

Dynamics of aging, coarsening and yielding in (dense) phase separating colloidal gels

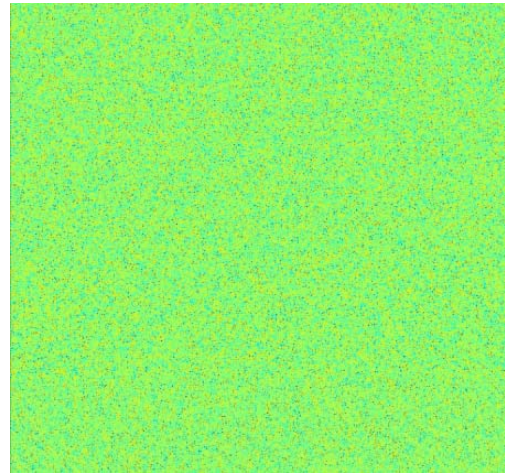
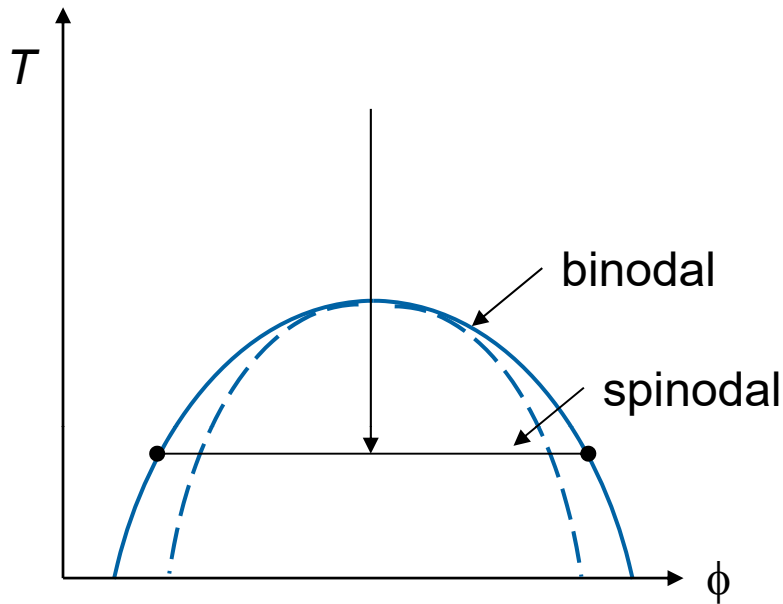


Matthew Helgeson



UC SANTA BARBARA
engineering

Using phase instability to control structure



Spinodal decomposition:
Cahn & Hilliard (1958)

$$\frac{\partial \phi}{\partial t} = D \nabla^2 (\phi^3 - \phi - \gamma \nabla^2 \phi)$$

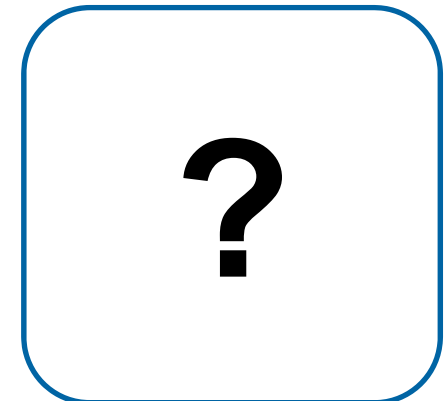
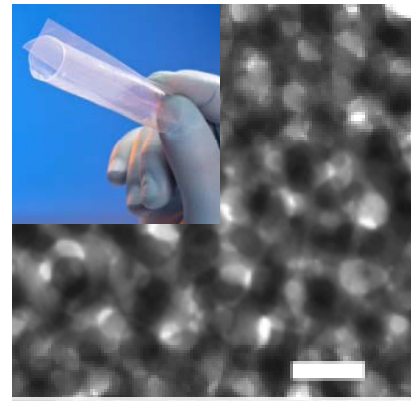
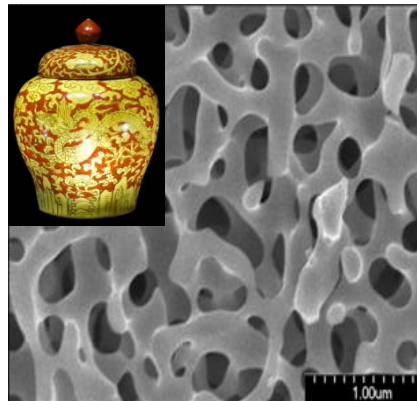
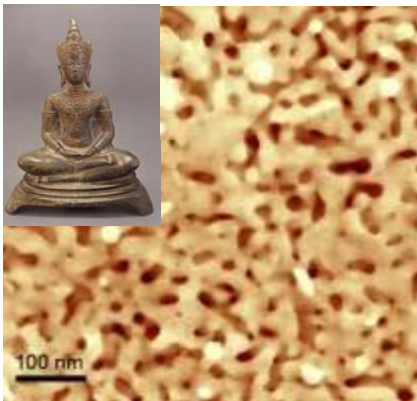
- Quench
- Anneal
- Temper

Metal alloys

Ceramics

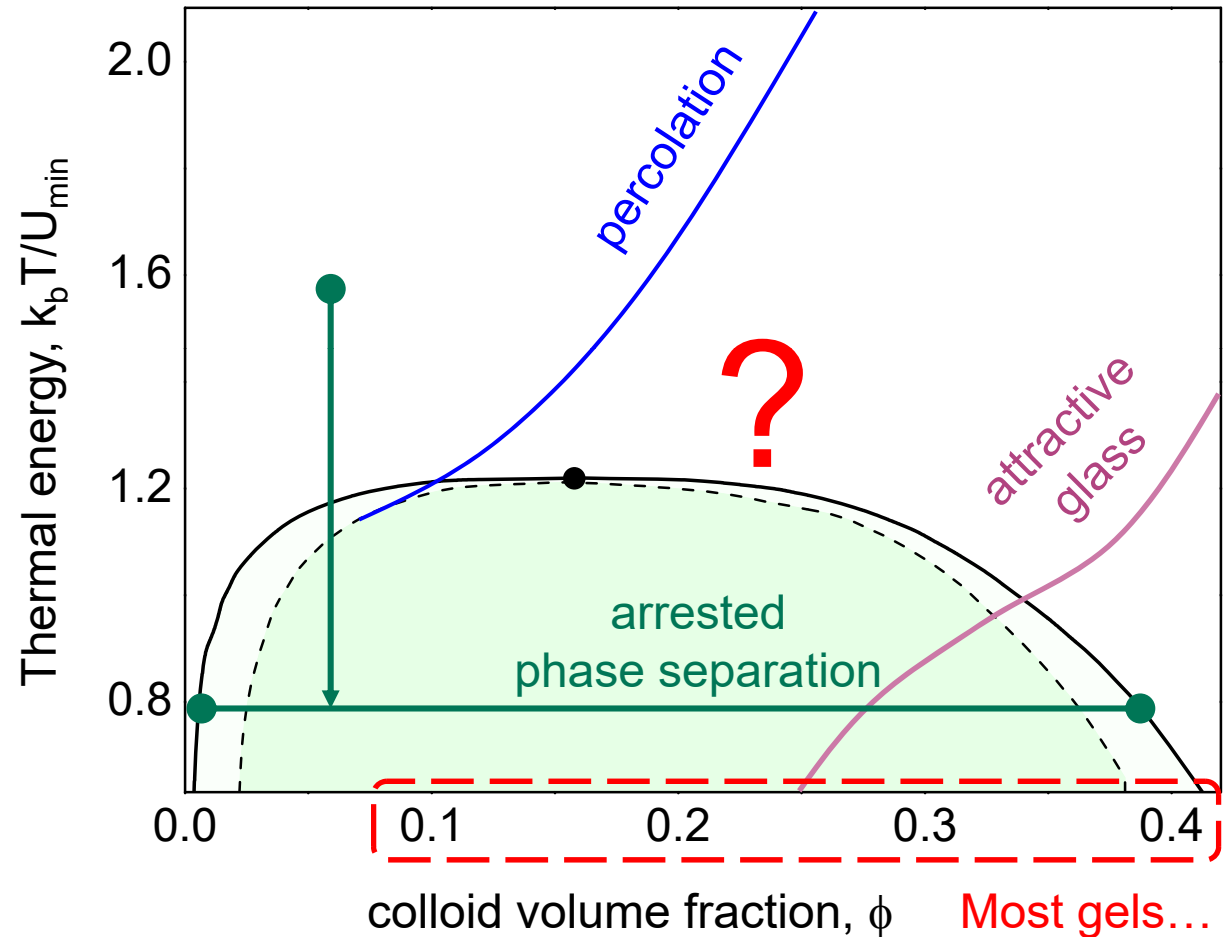
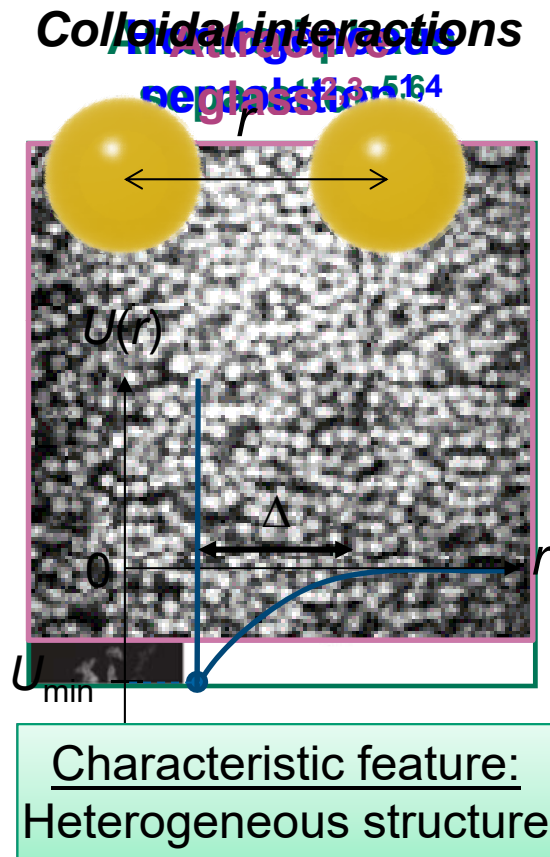
Polymer blends

Colloidal solids



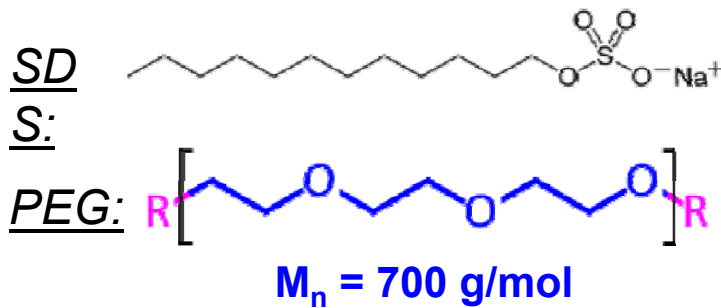
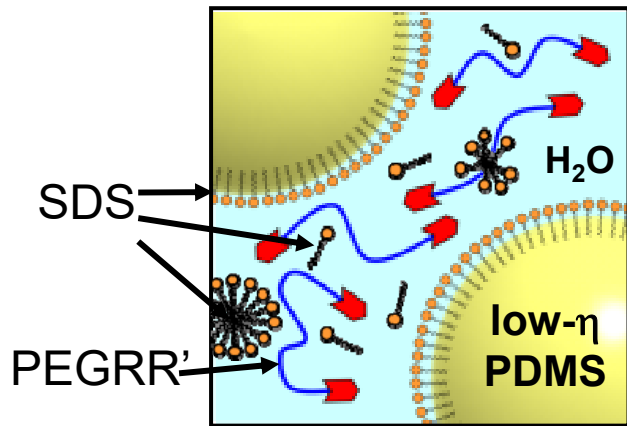
Colloidal gelation: a thermodynamic perspective

Colloidal phase diagram

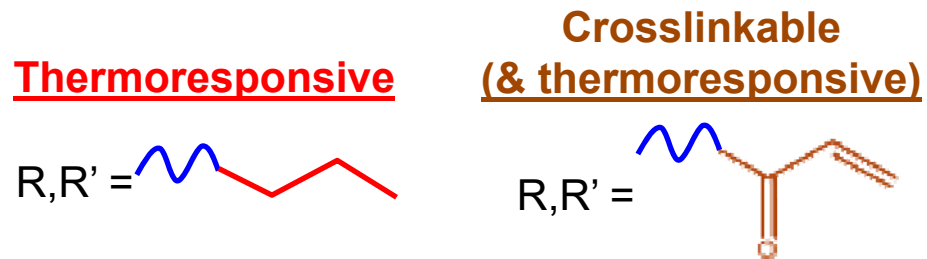


Challenge: How do we *experimentally* achieve dynamic, reversible control over colloidal attractions necessary to enable thermal processing?

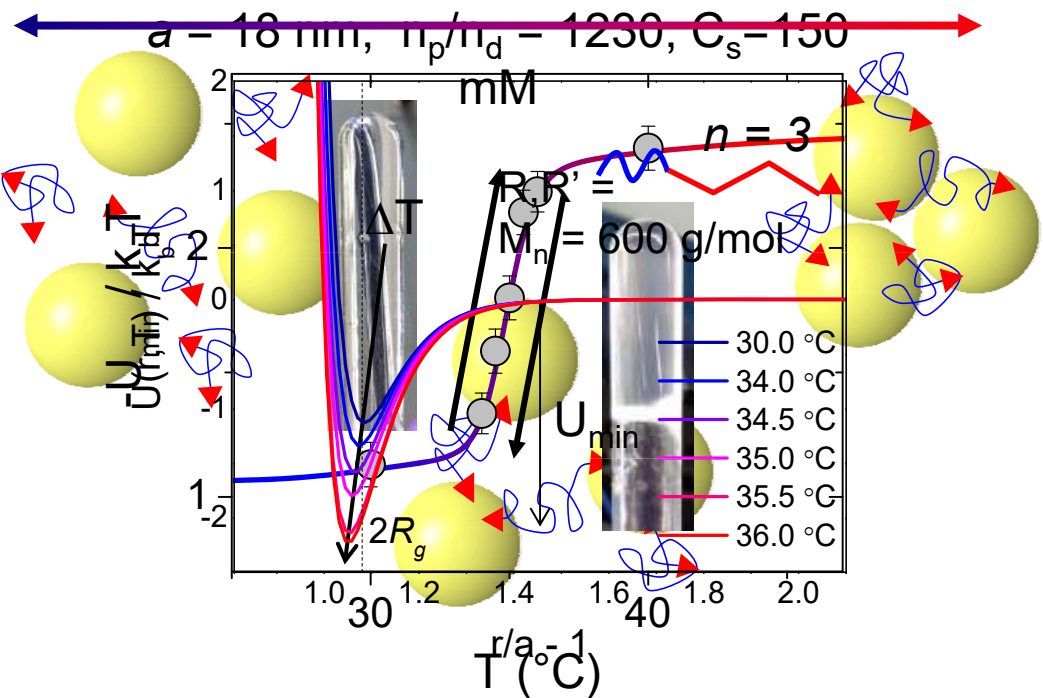
Thermoresponsive oil-in-water nanoemulsions¹⁻³



Thermosensitive polymers give rise to thermo-responsive polymer bridging.



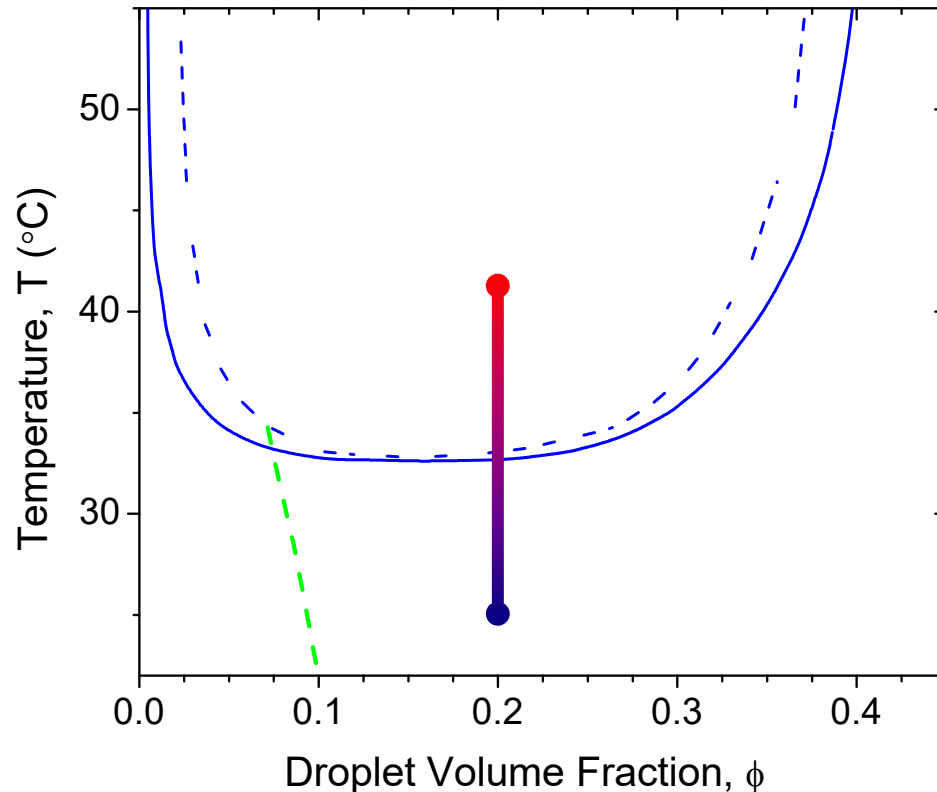
Interdroplet interactions (SANS)



- [1] M.E. Helgeson *et al.*, Nature Materials, 2012, 11(4): 344-352.
[2] J. Kim *et al.*, Soft Matter, 2013, 9(29): 6897-6910.



