capacity ➔ smaller μ, larger $\phi_m(\mu)$

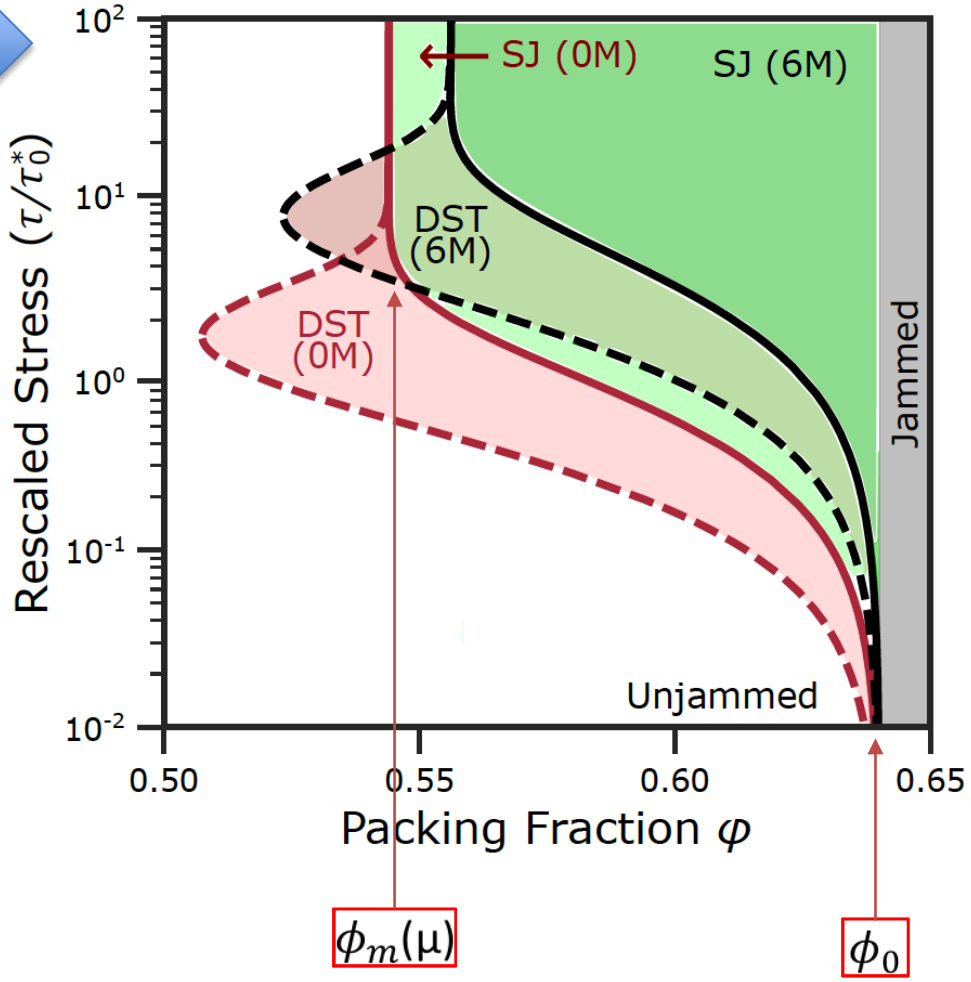
⬇

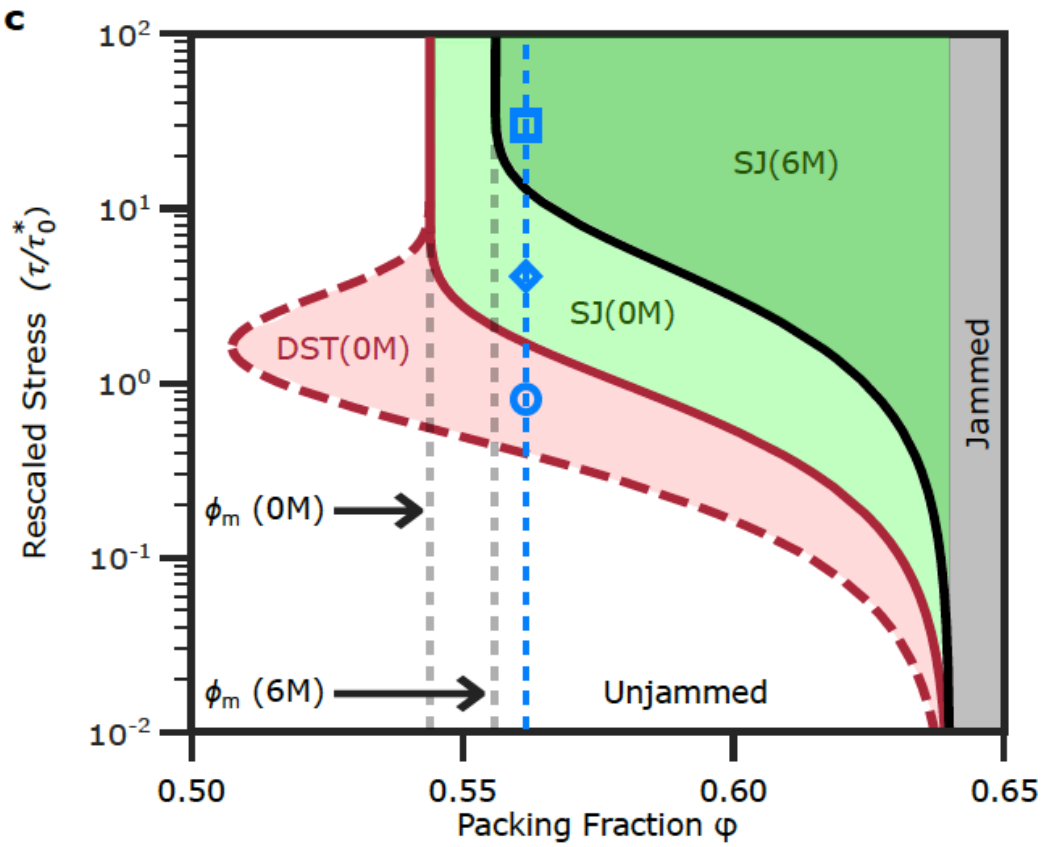
reduced SJ regime

Wyart & Cates (2014)



