NC STATE UNIVERSITY

Hsiao Lab
Re-imagining Interfaces

IFPRI
International Fine Particle Research Institute

Accelerated acoustic prediction of aging and failure

Wet Systems
(Project Review #1, 2024)

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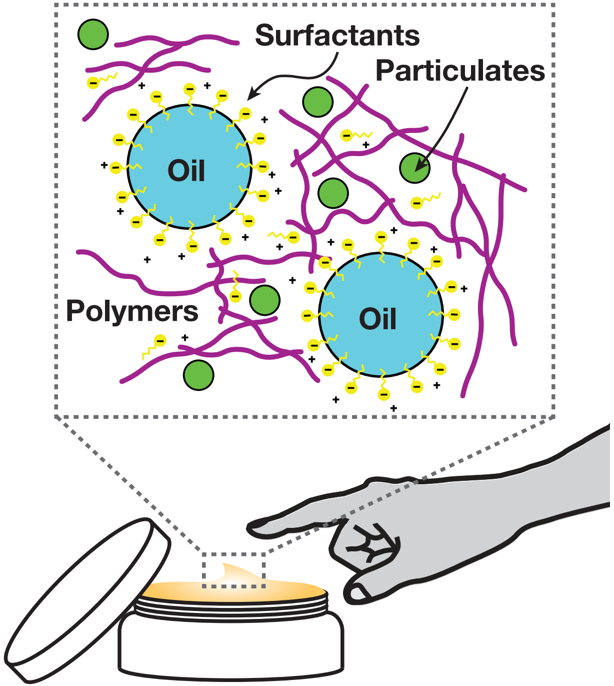
Shelf life of colloidal dispersions

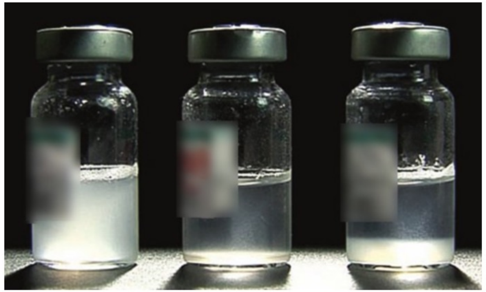
Formulation, stability, rheology of products



Farias, Hsiao & Khan, *ACS Appl Polym Mater* (2020).
Smith & Hsiao, *Chem Eng Prog* (2020).

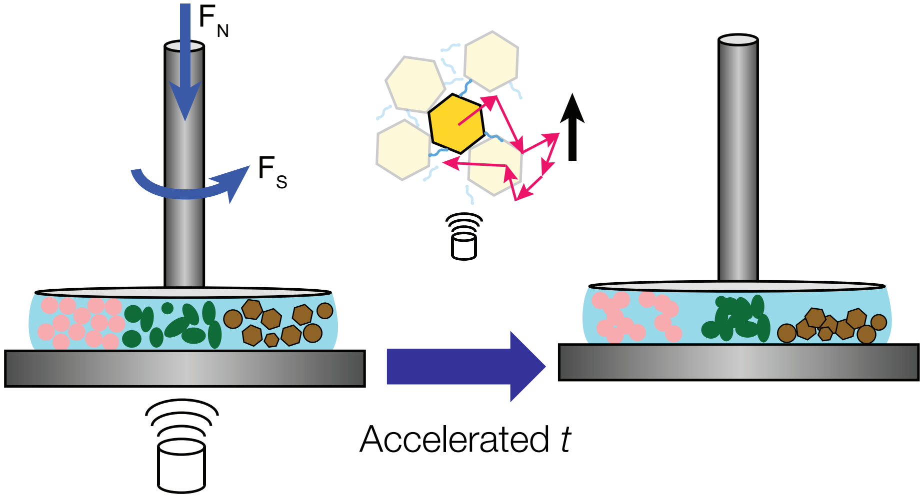
Phase separation or syneresis

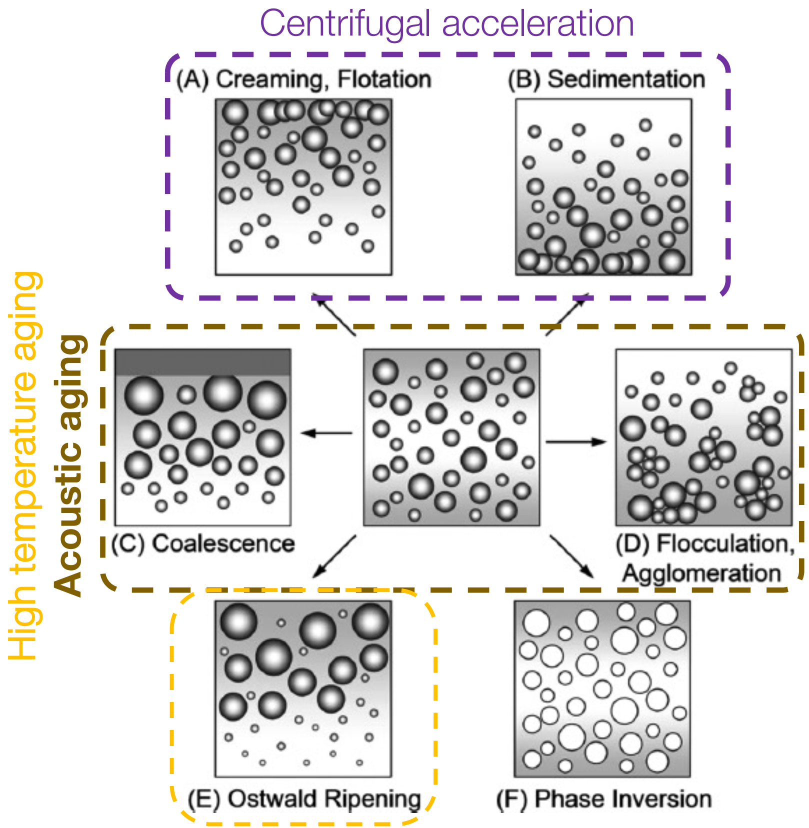
Vaccine stability



Resuspension of sediments

Project overview





Lerche & Sobisch, *J Dispersion Science & Technology* (2011).

