Coordinated measurements of particle interactions, microstructure, and rheology in colloidal gels

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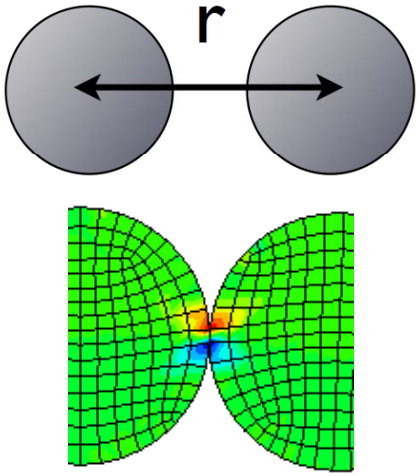
9th IFPRI Workshop on Particle Technology
June 2018

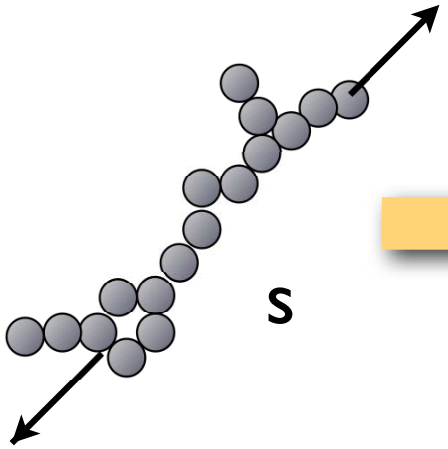
Mechanics of colloidal gels

Interactions



Double layer
van der Waals
Depletion
Solvation
Steric
Adhesion
Friction

Micromechanics

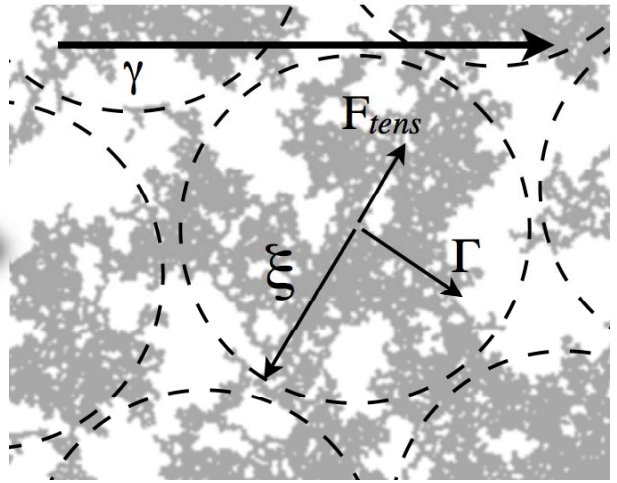


Bending rigidity

Tensile rupture force

Critical bending moment