Thermoresponsive gelation¹⁻³



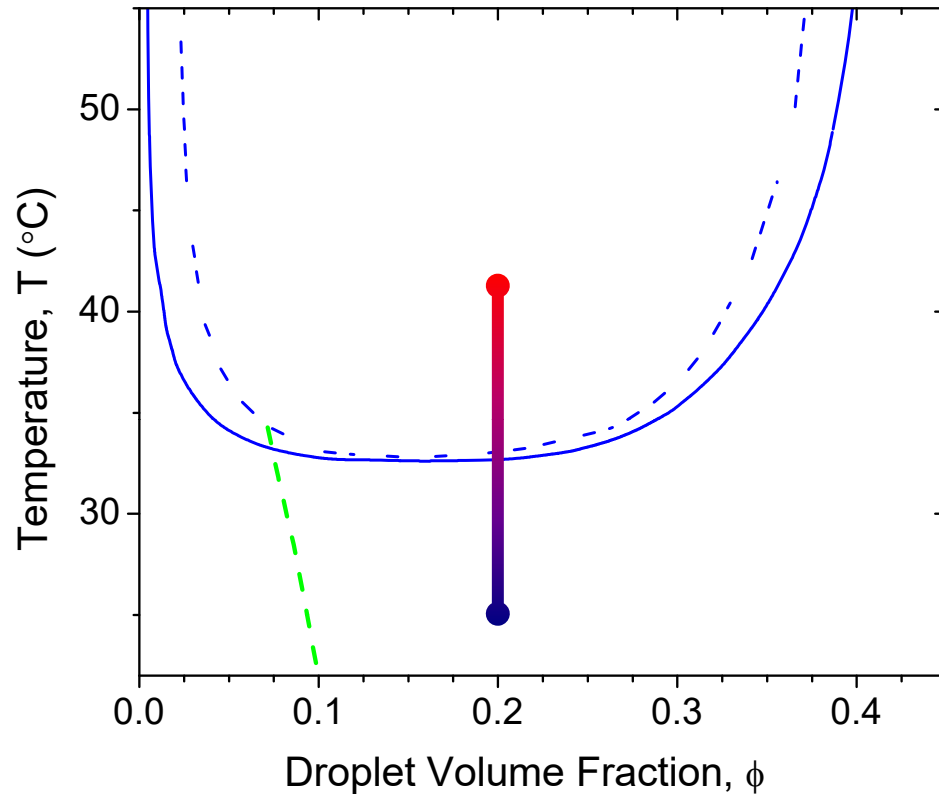
Thermoresponsive nanoemulsions allow for the formation of pristine colloidal gels with controlled thermal history.

What happens under a quench from the homogeneous fluid phase with a specific **quench depth** and **quench rate**?

[1] M.E. Helgeson *et al.*, *Soft Matter*, 2014, 10(17): 3122.

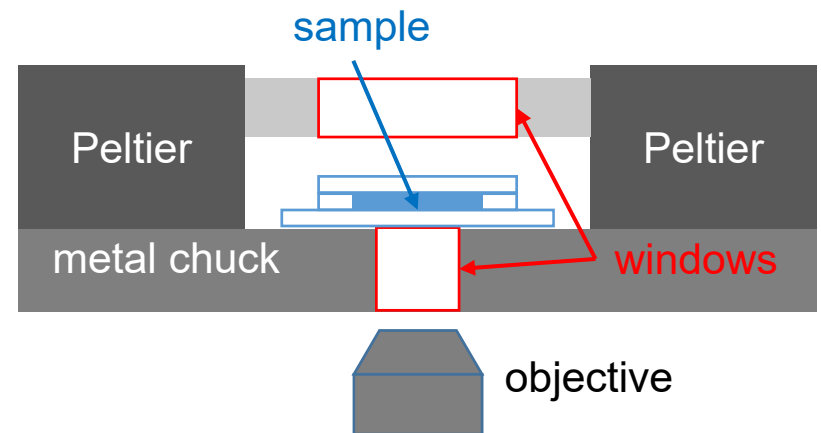
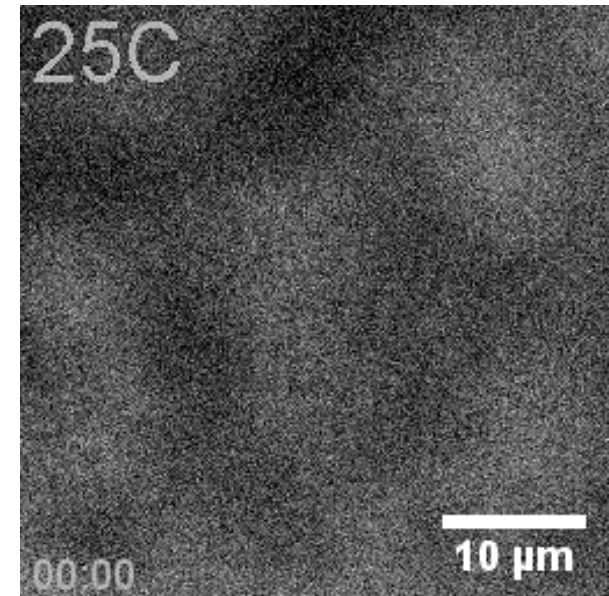
[2] Y. Gao *et al.*, *Soft Matter*, 2015, 11(32): 6360-6370

Thermoreversible gelation¹⁻³



What happens under a quench from the homogeneous fluid phase with a specific **quench depth** and **quench rate**?

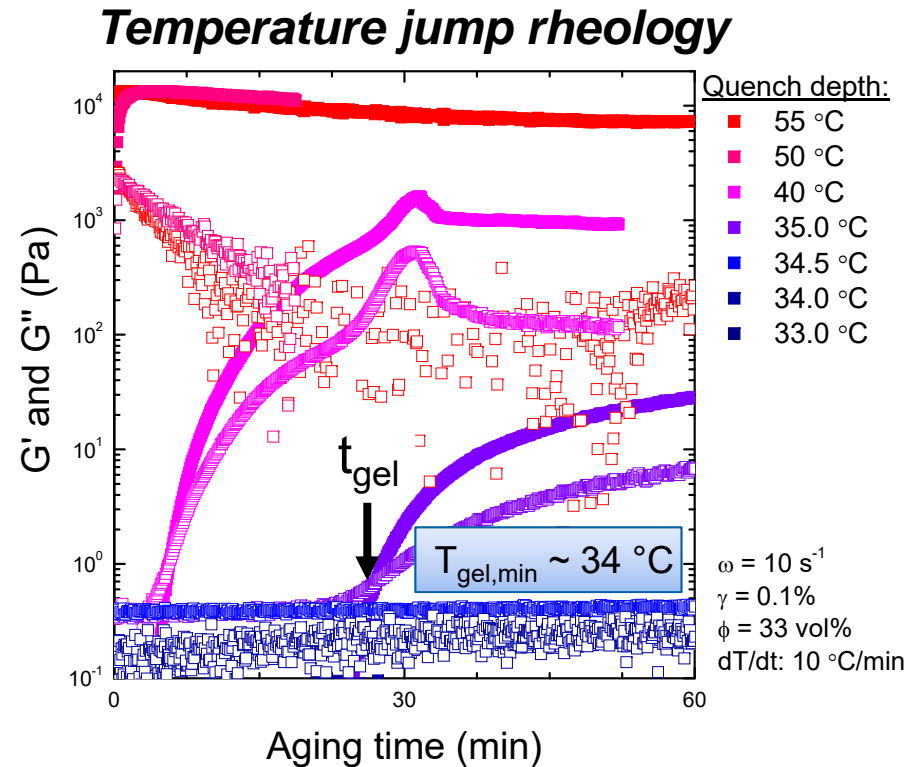
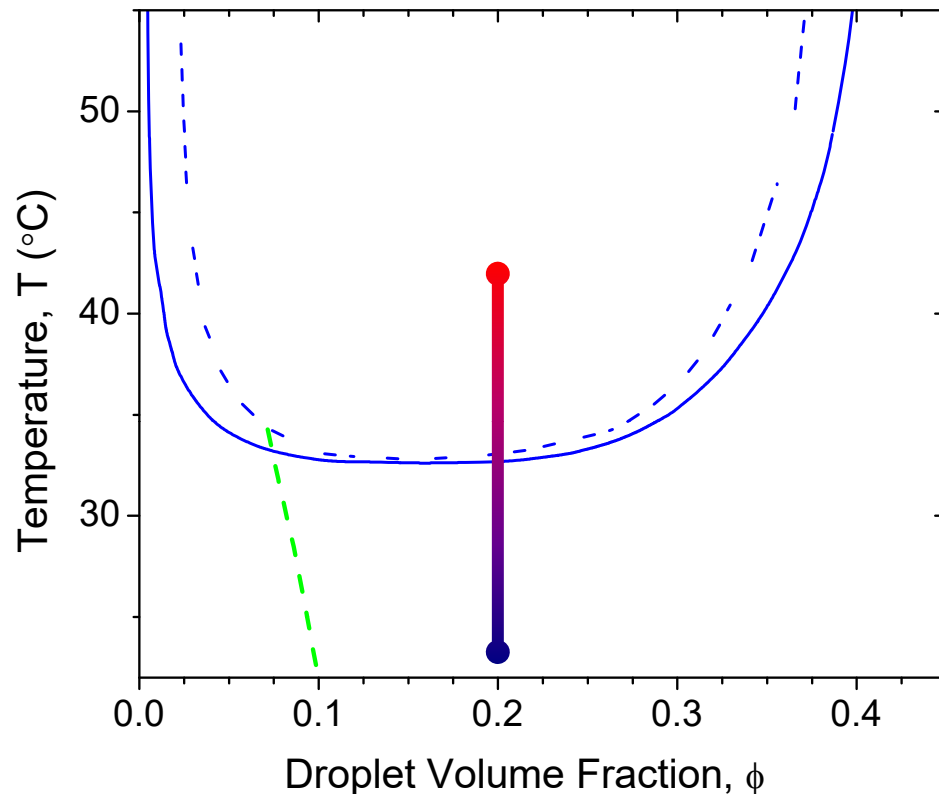
Bright field, Peltier T-control



[1] M.E. Helgeson *et al.*, *Soft Matter*, 2014, 10(17): 3122.

[2] Y. Gao *et al.*, *Soft Matter*, 2015, 11(32): 6360-6370

Thermoreversible gelation¹⁻³

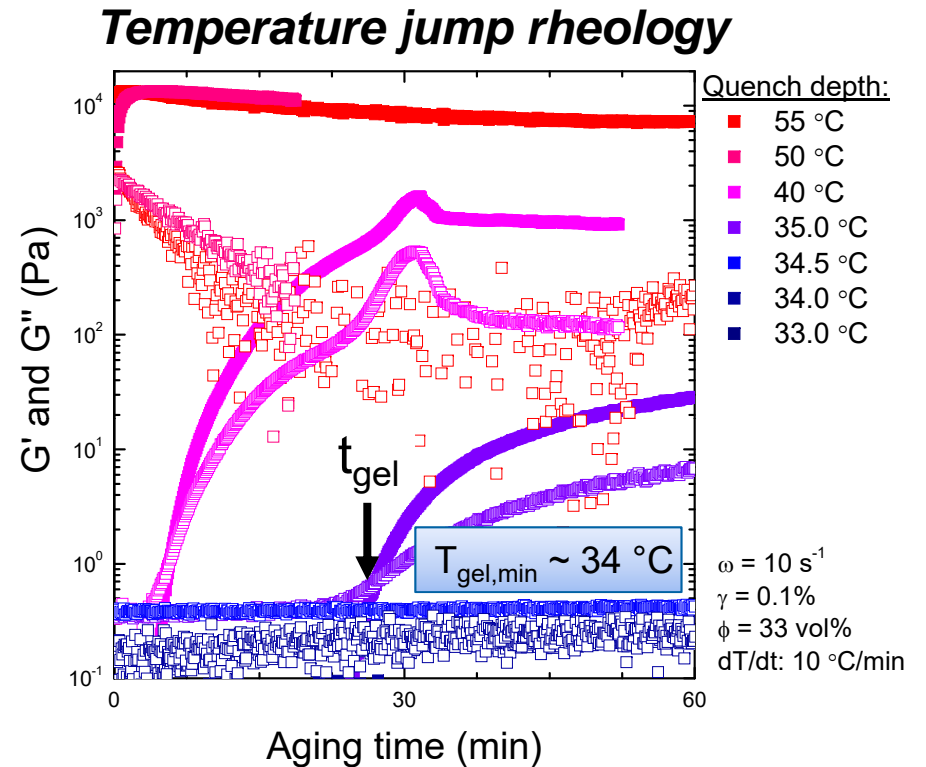
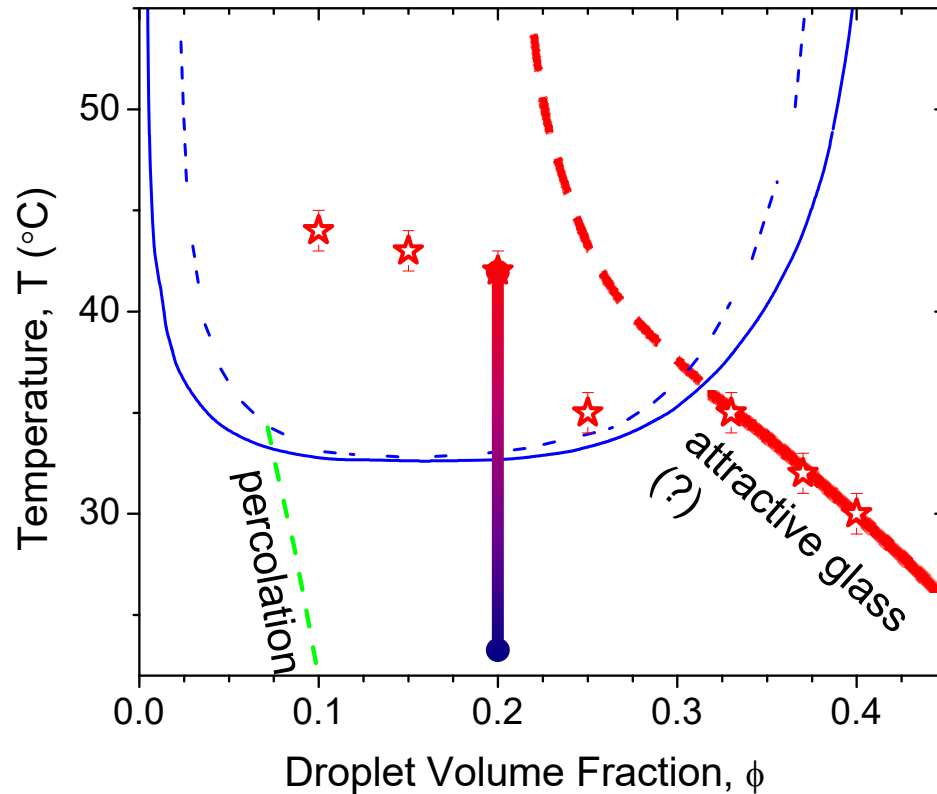


What happens under a quench from the homogeneous fluid phase with a specific **quench depth** and **quench rate**?

[1] M.E. Helgeson *et al.*, *Soft Matter*, 2014, 10(17): 3122.

[2] Y. Gao *et al.*, *Soft Matter*, 2015, 11(32): 6360-6370.