Goal: Develop a novel acoustic platform to speed up aging and failure in dispersions

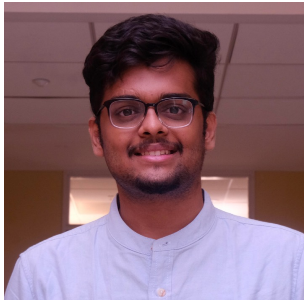
(Coalescence, flocculation, agglomeration)

Timeline and deliverables

STUDENTS	Shourie Yerabati, Nazanin Shakoury	YEAR ONE				YEAR TWO				YEAR THREE			
#	TASK TITLE	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1	Develop industry model formulations	✓	✓										
2	Develop academic model formulations		✓	✓	✓	✓							
3	*Ex situ* rheology with and without acoustics		✓	✓	✓	✓							
4	Imaging of particle dynamics					✓							
5	Generate stability phase diagrams												
6	Obtain predictive correlations of stability												

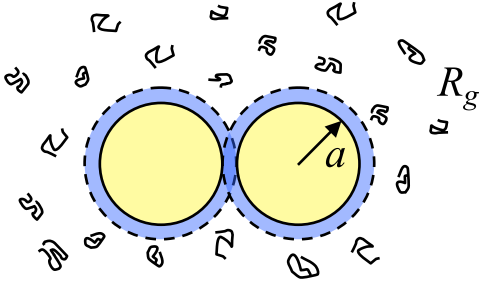
Major accomplishments this cycle:

- 3 model systems developed including commercial agrochemical dispersion, oil/water nanoemulsion, colloidal depletion gels
- Demonstrated that low-power acoustic aging does work!
- However, effect of acoustics is currently system dependent
- 4 IFPRI Liaison update meetings conducted
- Support of 2 PhD students working on different model systems
- 3 upcoming presentations at national conferences

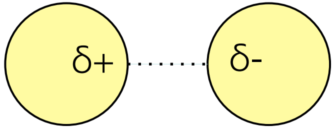


Background: colloidal forces responsible for stability

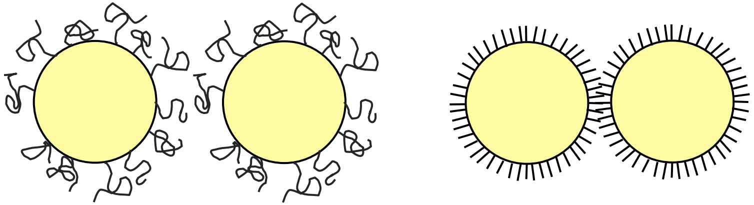
Destabilizing (causes aggregation)



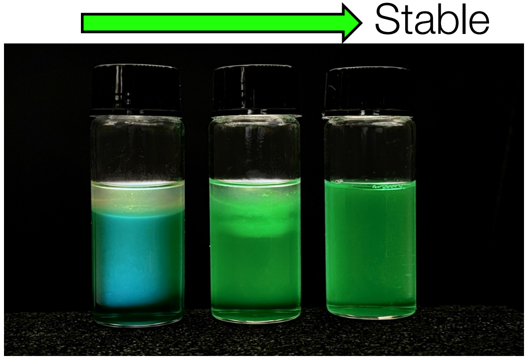
Depletion forces



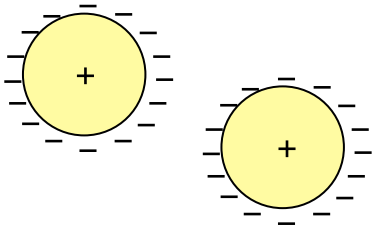
Van der Waals forces



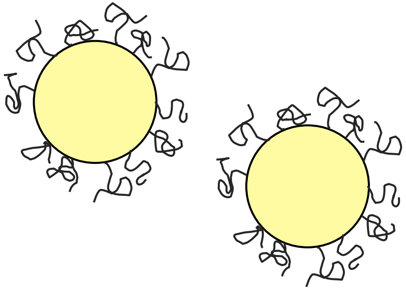
Thermal gelation



Stabilizing (reduces aggregation)