Experimentally calibrated model



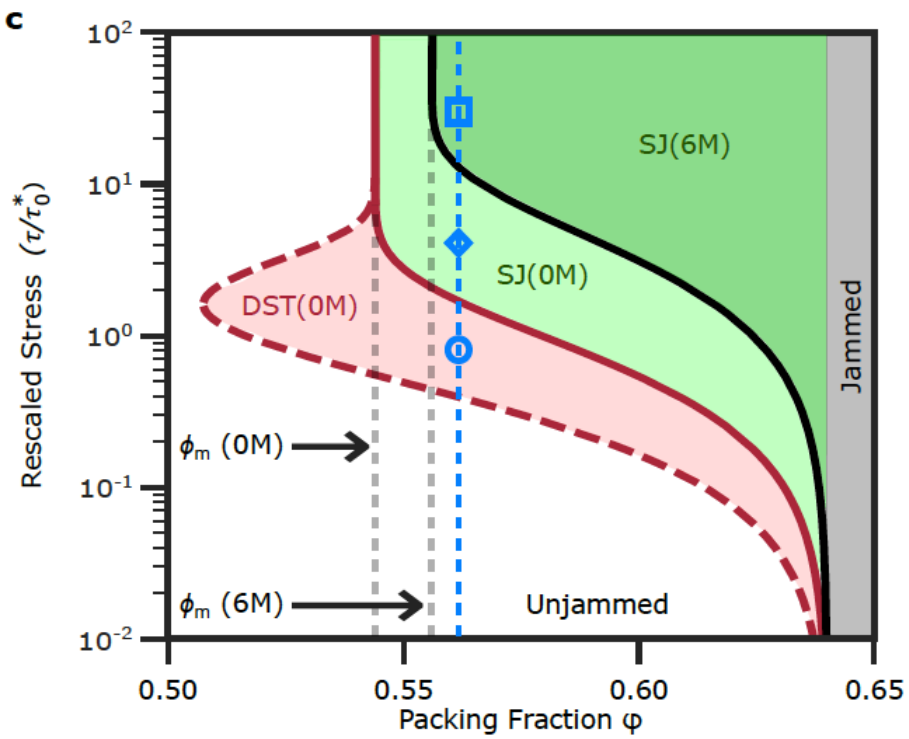


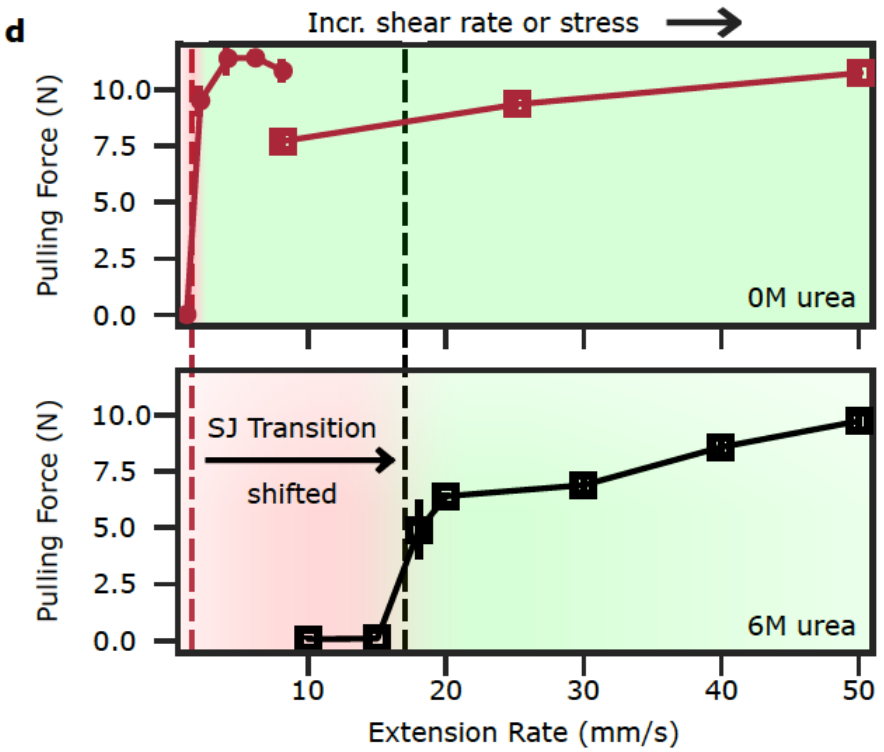
Get ϕ_m , ϕ_0, and τ^* from steady-state rheometry!

➔ See Endao Han's new preprint