Thermoreversible gelation¹⁻³

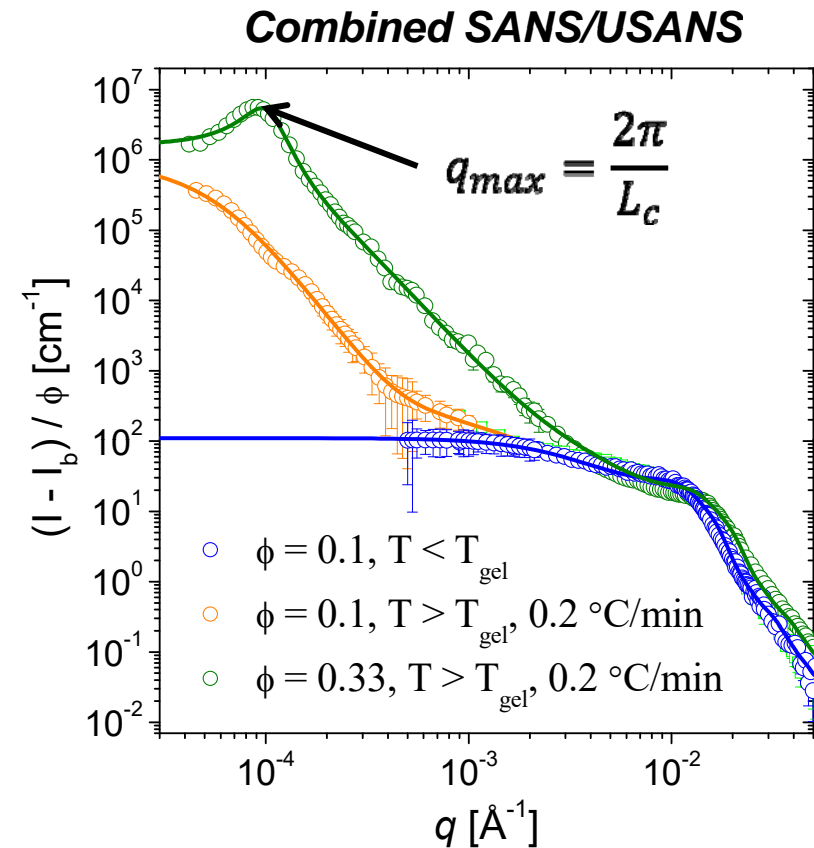
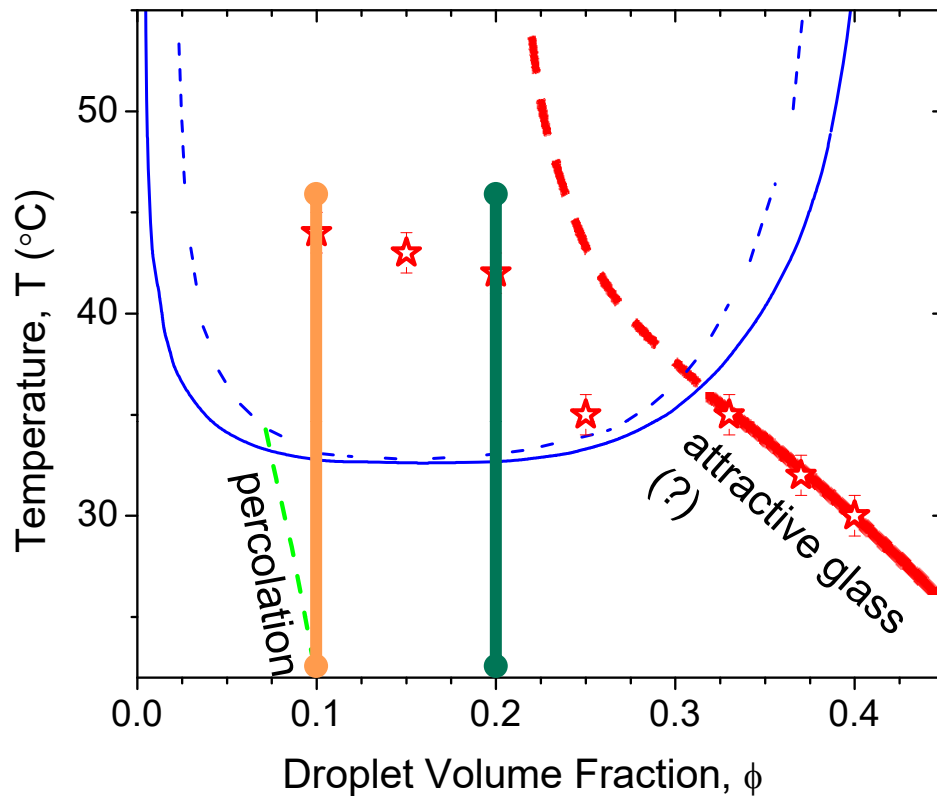


What happens under a quench from the homogeneous fluid phase with a specific **quench depth** and **quench rate**?

[1] M.E. Helgeson *et al.*, *Soft Matter*, 2014, 10(17): 3122.

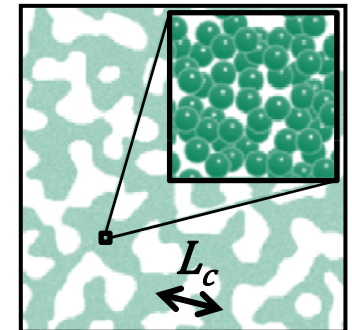
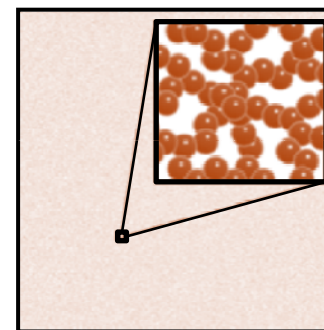
[2] Y. Gao *et al.*, *Soft Matter*, 2015, 11(32): 6360-6370

Thermoreversible gelation¹⁻³



Gel **morphology** depends significantly on the details of the quench (ϕ , dT/dt , T_{final}).

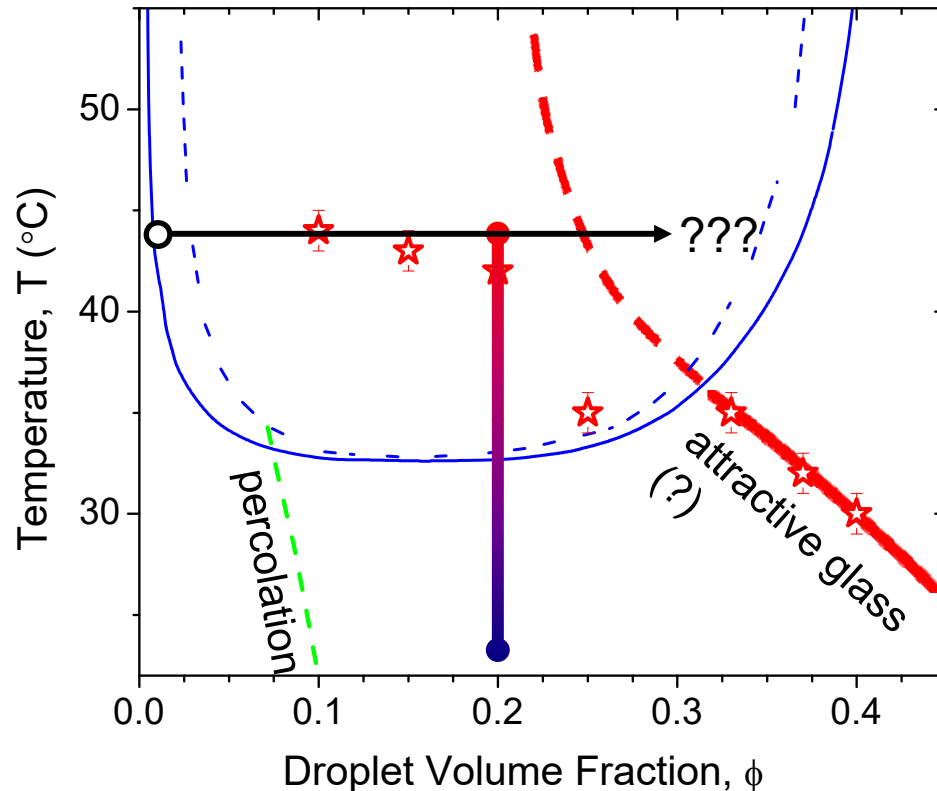
Homogeneous Phase separated



[1] M.E. Helgeson *et al.*, *Soft Matter*, 2014, 10(17): 3122.

[2] Y. Gao *et al.*, *Soft Matter*, 2015, 11(32): 6360-6370

Thermoreversible gelation¹⁻³



Open questions:

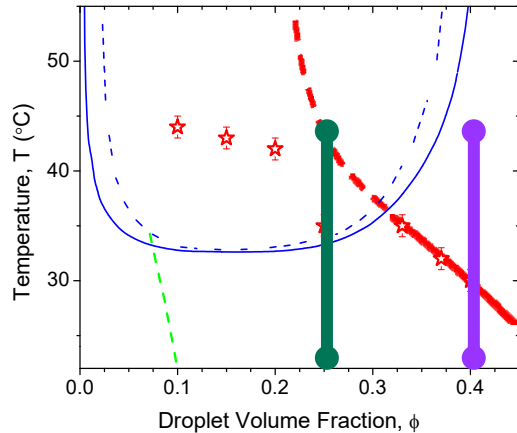
- How do the *kinetics* of gelation and aging and depend on the quench taken to the gel state?
- How does the arrested gel structure depend on the quench taken to the gelled state?
- What are the *micromechanical* processes that drive coarsening of gel structure?
- How does phase separated structure impart gel toughness?

[1] M.E. Helgeson *et al.*, *Soft Matter*, 2014, 10(17): 3122.

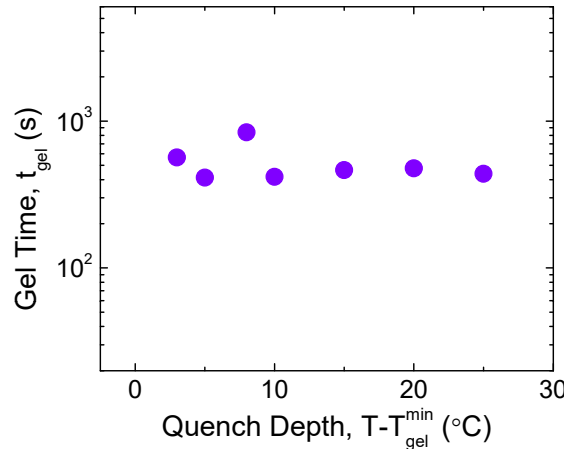
[2] Y. Gao *et al.*, *Soft Matter*, 2015, 11(32): 6360-6370

Kinetics of gelation

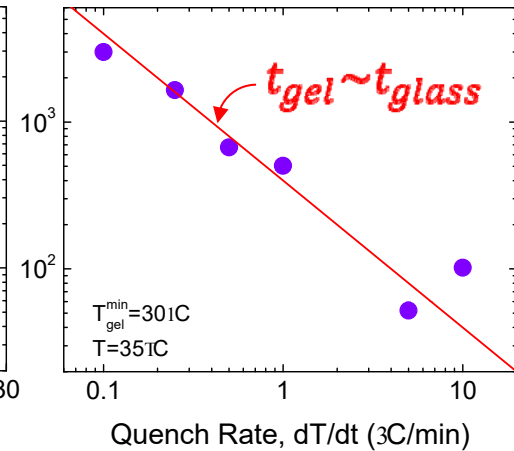
$\phi = 0.40$ (attractive glass)



Fixed quench rate
($dT/dt = 5 \text{ }^\circ\text{C/min}$)



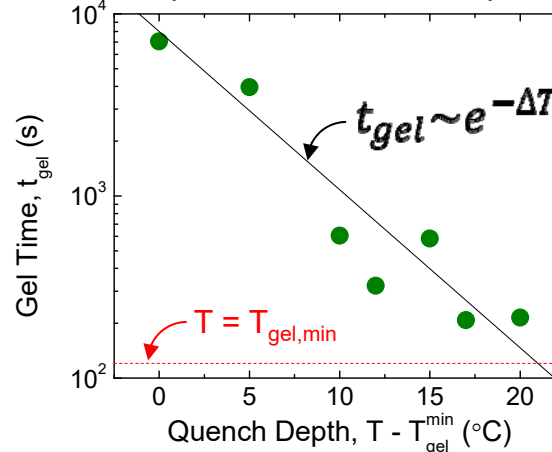
Fixed quench depth
($T_{final} = 40 \text{ }^\circ\text{C}$)



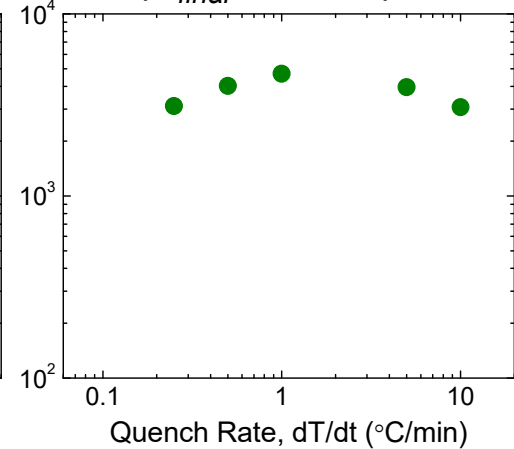
Attractive glass arrests
immediately upon crossing
the arrest line when
approached from the
homogeneous liquid state.

Phase separated gel arrests
exponentially quicker with
increasing quench depth.

Fixed quench rate
($dT/dt = 5 \text{ }^\circ\text{C/min}$)

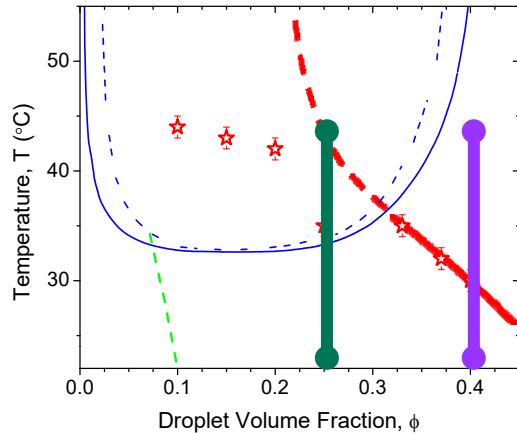


Fixed quench depth
($T_{final} = 40 \text{ }^\circ\text{C}$)

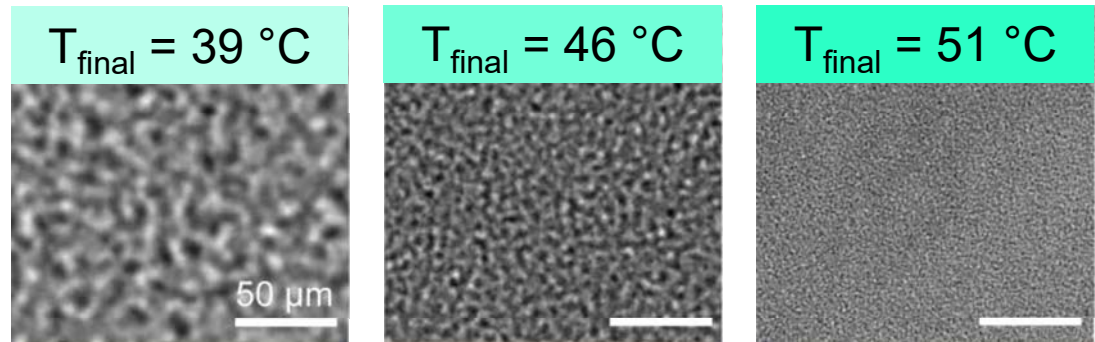


Kinetics of gelation

$\phi = 0.40$ (attractive glass)



Quench depth \rightarrow

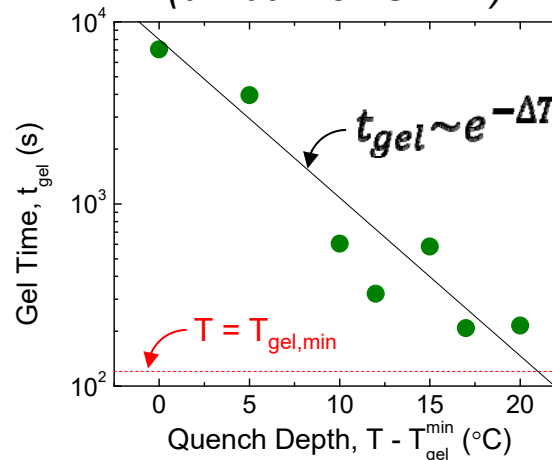


Increasing quench depth interrupts phase separation at an earlier stage of coarsening.

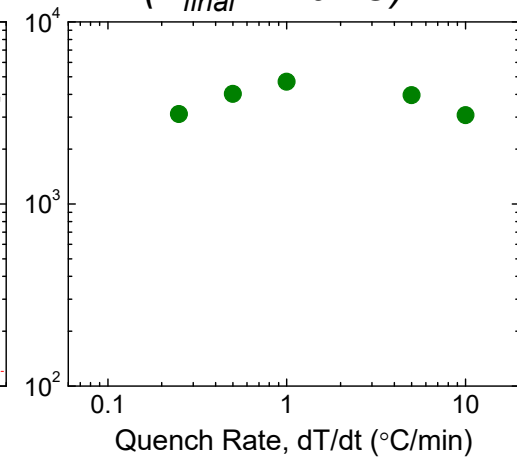
Attractive glass arrests **immediately** upon crossing the arrest line when approached from the homogeneous liquid state.

Phase separated gel arrests **exponentially quicker** with increasing quench depth.