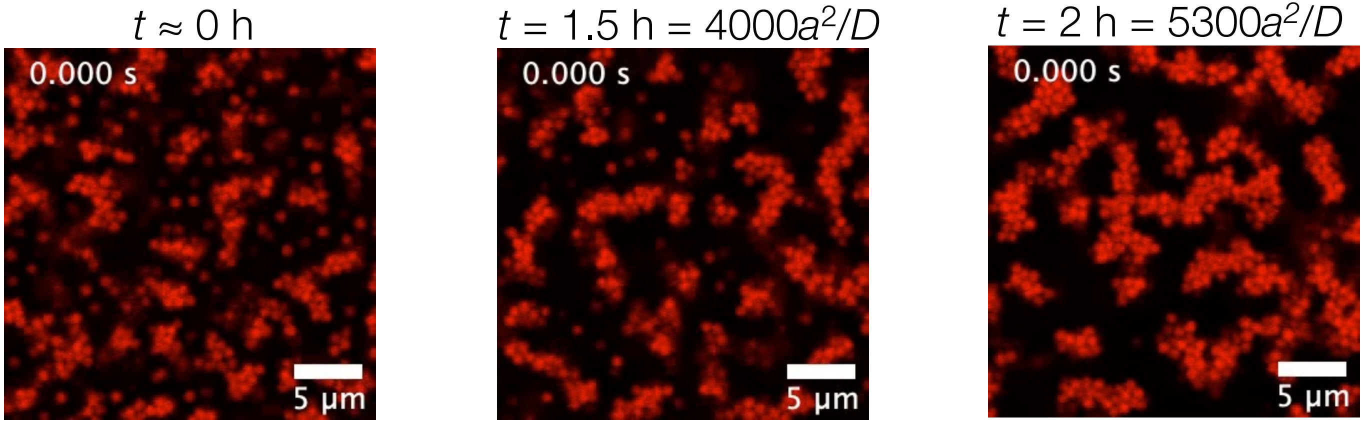
Electrostatics

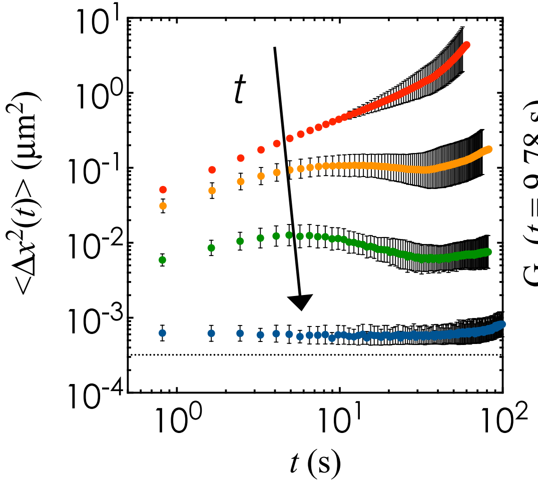


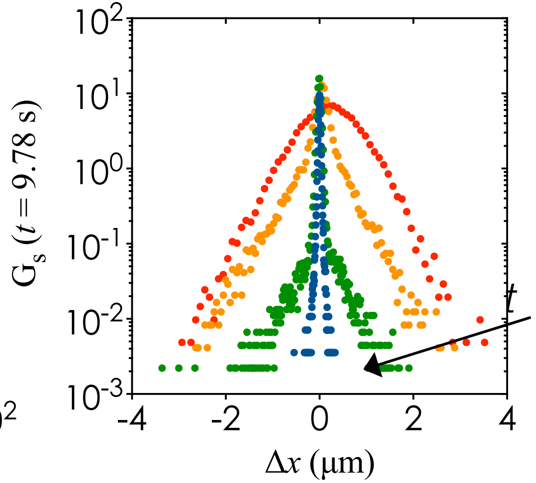
Steric layer grafting

Background: Example of natural aging in a colloidal gel

$2a$ = 800 nm
ϕ = 0.20
U/kT = 6

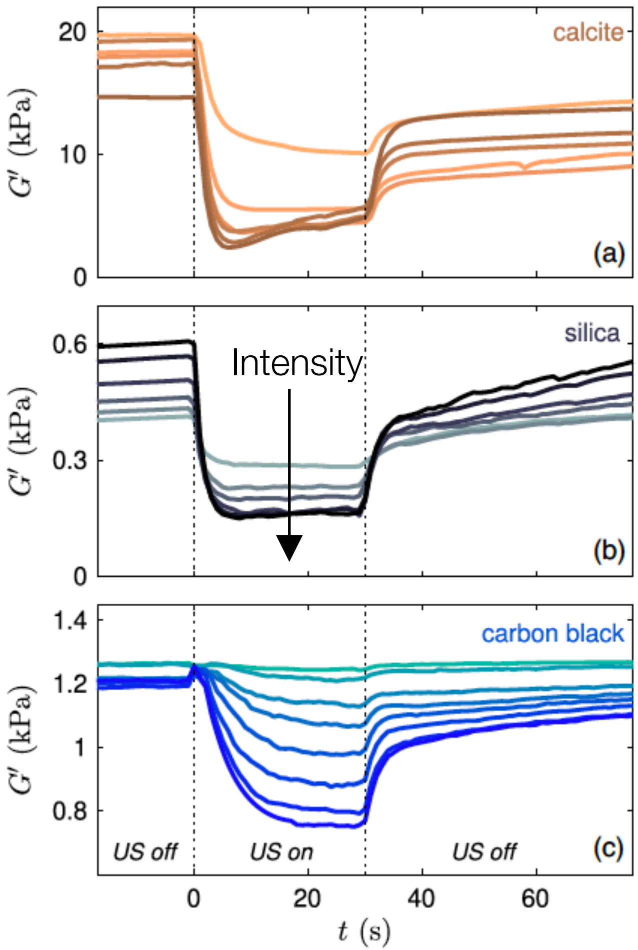


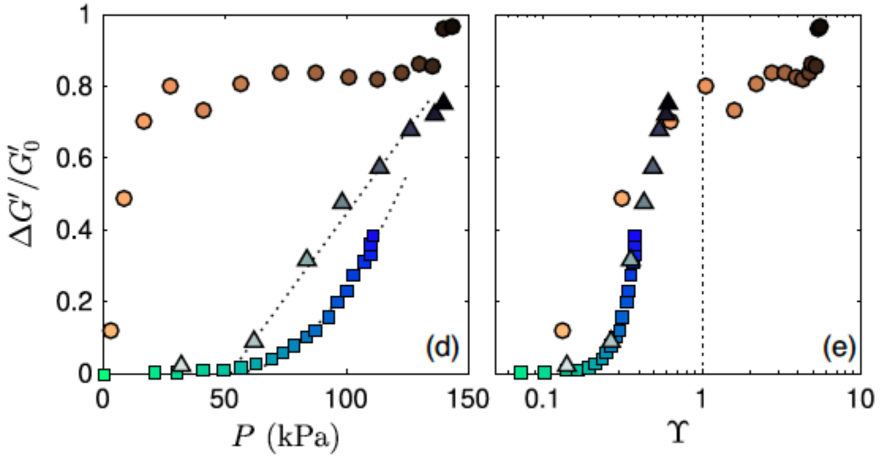




Hsiao & Solomon *et al.*, *Soft Matter* (2014).