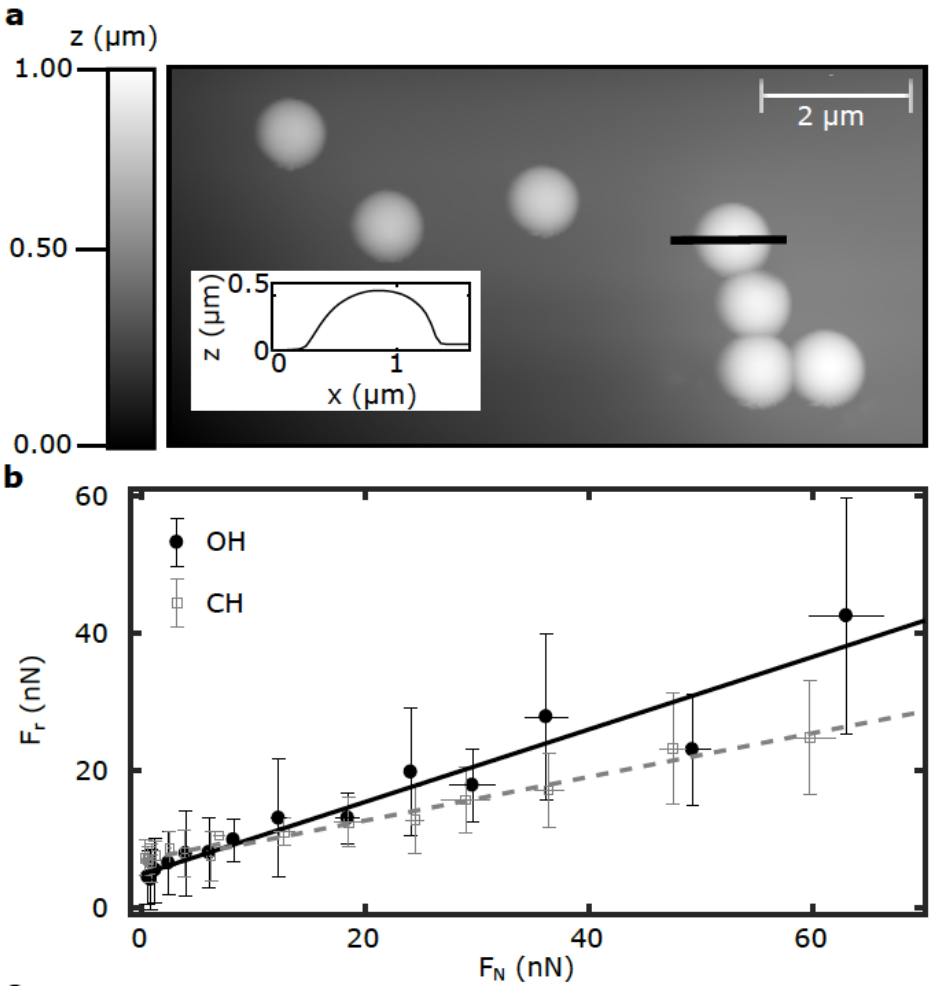
- Move DST-SJ boundary by controlling friction via hydrogen bonding capacity
- At fixed packing fraction: Onset stress for SJ (and also DST) shifts