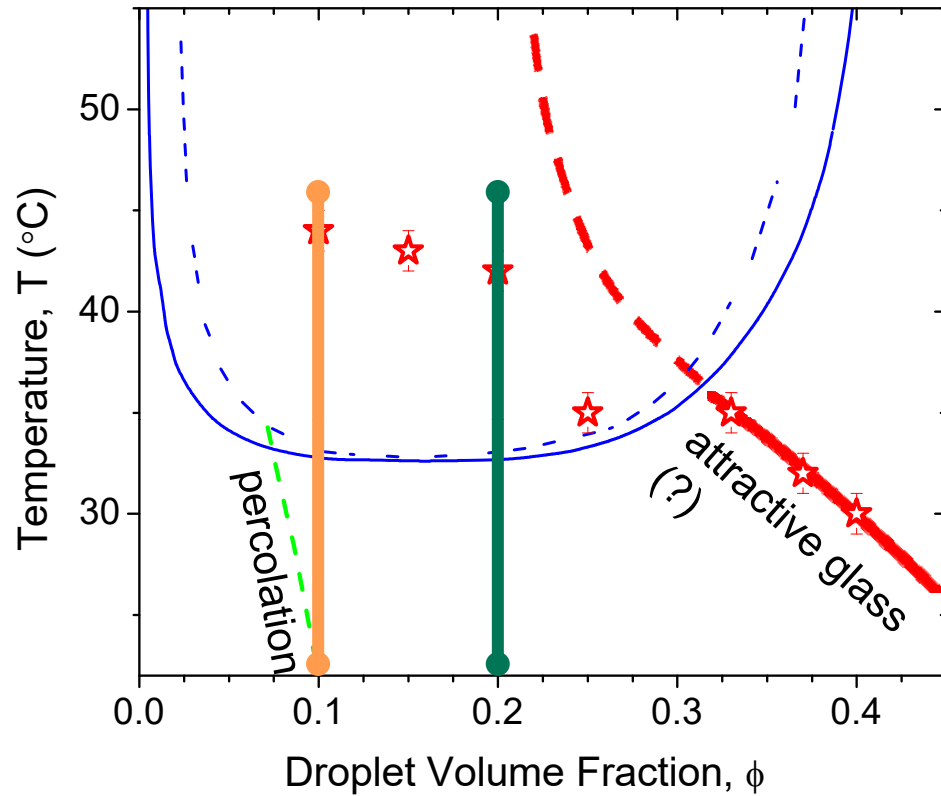
Fixed quench rate
($dT/dt = 5 \text{ }^\circ\text{C}/\text{min}$)



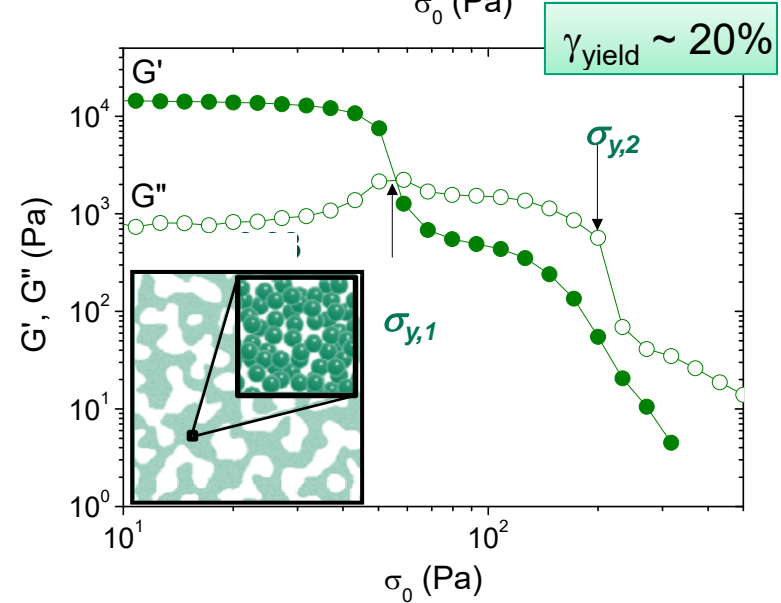
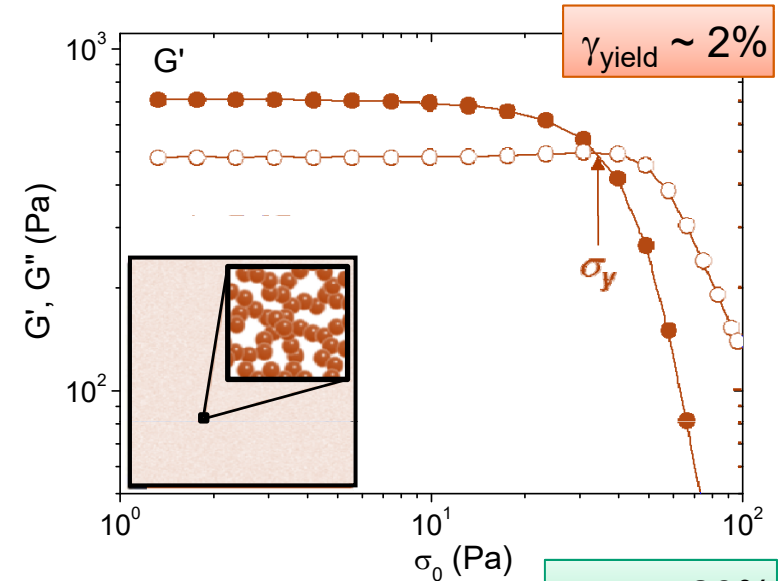
Fixed quench depth
($T_{\text{final}} = 40 \text{ }^\circ\text{C}$)



Kinetics of gelation



Gel *rheology* depends significantly on the details of the quench (ϕ , dT/dt , T_{final}).



[1] M.E. Helgeson *et al.*, *Soft Matter*, 2014, 10(17): 3122.

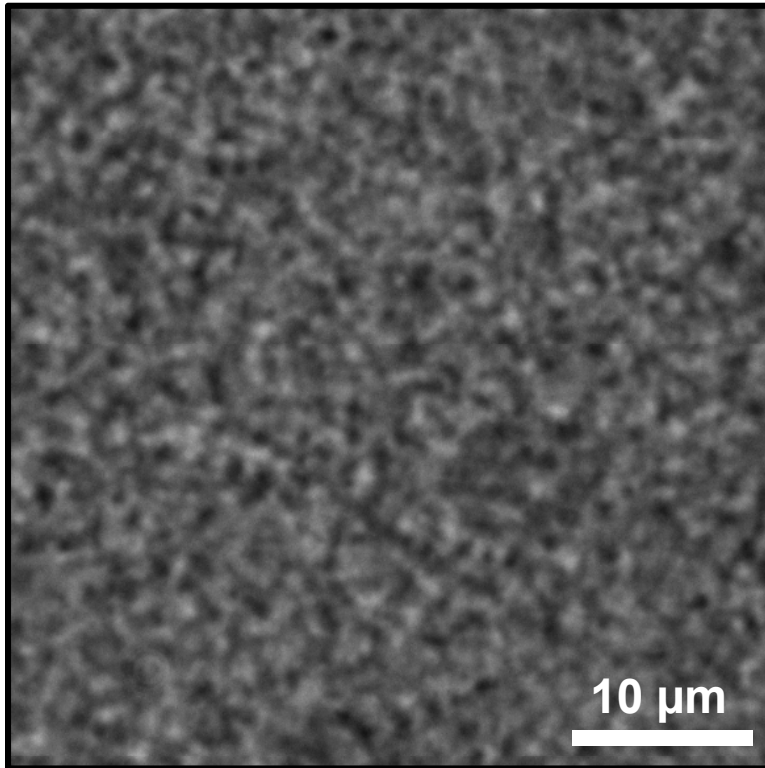
[2] J. Kim *et al.*, *Journal of Rheology*, 2014, 58(5): 1259.

Conclusions, Part 1

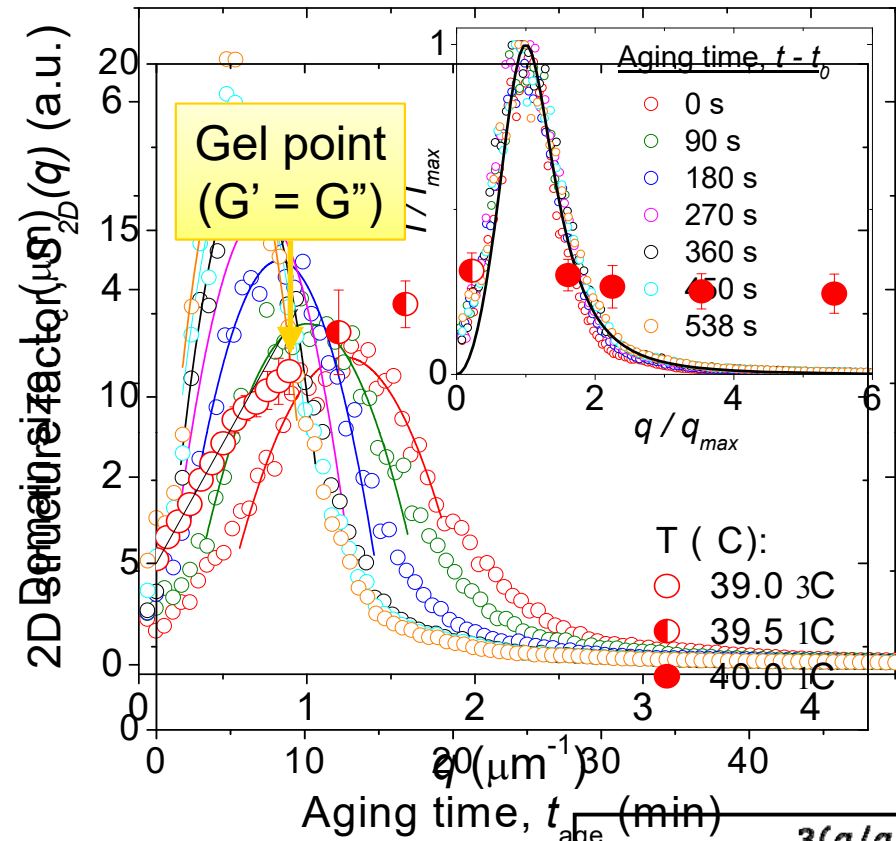
- Thermoresponsive systems can lead to a range of different gel morphologies depending on the details of the thermodynamic (ϕ , T_{final}) and kinetic (dT/dt) path taken to the gelled state
- Attractive glasses formed in the homogeneous fluid phase arrest immediately upon crossing the arrest temperature
- The arrested structure of gels formed by interrupted phase separation can be tuned with quench depth into the spinodal regime
- Thermal processing can be used to achieve gels with “toughened” rheology (multi-stage or delayed yielding)

Monitoring structure during quenching

Coarsening of phase separation



Analysis of static images by texture analysis microscopy.^{1,2}



Late-stage spinodal coarsening:³ $I/I_{max} = \frac{3(q/q_{max})^2}{2+(q/q_{max})^6}$

Coarsening by spinodal decomposition, which arrests at the mechanical gel point.



Anomalous dynamics in *arrested* colloidal gels

“Superdiffusive behavior”

$$\lim_{t \rightarrow \infty} g(q, t) \sim \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right]; \quad \beta = 1.3 - 1.7, \quad \tau \sim q^{-1}$$

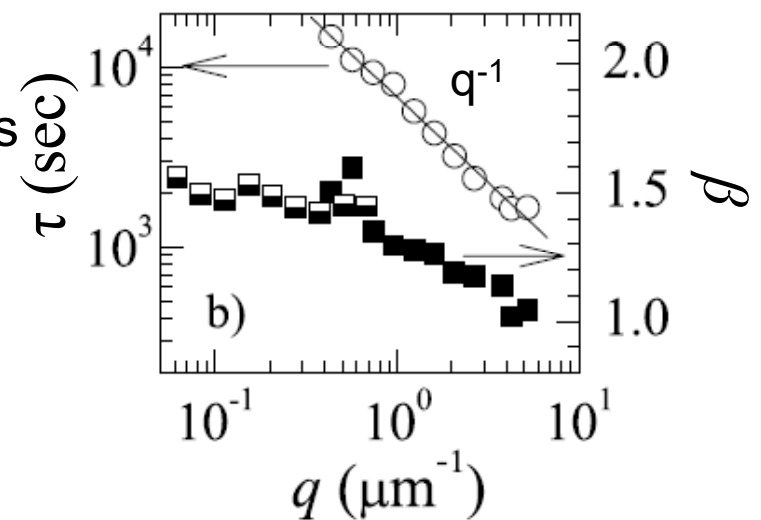
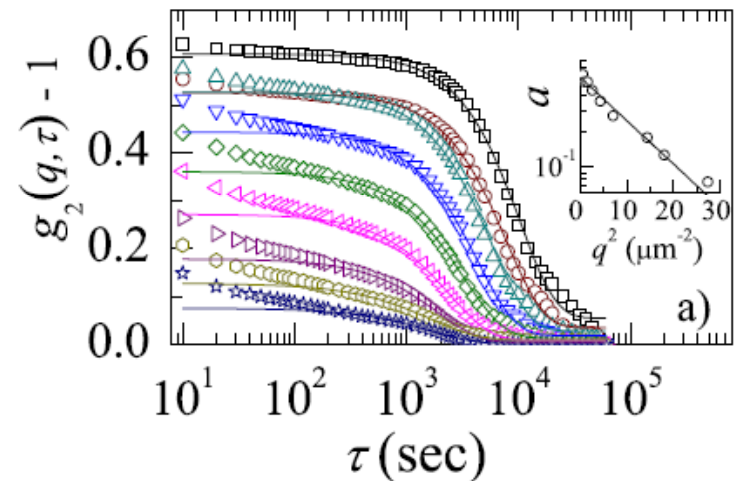
Cipelletti et al., *Phys Rev. Lett*, 2000, 84: 2275

Bouchaud and Pitard, *Eur. Phys. J. E*, 2001, 6: 231–236

Duri and Cipelletti, *Europhys. Lett.*, 2006, 76(5): 972–978

Chung et al., *Phys Rev. Lett.*, 2006, 96, 228301.

Angelini et al., *Soft Matter*, 2013, 9:10955–10959.



Hypothesis: gel aging produces residual stresses, which relax through “microyielding”.

Assume: Yielding events occur as force dipoles acting on an elastic medium over time scale τ_c .

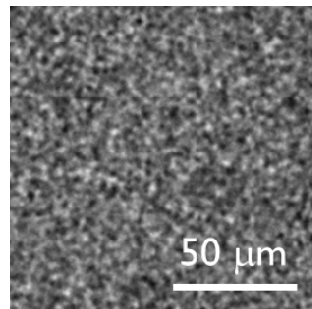
Questions:

- What is the physical nature of “microyielding”? (i.e. what does it look like?)
- Is there an associated structural feature?
- Do superdiffusive dynamics occur *during* gelation?

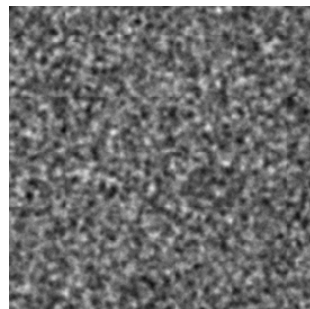
Tracking microdynamics of coarsening

Differential dynamic microscopy (DDM)¹⁻³

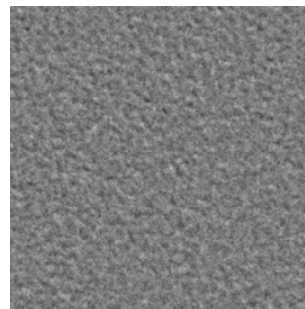
Micrographs (*Real space, \mathbf{x}*)



—

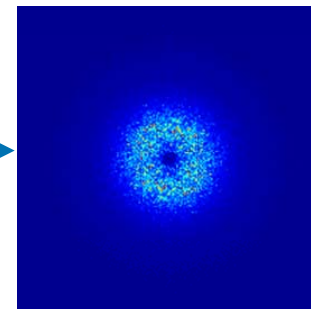


=



→
FFT

Reciprocal space, \mathbf{q}



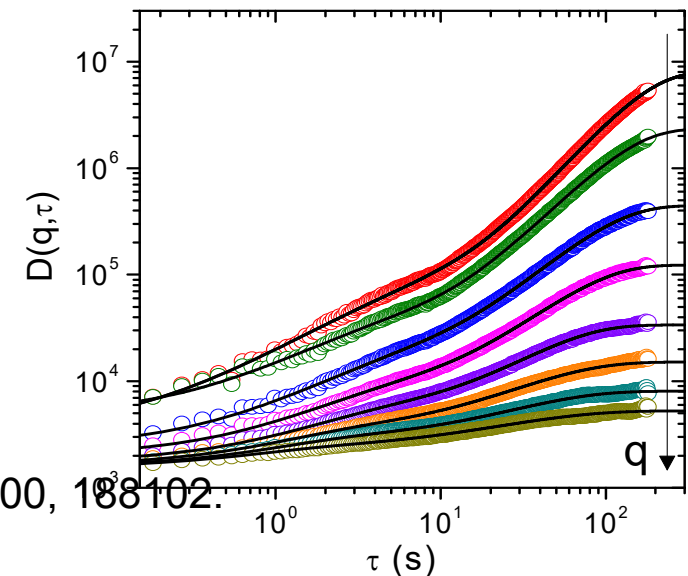
$$I(\mathbf{x}, t + \Delta t) - I(\mathbf{x}, t) = \Delta I(\mathbf{x}, t; \Delta t)$$

$$\Delta \hat{I}(\mathbf{q}, t; \Delta t)$$

Dynamic structure function:

$$D(\mathbf{q}, t) = \underbrace{A(\mathbf{q})}_{\text{total}} \left[\underbrace{1 - \frac{g(\mathbf{q}, t)}{g(\mathbf{q}, 0)}}_{\text{coherent}} \right] + \underbrace{B(\mathbf{q})}_{\text{incoherent}}$$

MATLAB code for DDM analysis available at:
<http://engineering.ucsb.edu/~helgeson/>



[1] R. Cerbino and V. Trappe, Physical Review Letters, 2008, 100, 188102.