Background: Acoustic effects on dispersions





Gibaud *et al. Phys Rev X* (2020).

- Too high of a power leads to yielding
- Acoustic pressure should be matched to the bulk yield stress

$$P = 2\pi f a \rho c$$

Acoustic pressure [=] Pa

(Frequency) x (Amplitude) x (Density) x (Speed of sound)

Experimental conditions and setup

Natural aging

- Room temperature
- Dry, dark place
- Aged for 30 days

Heat aging

- T = 40, 54 °C
- Aging t = 30 days
- Waiting t = 1 day

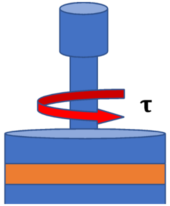
Acoustic aging $P = 2\pi f a \rho c$

High-power ultrasonication

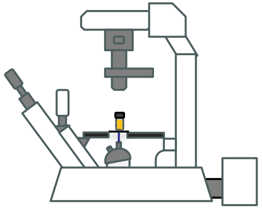
- Power = 150-260 W
- Frequency = 25 kHz
- Displacement = 15-26 μm
- Acoustic pressure = 3-5 MPa
- Aging t = 24 mins
- Waiting t = 3 days

Low-power acoustic setup

- Frequency = 20 kHz
- Max displacement ~ μm
- Acoustic pressure ~ 10^2 Pa
- Aging t = 120 mins
- Waiting t = 3 days



Ex situ rheology:
Viscoelasticity and yield stress



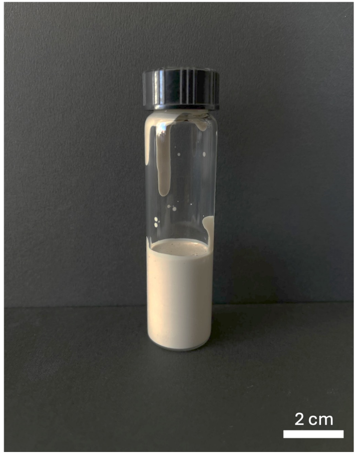
Ex situ confocal microscopy:
Microstructure and dynamics

Yield stress of reference materials: Toothpaste (10 Pa), ketchup (20 Pa), vaccine adjuvants (10^{-3} Pa), agrochemical dispersions (1 Pa)

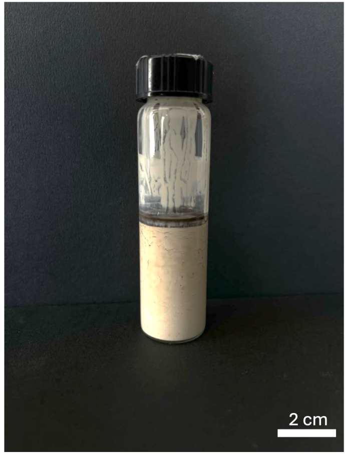
Model system 1: commercial samples from IFPRI

System: 30-50 wt% colloidal solids, 1-3 wt% surfactants, <10 wt% dispersant, trace rheology stabilizers
Aqueous media

Fresh sample
t_w = 0 days



Naturally aged
t_w = 30 days



Heated to 54°C, 70°C
t_a = 30 days
t_w = 1 day

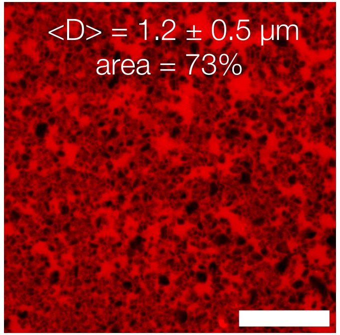
High power acoustics
(~MPa)
t_a = 2 h
t_w = 3 days

Low power acoustics
(~10^2 Pa)
t_a = 2 h
t_w = 3 days

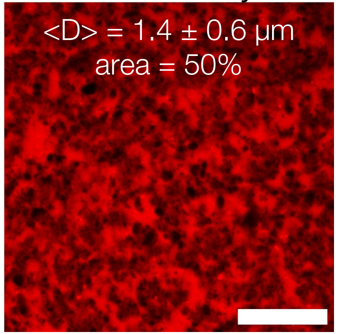
Confocal micrographs of commercial samples

Naturally aged

Fresh sample



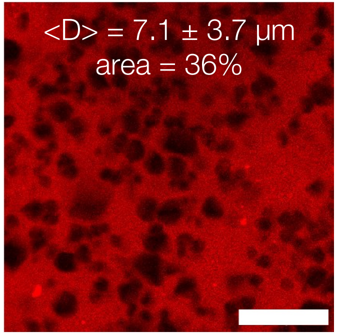
After 30 days



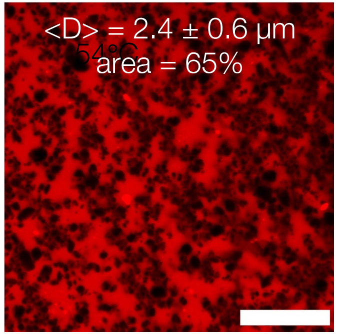
Heat aged

(t_a = 30 days, t_w = 6 h)