Pull test = facile method for detecting shear jamming





Measure frictional interactions directly



Extract friction from lateral deflection force during slow, 100nm AFM scans near apex
>> scale of molecular interactions

Comtet et al. (Nature Comm 8, 2017):
fast oscillatory probe, few nm amplitude

μ = 0.53

μ = 0.3

Open Questions & New Opportunities

- Particle-particle hydrogen bonds vs solvation layers?
- Atomistic modeling of particle-particle hydrogen bonding?
- Hydrogen bonds reversible in protic solvent like water. Individual time scale for bond formation or breaking ~10^{-12}s….but collective behavior?
- SJ with small attractive interactions?

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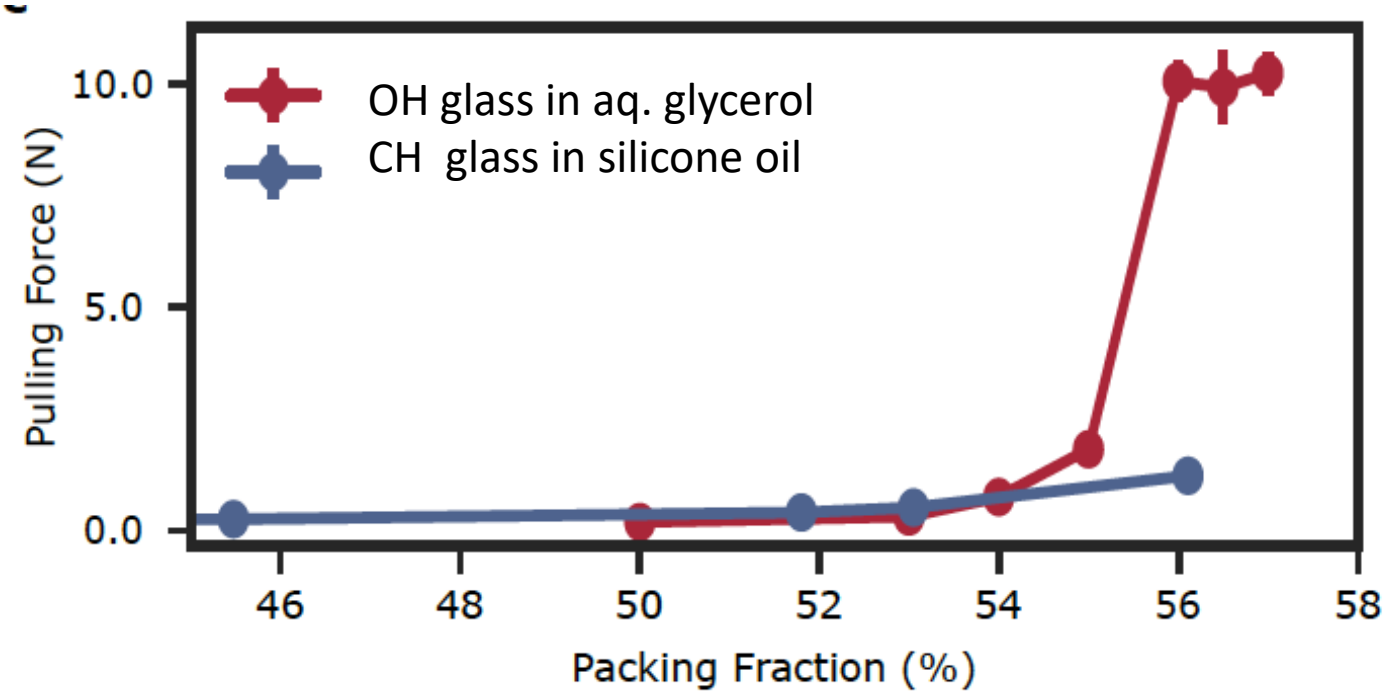
- Design targeted SJ behavior by tailoring particle surface & solvent!

Design surface chemistry & solvent to elicit shear jamming



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- Similar scenarios for non-aqueous systems?