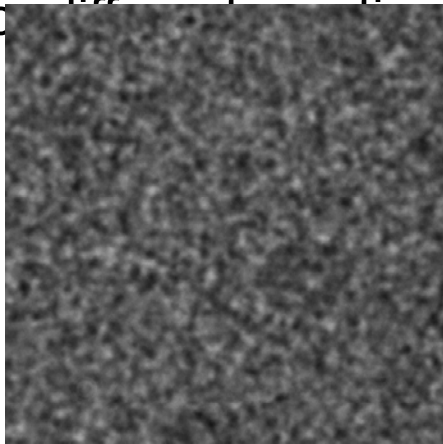
[2] A.V. Bayles *et al.*, Soft Matter, 2016, 12: 2440 - 2452.

[3] Y. Gao, J. Kim and M.E. Helgeson, Soft Matter, 2015, 10(17): 3122.

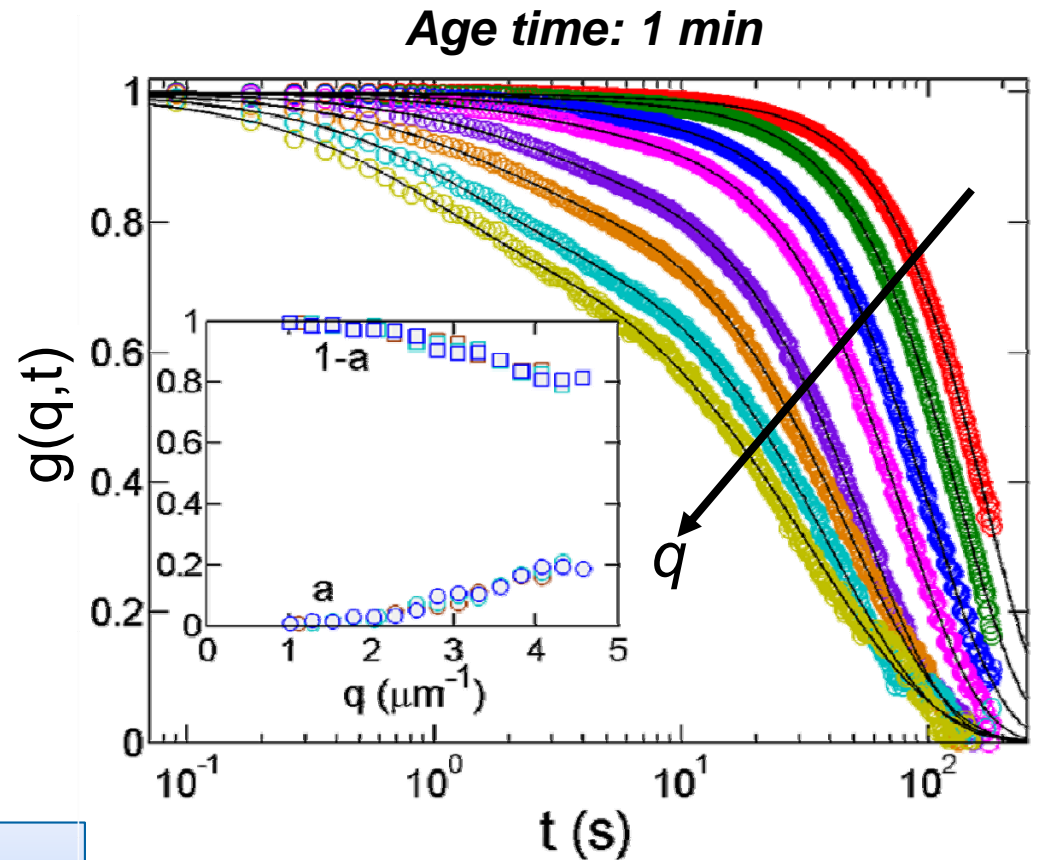
Tracking microdynamics during coarsening with DDM

DDM analysis:

- Divide video into 2 min intervals
- DDM for different times



$$D(q,t) = A(q)[1 - g(q,t)] + B(q)$$



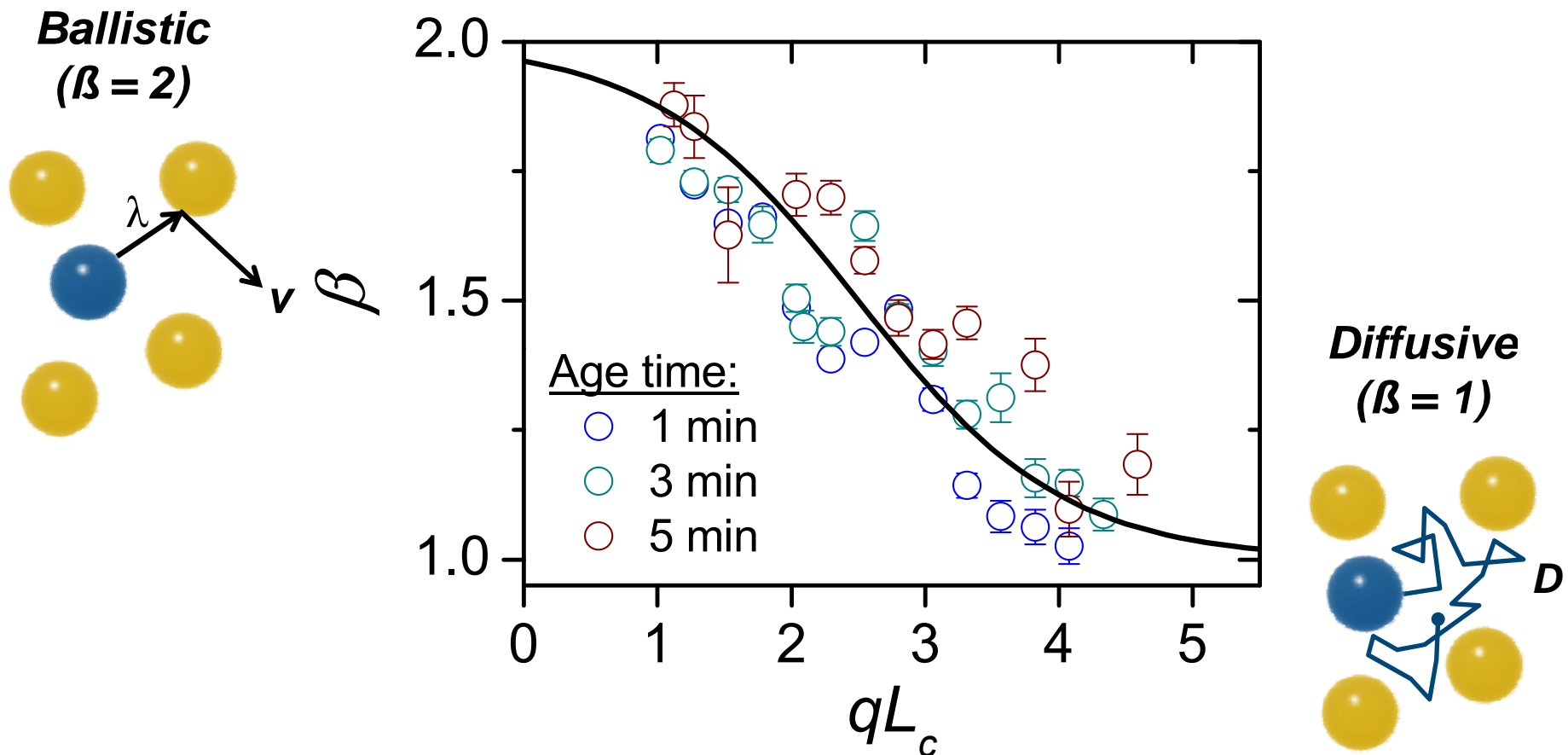
Fast mode: overdamped fluctuations of network strands in dense phase¹

Slow mode: superdiffusive motion ($\beta >$

$$g(q,t) = a \exp\left[-\left(\frac{t}{\tau_1}\right)\right] + (1-a) \exp\left[-\left(\frac{t}{\tau_2}\right)^\beta\right]$$



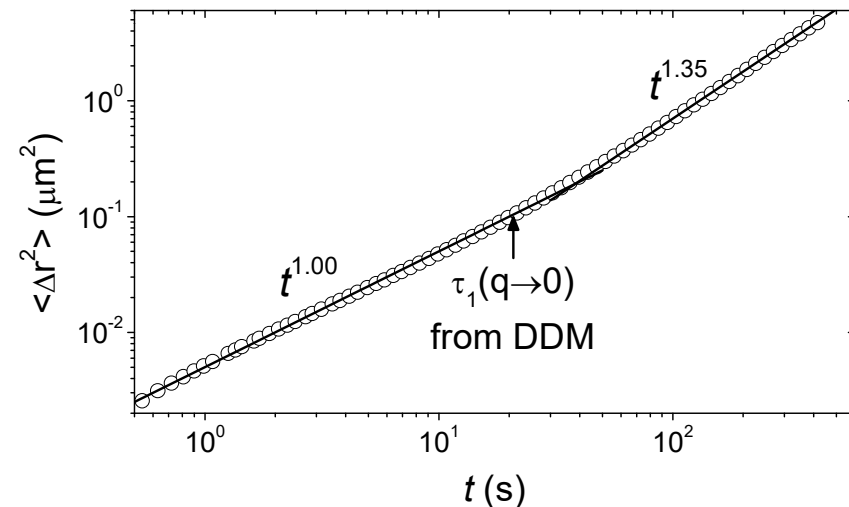
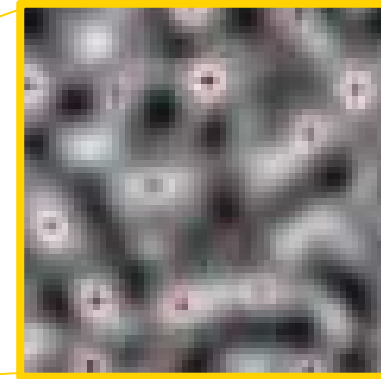
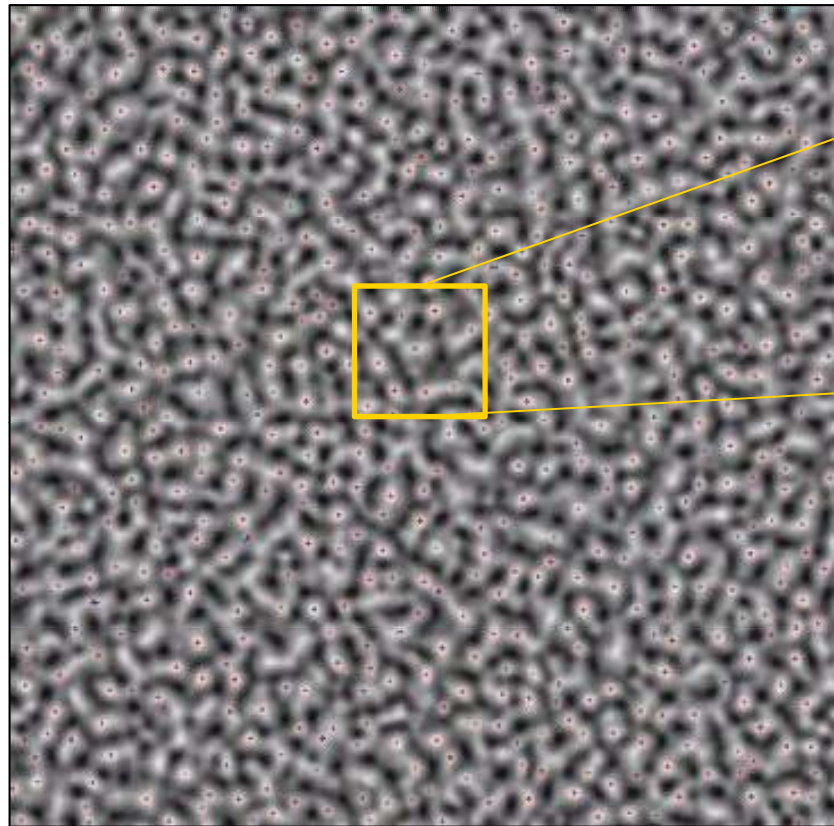
What causes superdiffusive dynamics?



Hypothesis: superdiffusion arises from long-range motion of individual dense domains, which decays to diffusive motion within domains...



Identifying the source of superdiffusive motion



Domain tracking confirms that superdiffusive dynamics occurs by intermittent motion of individual dense domains, which move like rigid objects.



Conclusions, Part 2

- For quenches into the spinodal, phase separation precedes gelation, and becomes arrested at the macroscopic gel point, with slow coarsening continuing after the gel has formed
- Coarsening of phase separation coincides with superdiffusive motion of the gel network
- “Microyielding” events arise due to the intermittent relaxation of stresses built up by spinodal-like coarsening of the “interfaces” between dense domains
- Presumably, the microdynamics of coarsening and aging can be tuned with quench...

Yielding – a naïve description

The yield point

- Yield strain: γ_y
- Yield stress: σ_y

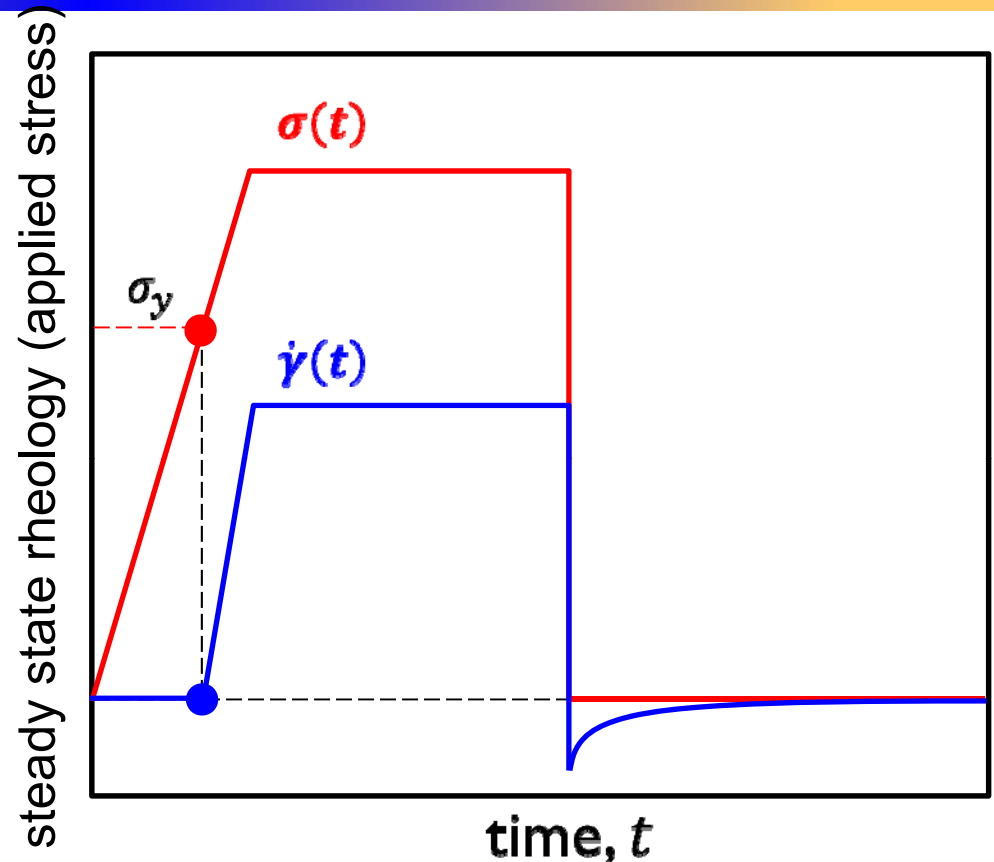
“Simple” yielding:

$$\sigma < \sigma_y: \quad \sigma(\gamma) = G\gamma$$

$$\sigma > \sigma_y: \quad \sigma(\gamma) = G\gamma + \eta\dot{\gamma}$$

Bingham: $\eta = \text{const.}$

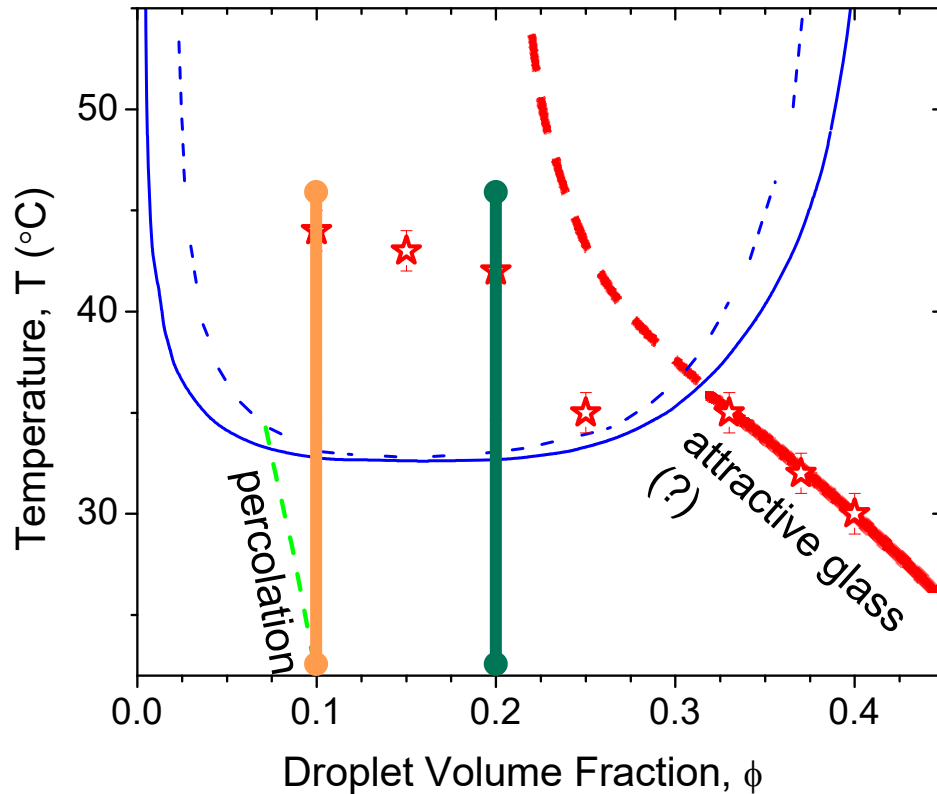
Herschel-Bulkley: $\eta = K\dot{\gamma}^{n-1}$