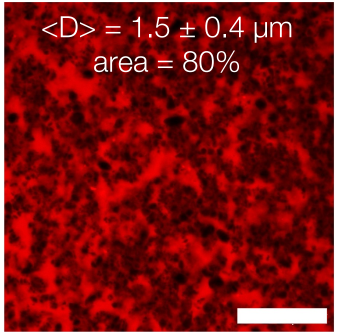
70°C



54°C



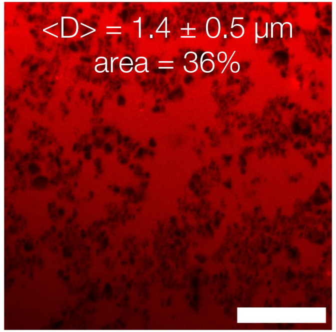
40°C



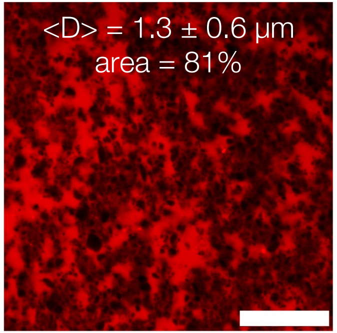
Acoustic aged

(t_a = 2 h, t_w = 3 days)

High power

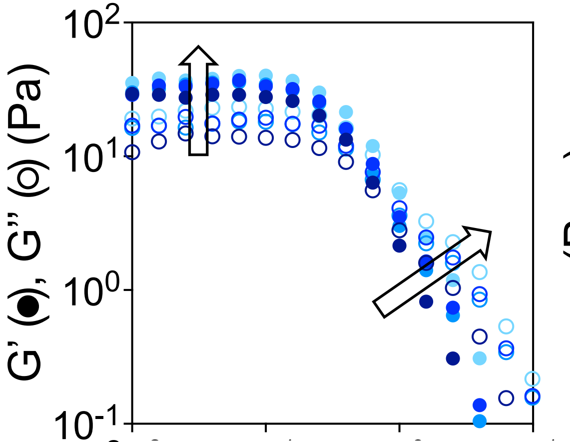


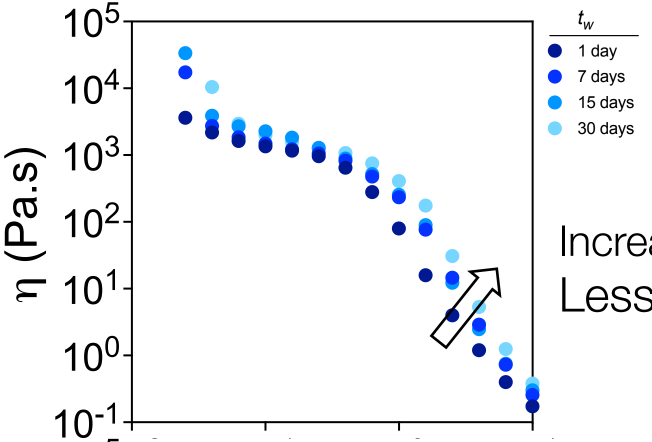
Low power

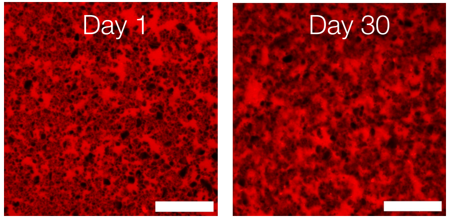


Scale = 20 μm

Ex situ rheology of commercial samples

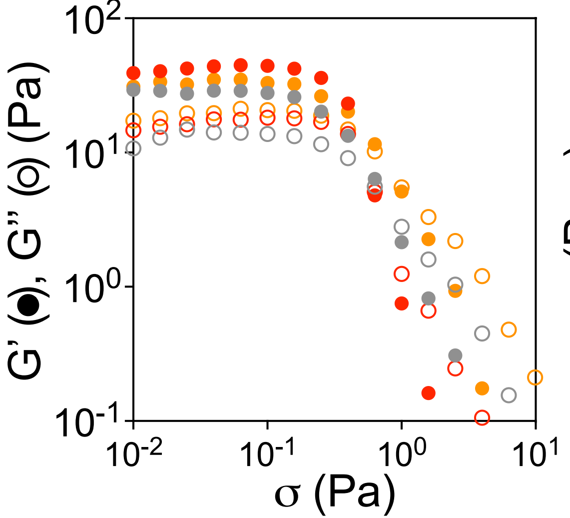


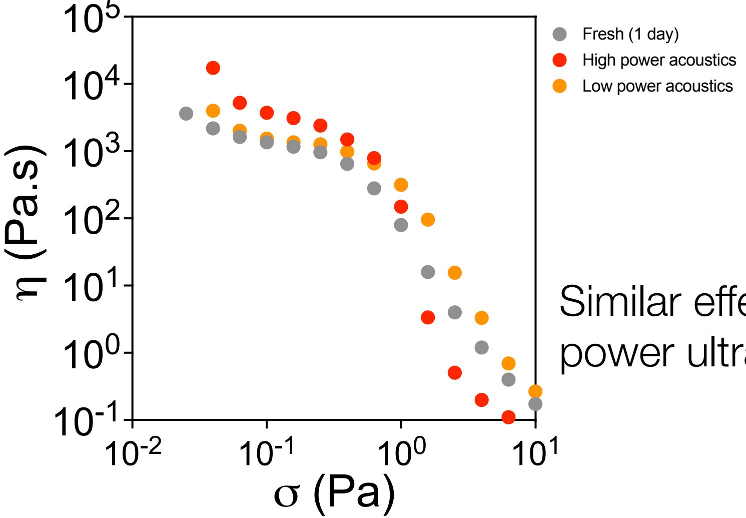


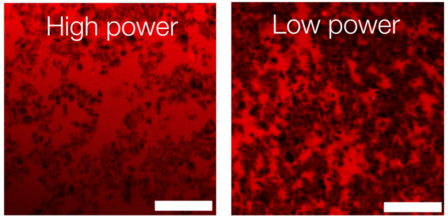


Increased G' and η

Less shear thinning



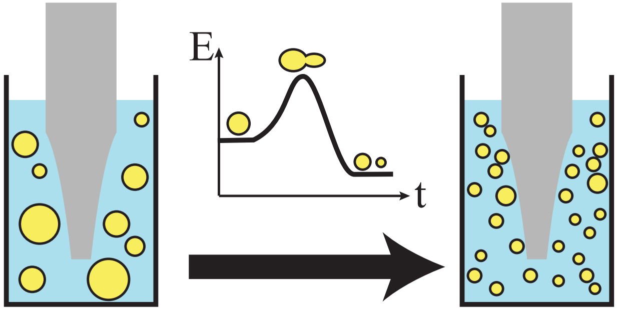


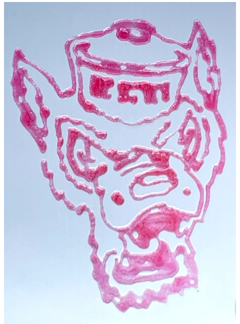


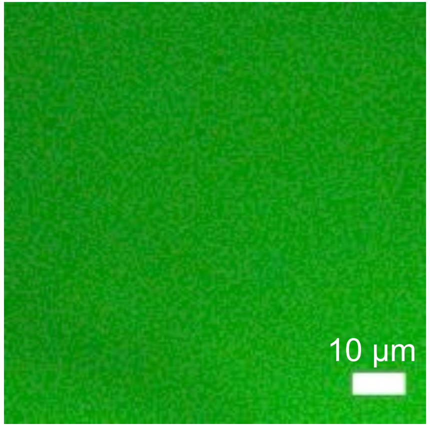
Similar effects seen with low power ultrasound

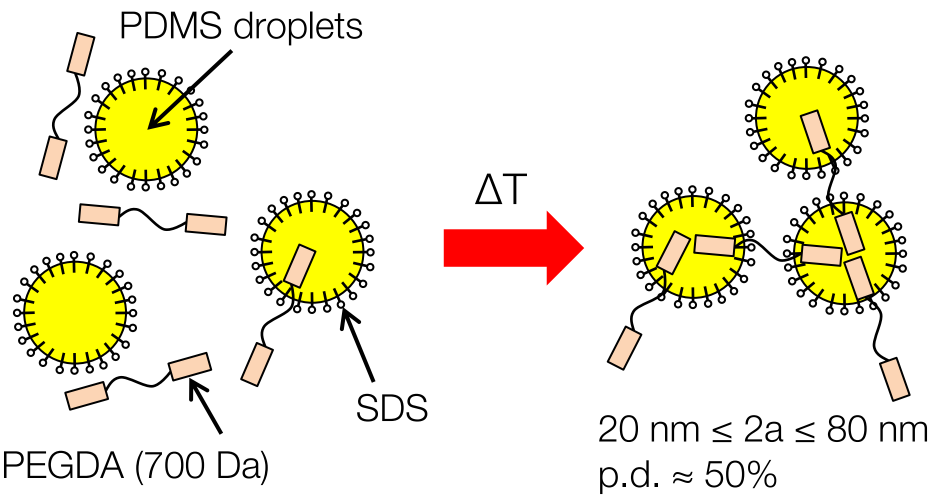
Scale = 20 μm

Model system 2: heat sensitive o/w nanoemulsions

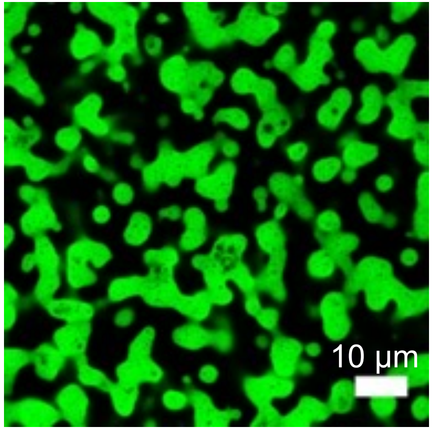






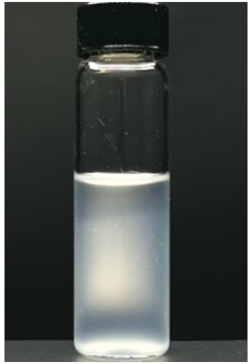
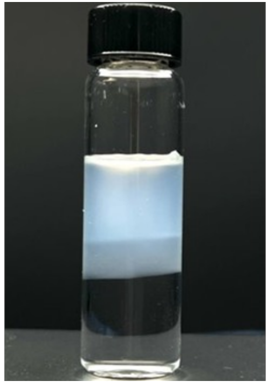
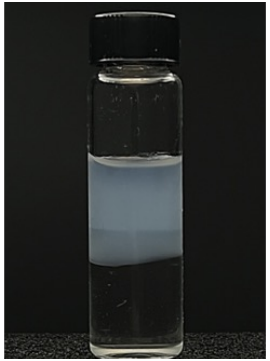