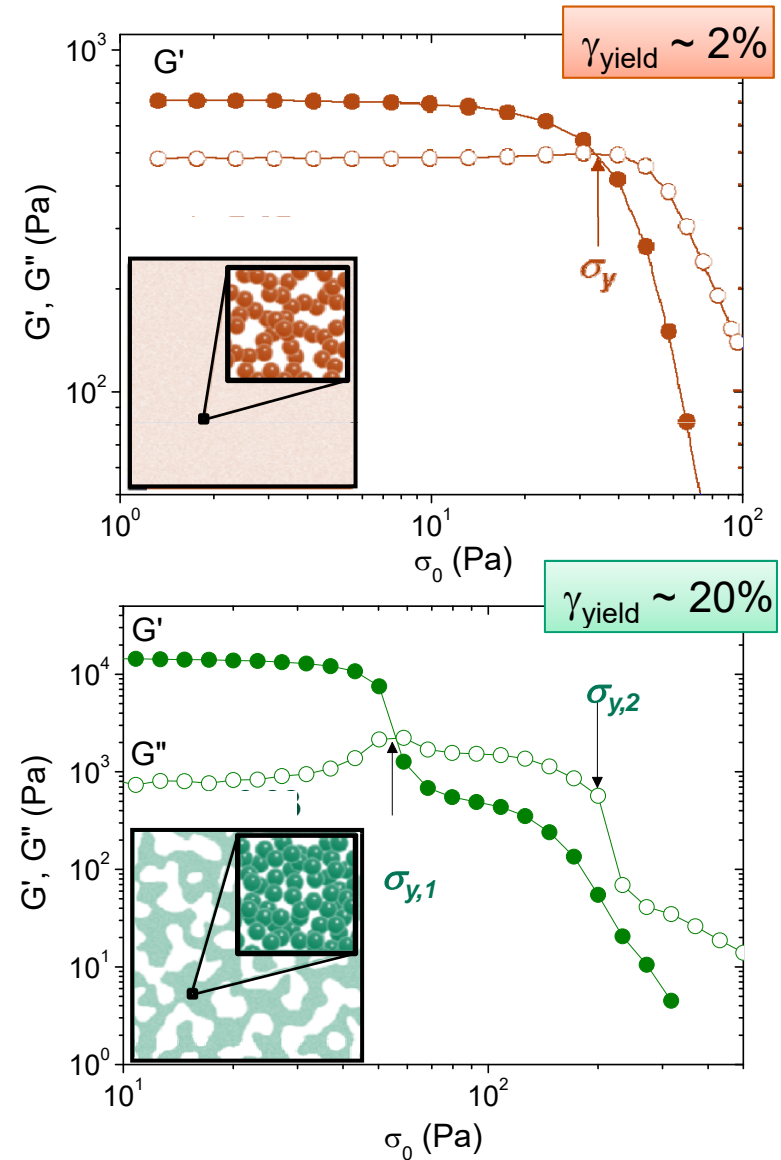
Objectives:

1. What happens at the **yield “point”**? Is it a “point”?
2. How does **micro-/mesostructure** influence yielding?
3. How do we use structure to rationally **engineer yielding**?

“Toughening” gels through interrupted phase separation



Gel *rheology* depends significantly on the details of the quench (ϕ , dT/dt , T_{final}).



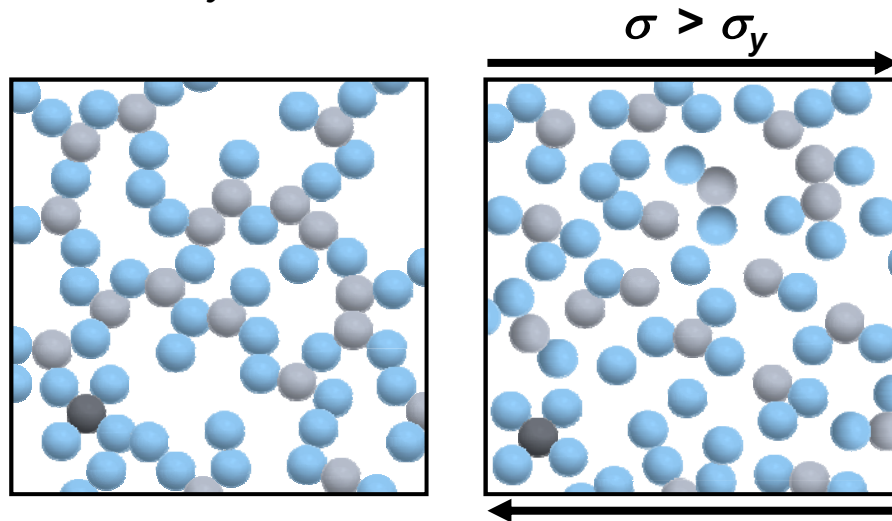
[1] M.E. Helgeson *et al.*, *Soft Matter*, 2014, 10(17): 3122.

[2] J. Kim *et al.*, *Journal of Rheology*, 2014, 58(5): 1259.

Type 1: “Simple” yielding in “simple” colloidal gels

Characteristic signatures:

- $\sigma < \sigma_y$: elastic-like behavior
- $\sigma \sim \sigma_y$: rate-dependent yielding
- $\sigma > \sigma_y$: flow (eventually)

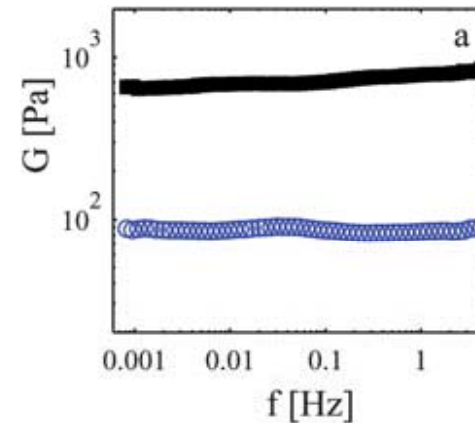


Hypothesis: “Simple” yielding occurs due to (microscopically) homogeneous rupture of cluster bonds.

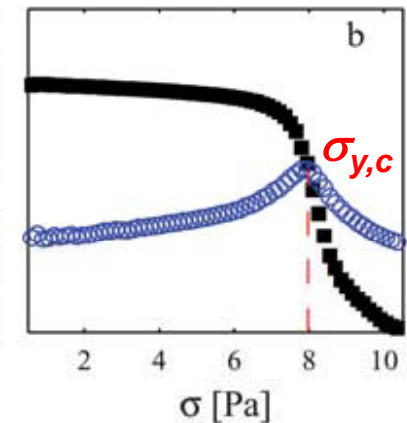
Carbon black gel ($\phi = 0.033$)

Gibaud et al., Soft Matter, 2010, 6: 3482-3488.

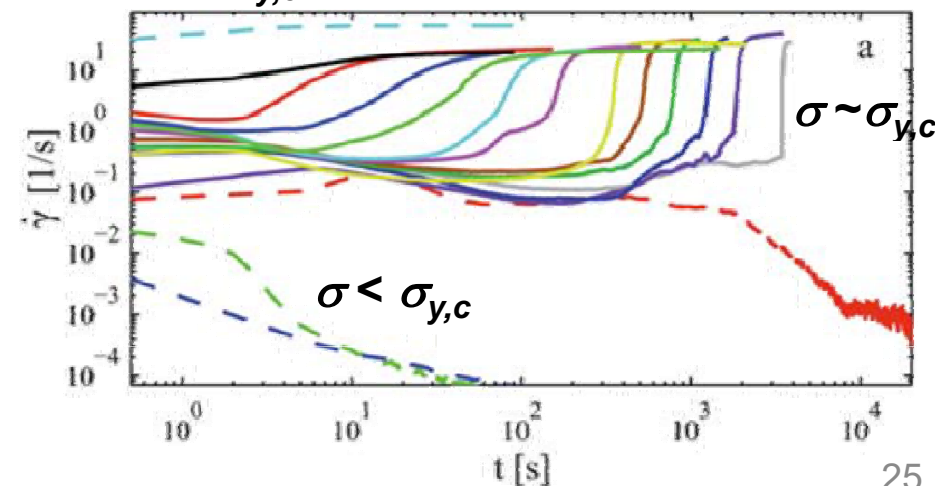
Linear viscoelasticity



LAOS



$\sigma > \sigma_{y,c}$ *Creep*

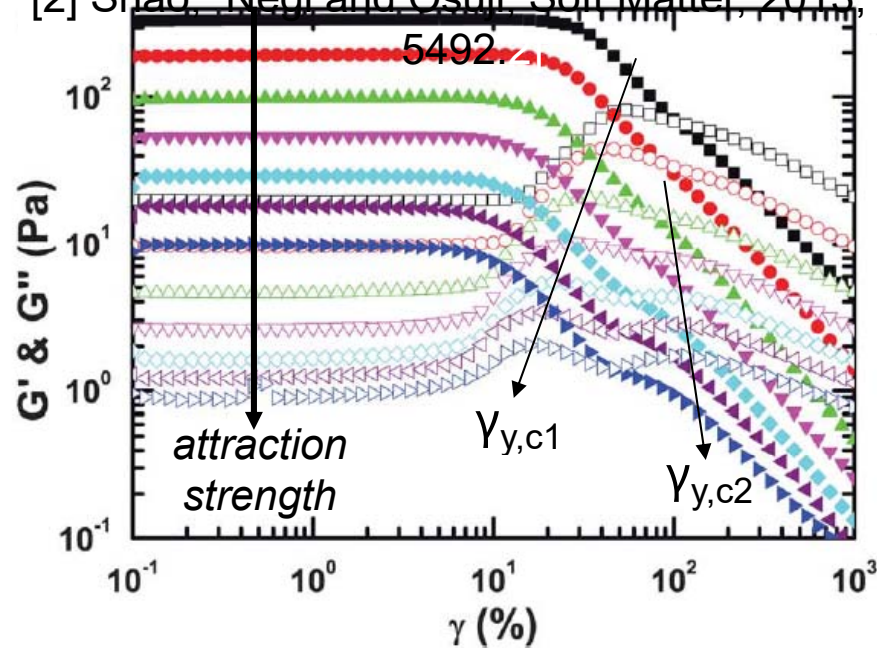


Type 2: “Two-step” yielding in colloidal gels

Large amplitude oscillatory shear (LAOS)^{1,2}

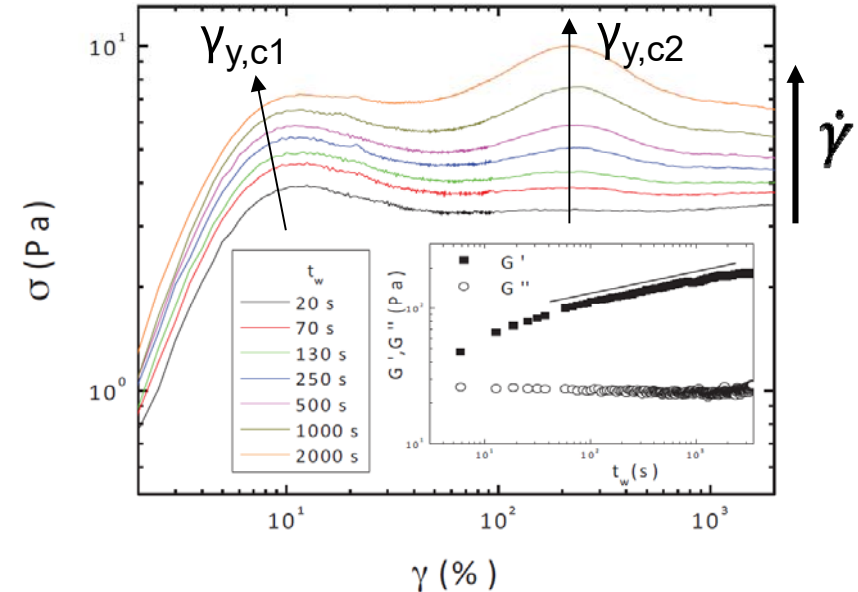
[1] Koumakis and Petekidis, *Soft Matter*, 2011, 7: 2456.

[2] Shao, Negi and Osuji, *Soft Matter*, 2013, 9:



Step shear rate³

[3] Koumakis *et al.* (unpublished)



Common Features:

- Local maxima in σ , G^* , G'' with increasing strain/strain amplitude
- Critical yield points depend significantly on applied strain rate/frequency

Hypothesis: two dynamic processes

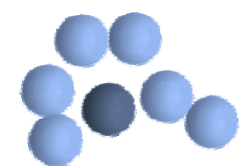
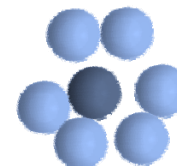
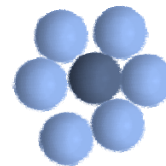
$\gamma_1 < \gamma < \gamma_2$ – Bond rupture, rearrangement

$\gamma > \gamma_2$ – Cage breakage, network failure

$\gamma < \gamma_1$

$\gamma_1 < \gamma < \gamma_2$

$\gamma > \gamma_2$

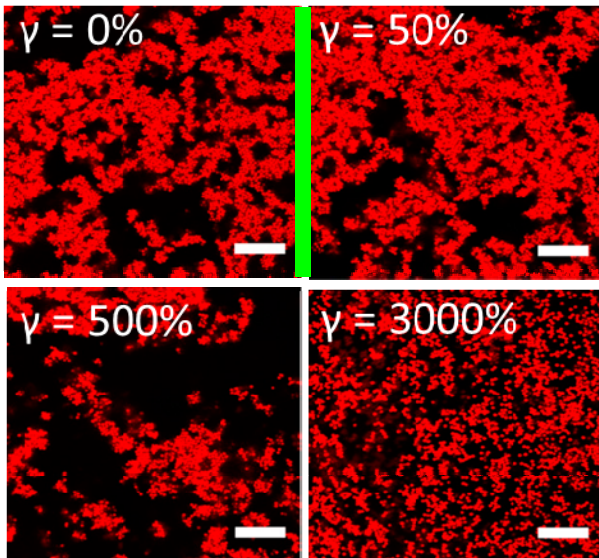


Structure during two-step yielding?