20 nm ≤ 2a ≤ 80 nm
p.d. ≈ 50%
$0.1 \leq \phi \leq 0.33$

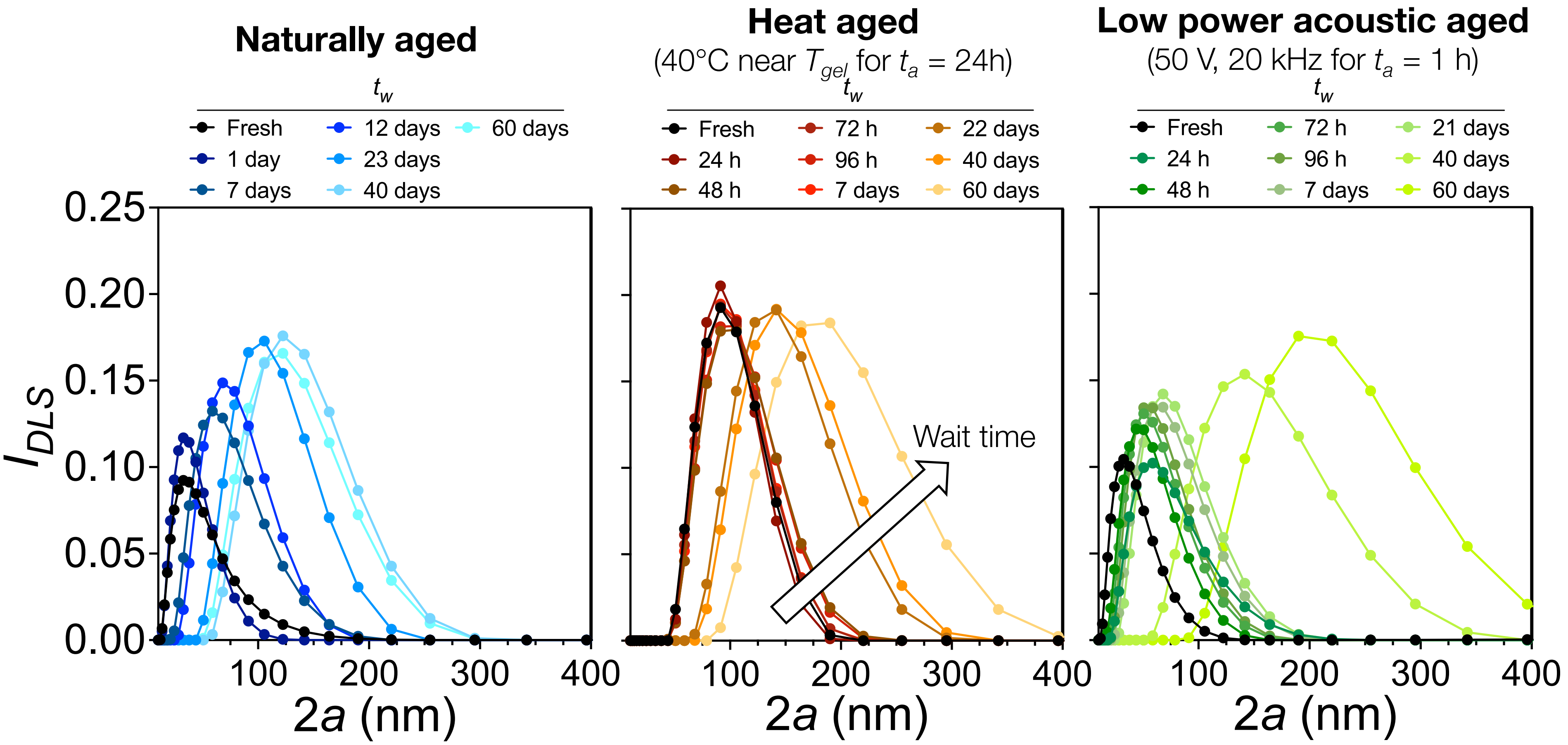


Hsiao & Doyle, *Soft Matter* (2015).

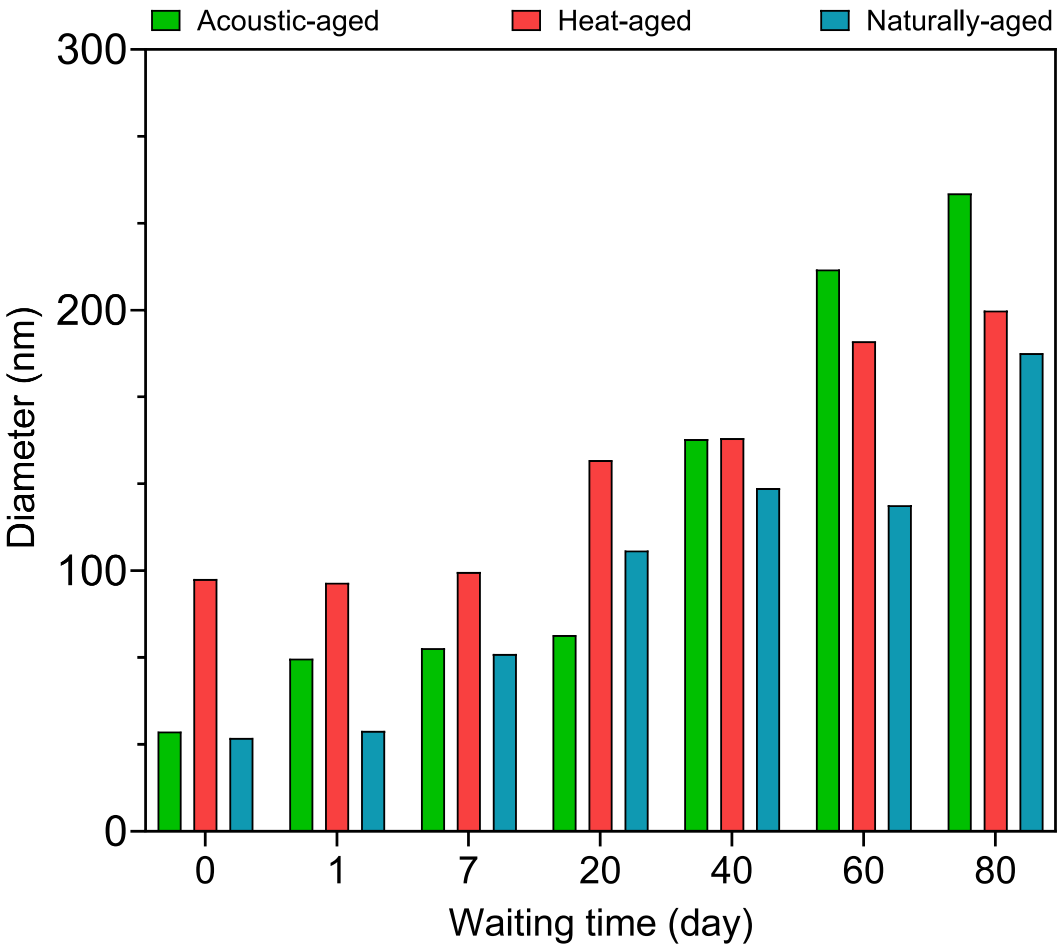
Vial images of aged nanoemulsions

	Naturally aged	**Heat aged** (40°C near T_{gel} for t_a = 24h)	**Low power acoustic aged** (50 V, 20 kHz for t_a = 1 h)
t_w = 20 days			
t_w = 90 days			

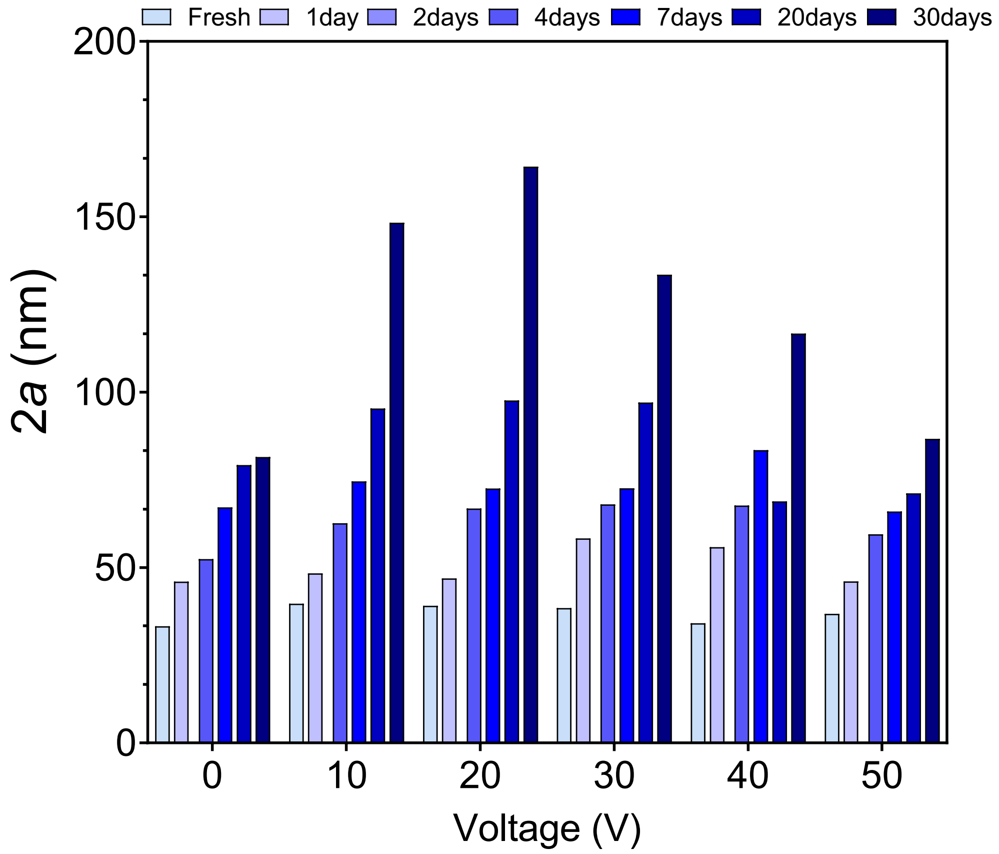
Droplet growth kinetics with different aging methods



Droplet growth kinetics with different aging methods



Effect of acoustic power on droplet growth



f = 20 kHz, t_w = 30 days

Sample	***2a* (nm)**
10 V	148
20 V	164
30 V	134
40 V	117
50 V	87
Natural	82

- Fastest aging at 20V applied power
- Delayed particle growth with differences most significant at $t_w \geq$ 20 days
- Possible "resonant" pressure that matches Brownian pressure

Summary and future plans

Low power acoustic platform works for accelerating destabilization!

STUDENTS	Shourie Yerabati, Nazanin Shakoury	YEAR ONE				YEAR TWO				YEAR THREE			
#	**TASK TITLE**	**Q1**	**Q2**	**Q3**	**Q4**	**Q1**	**Q2**	**Q3**	**Q4**	**Q1**	**Q2**	**Q3**	**Q4**
1	Develop industry model formulations	✓	✓										
2	Develop academic model formulations		✓	✓	✓	✓							
3	*Ex situ* rheology with and without acoustics		✓	✓	✓	✓							
4	Imaging of particle dynamics					✓							
5	Generate stability phase diagrams												
6	Obtain predictive correlations of stability												

Upcoming plans for Y2:

- Continue developing model colloidal gel dispersions based on discussion with IFPRI partners
- Construct acoustic transducers for *in situ* confocal microscopy and rheometry
- Imaging of single particle dynamics with *in situ* acoustic application
- Correlation of accelerated dynamics with real-time aging with bulk measurements
- Towards understanding how acoustics target certain destabilization mechanisms