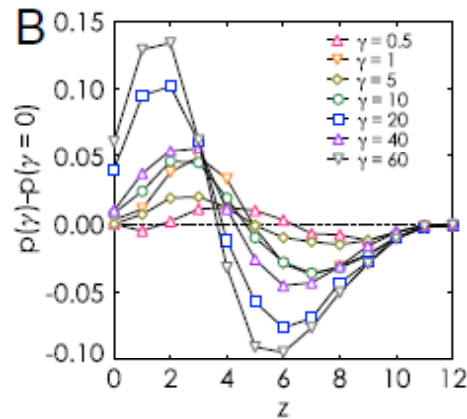
Visualization after step strain

[1] Rajaram and Mohraz, Phys. Rev. E 84, 011405 (2011)

[2] Hsiao *et al.*, PNAS 109(40), 16029-16034 (2012)



bond # distribution



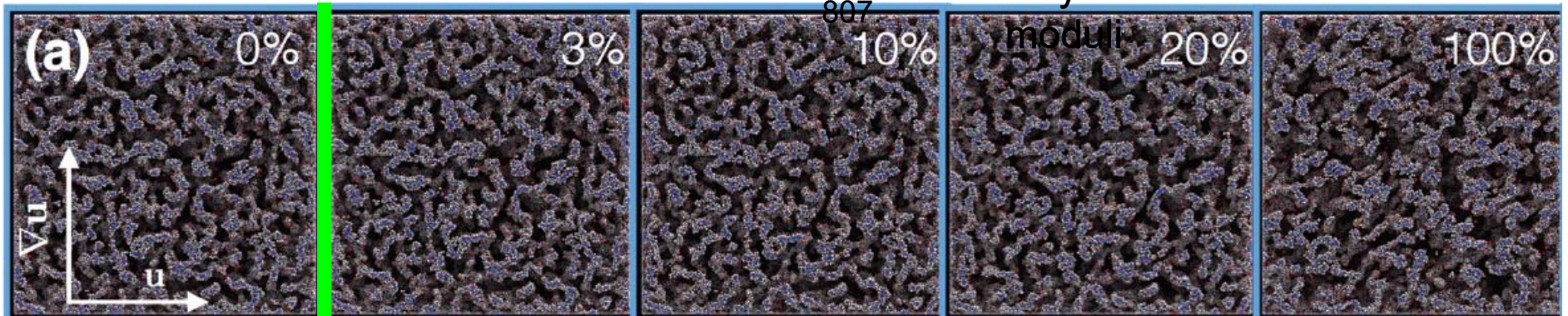
Challenges:

- Pre-shear protocols can irreversibly disrupt gel structure
- Hard to resolve microstructural changes at small strains
- Local descriptors only show significant changes for $\gamma \gg \gamma_{y,c}$

Large-scale LAMMPS simulations vs. Rheological measurements

[3] B.J. Landrum, W.B. Russel, and R.N. Zia. Journal of Rheology, 2016, 60(4), 783-807

only consider linearized moduli



Large amplitude oscillatory shear (LAOS)

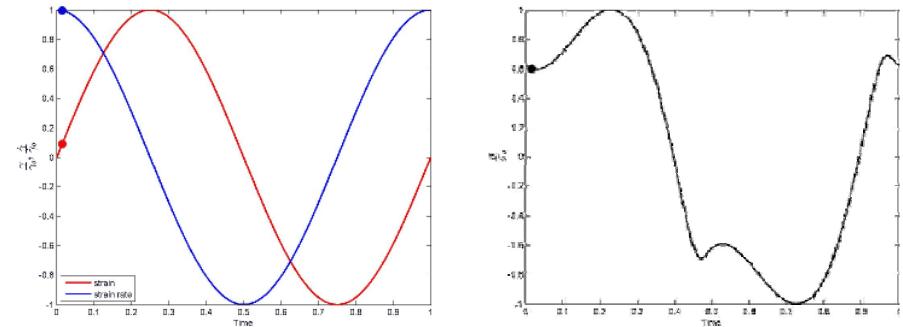
$$\gamma(\omega, t) = \gamma_0 \sin \omega t$$

$$\dot{\gamma}(\omega, t) = \gamma_0 \omega \cos \omega t$$

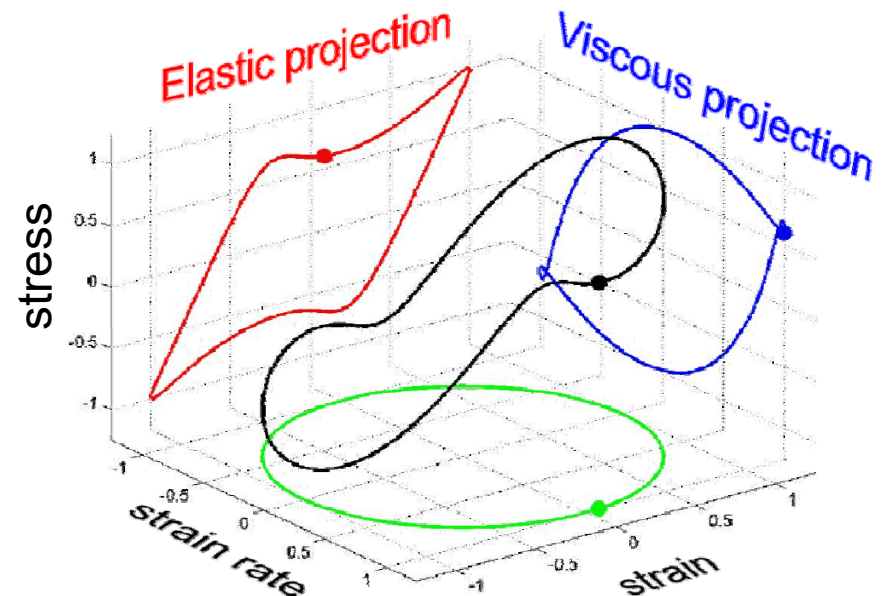
Nonlinear viscoelasticity:

$\sigma(\omega, t) \neq \sigma_0 \sin(\omega t + \delta)$
 G' , G'' no longer adequate!

strain, strain rate vs. time stress vs. time



Lissajous-Bowditch curve



Opportunity:

LAOS probes entire (rate-dependent) yielding process in a single, time-stationary measurement.

Challenge:

How do we extract *meaningful* properties from a complex, nonlinear stress response?



UC SANTA BARBARA
chemical
engineering

Approach to nonlinear analysis of LAOS

Sequence of physical processes (SPP)!

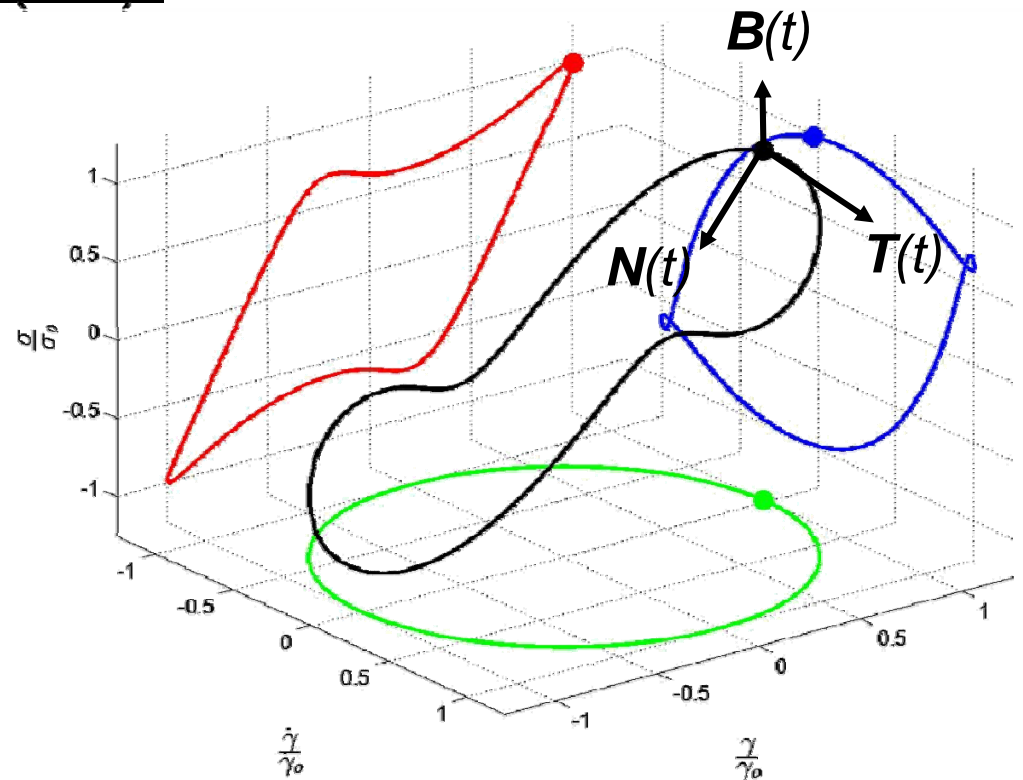
Binormal vector:

$$\mathbf{B}(t) = [B_\gamma(t) \quad \omega B_\dot{\gamma}(t) \quad B_\sigma(t)]$$

Phase: $\frac{B_\gamma}{|\mathbf{B}|} = \cos \delta(t) = \frac{G_R''(t)}{G_R'(t)}$

Modulus: $\frac{B_\sigma}{|\mathbf{B}|} = \frac{1}{\sqrt{1 + G_R^*(t)^2}}$

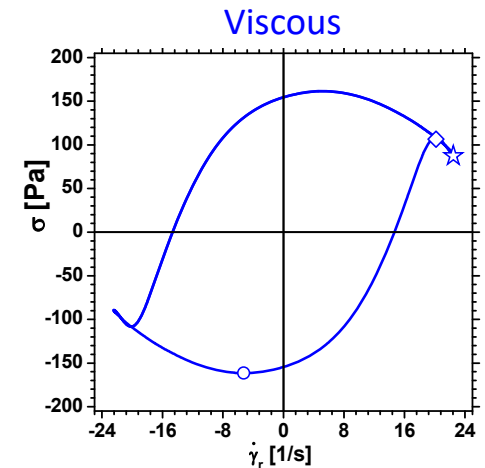
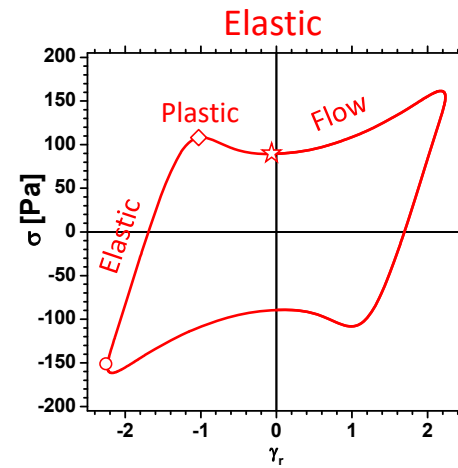
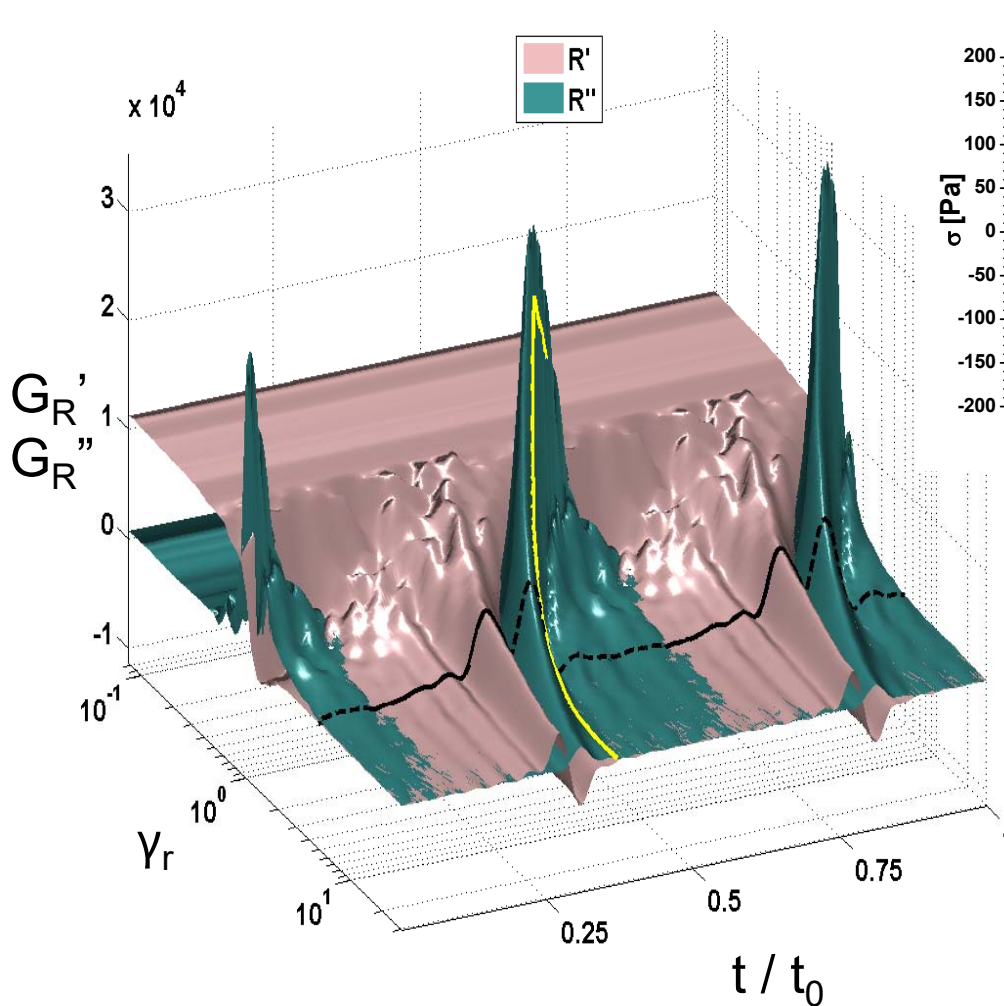
Frenet–Serret frame



SPP allows calculation of instantaneous, physically meaningful analogues of elastic, $G_R'(t)$, and viscous, $G_R''(t)$, moduli.



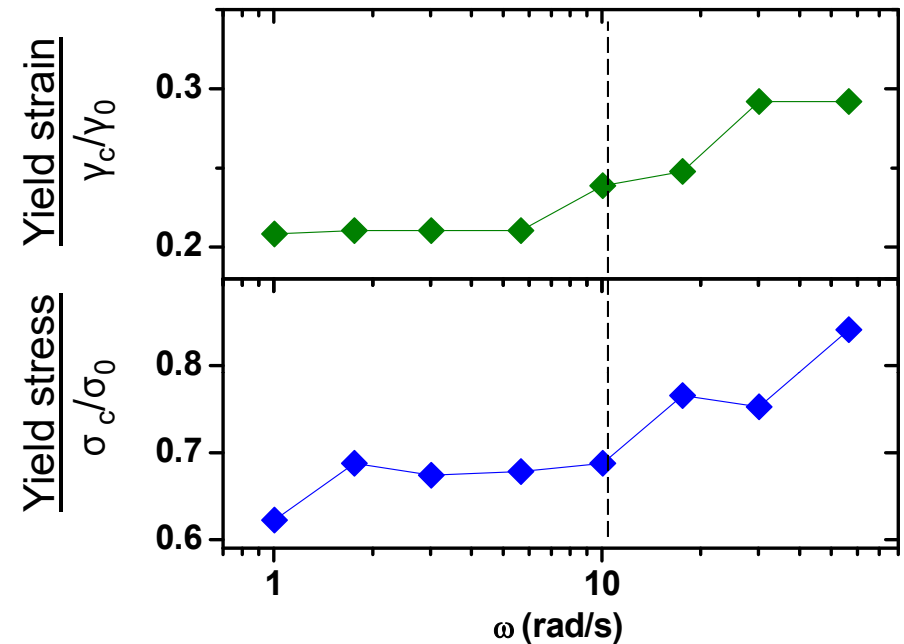
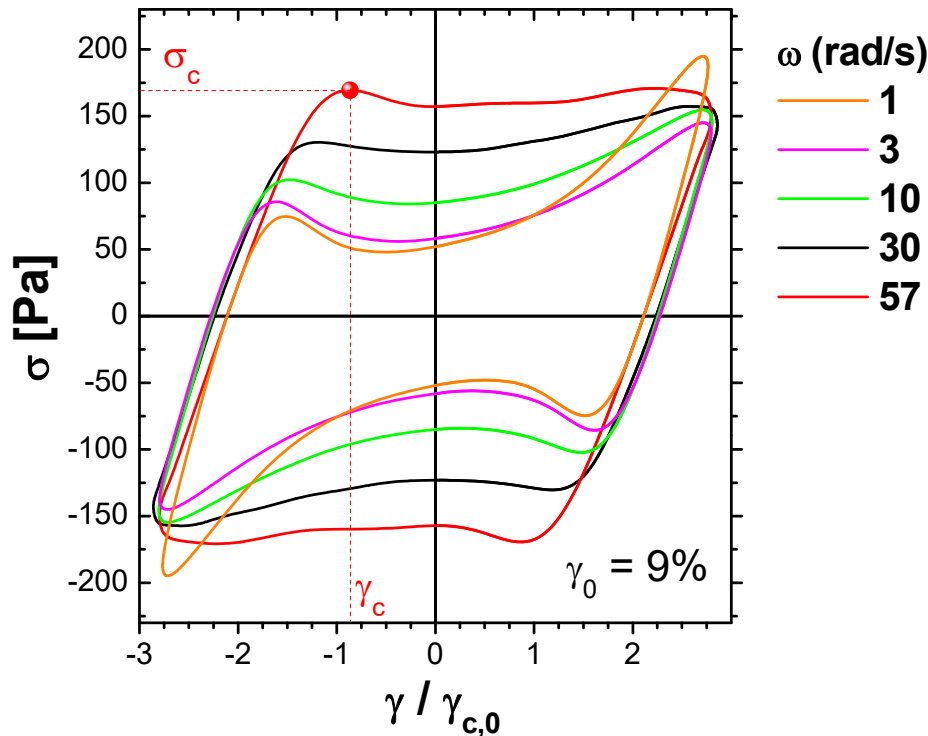
Instantaneous non-linear measures



$$\Delta I^2 / \langle \Delta I^2 \rangle_t$$



Frequency-dependence of “two-step” yielding



Observations:

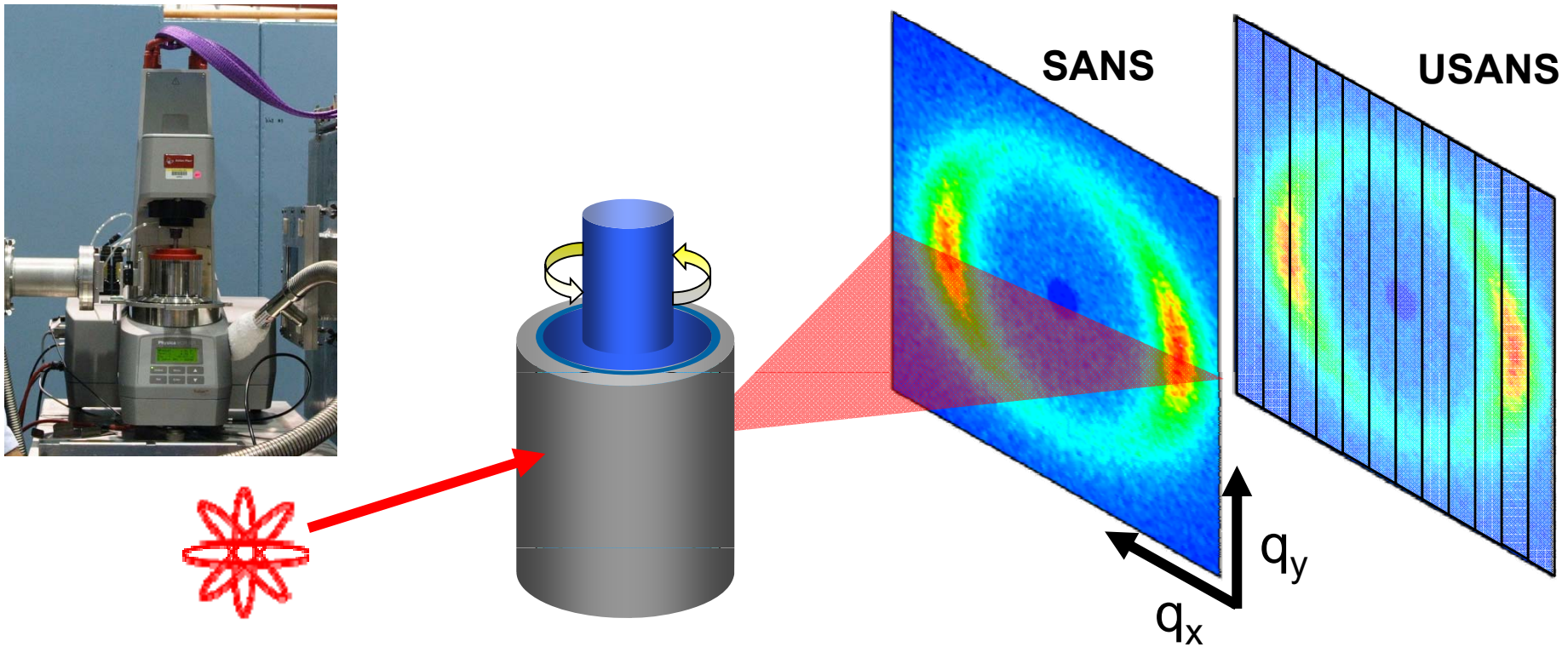
- “Two-step” yielding disappears at sufficiently high frequencies.
- Gel “toughens” above a critical frequency.

Questions

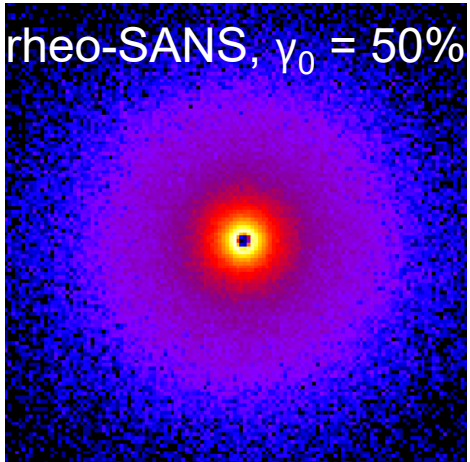
- What microstructural processes accompany the onset of yielding?
- What causes a rate-dependence of critical yield stress and strain?



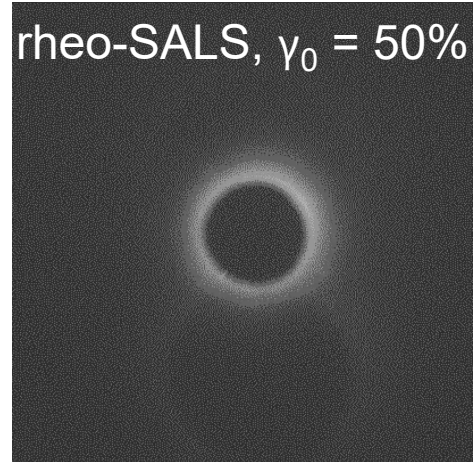
Rheo-SANS/USANS – simultaneous structure and rheology



rheo-SANS, $\gamma_0 = 50\%$



rheo-SALS, $\gamma_0 = 50\%$



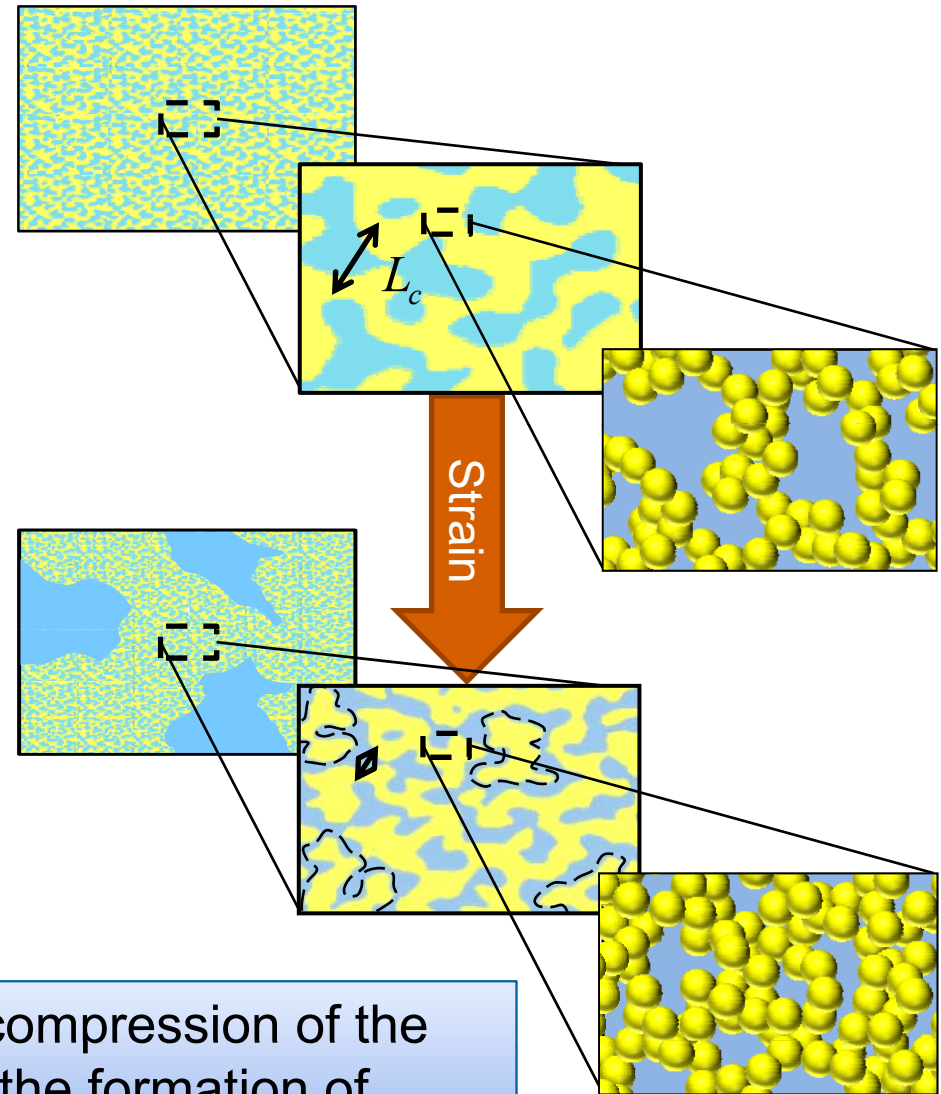
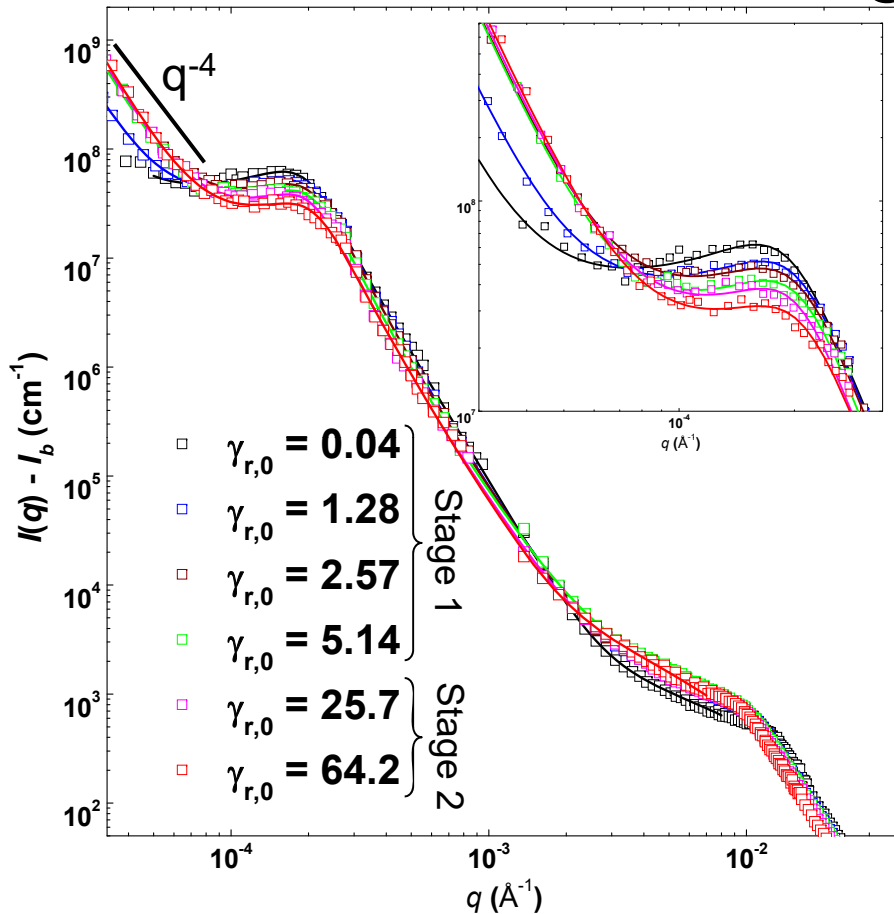
SANS:

- Structural resolution: 1-200 nm
- Structural anisotropy (2D detector)

USANS:

- Structural resolution: 200 nm - 20 μm
- Averages anisotropy (1D detector)

Rheo-USANS reveals structure in yielding regimes

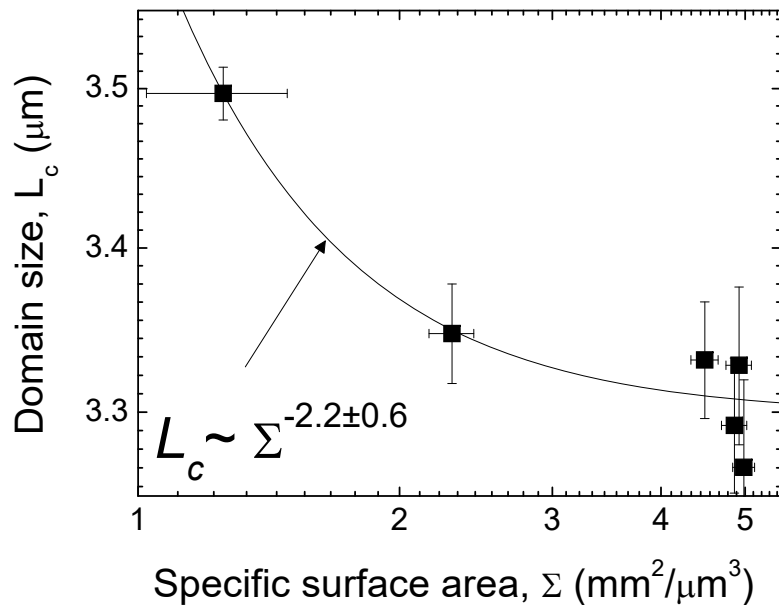
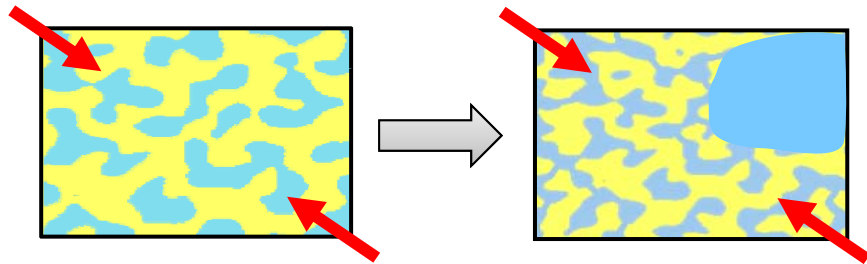


Initial stage of yielding dominated by compression of the phase separated structure, leading to the formation of large voids.

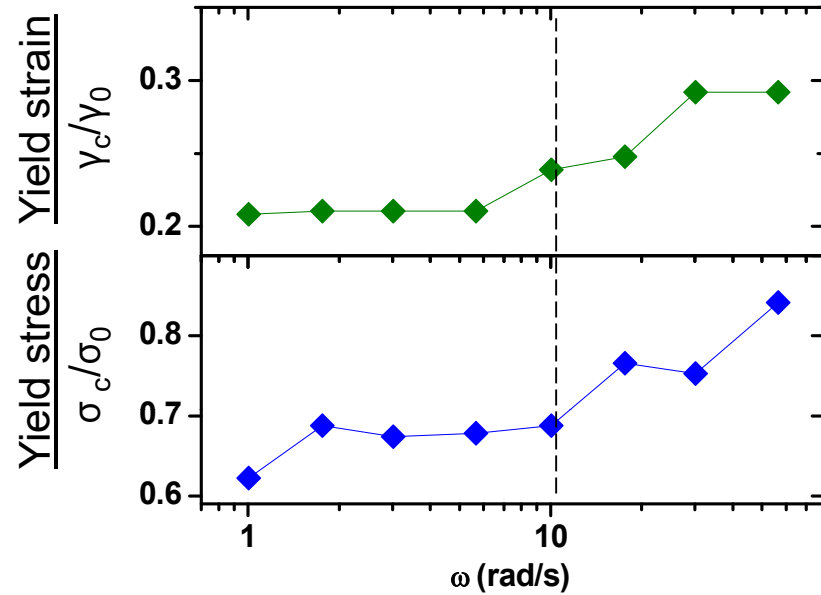
[1] J. Kim *et al.*, J. Rheology, 58(4): 1359-1390, 2014.

Rheo-USANS reveals source of rate-dependent yielding

Sp. surface area $\Sigma = \frac{\lim_{q \rightarrow 0} (I(q) q^4)}{2\pi(\Delta\rho)^2}$



Isometric compression: $L_c \sim \Sigma^{-3/2}$



Poroelastic drainage model:

Darcy's Law: $t_{drain} \sim \frac{\eta_s L_c^2}{k_{abs} \sigma}$

$t_{drain} \sim 0.1 \text{ s}$

Draining fractal: $k_{abs} \sim \frac{d^2}{72} \frac{\phi^3}{(1-\phi)^2 \tau^2}$

“Two-step” yielding due to poroelastic drainage from phase separated structure.

Conclusions, Part 3

- Gels with heterogeneous structure due to interrupted phase separation exhibit delayed yielding
- When using large amplitude oscillatory rheology to probe yielding, intercycle measures (G' and G'') are inadequate
- Combined LAOS analysis and rheo-SANS measurements indicate that delayed yielding is enhanced at high deformation rates due to poroelastic drainage from the phase separated structure
- Presumably, the time scale of poroelasticity can be tuned with quench and aging due to coarsening and arrest of phase separation at different length scales

Take-home message

- Thermal processing opens up **new opportunities to control** the structure and mechanical properties of dense attractive colloidal systems
- The kinetics of coarsening, aging and yielding in gels forming by interrupted phase separation is driven by ***mechanical processes at the dominant length scale of phase separation***, and not necessarily the particle scale

Tuan Nguyen



Juntae Kim



Yongxiang Gao



NSF DMR 1720256



UNIVERSITY OF CALIFORNIA SANTA BARBARA



UC SANTA BARBARA
chemical
engineering