Gel rheology

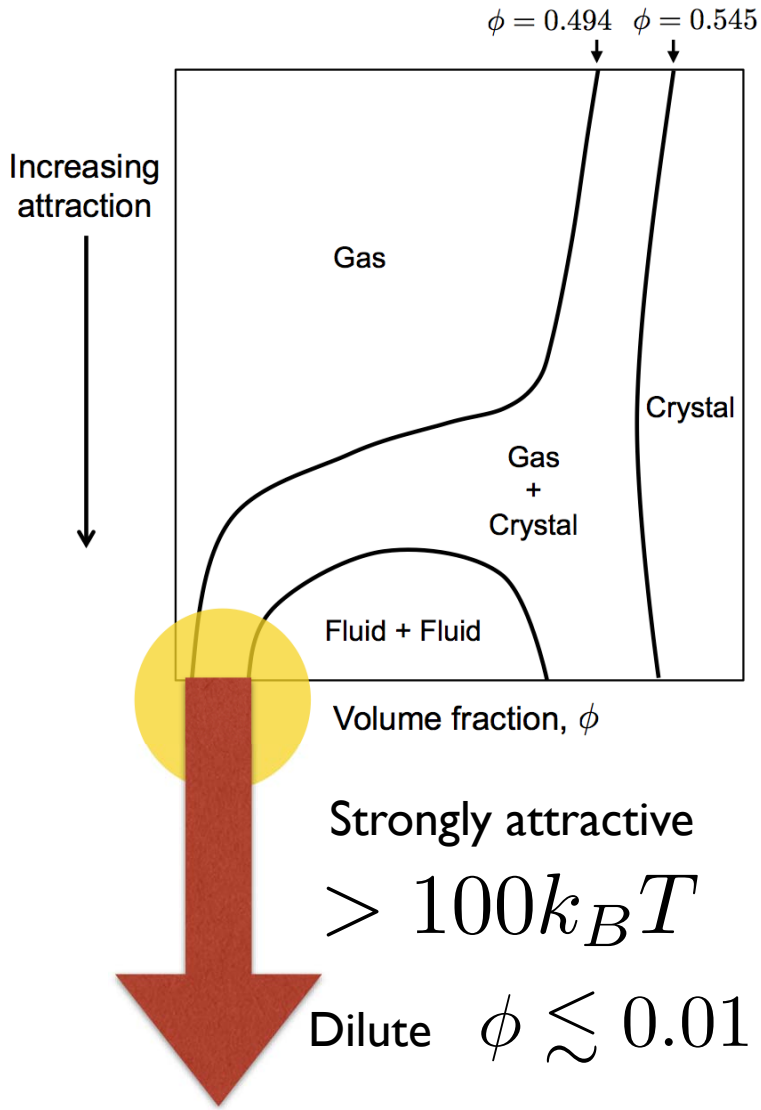


Yield stress (strength)

Elastic modulus

Strong attraction – fractal aggregates

Phase diagram
short range attraction



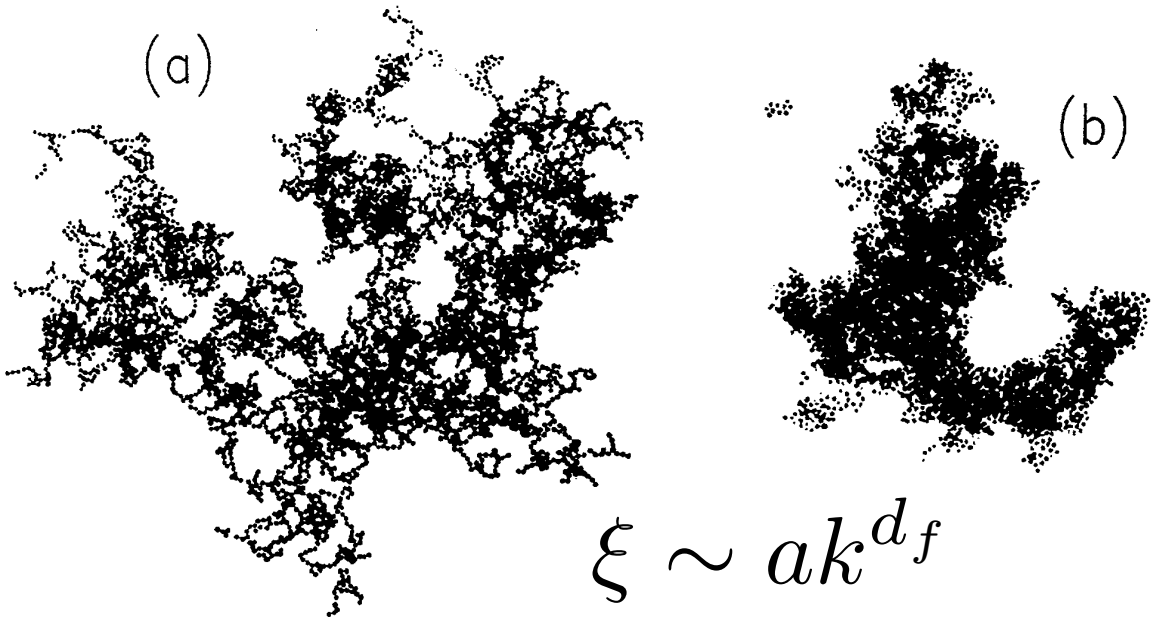
Strongly attractive

$> 100 k_B T$

Dilute $\phi \lesssim 0.01$

7.2nm Au particles

D. Weitz and M. Oliveria, Phys. Rev. Lett. 52, 1433 (1984).
D. Weitz, J. Huang, M. Lin, and J. Sung, Phys. Rev. Lett. 53, 1657 (1984).



$$\xi \sim a k^{d_f}$$

d_f *Fractal dimension*

Diffusion limited

$d_f \approx 1.7 - 1.8$

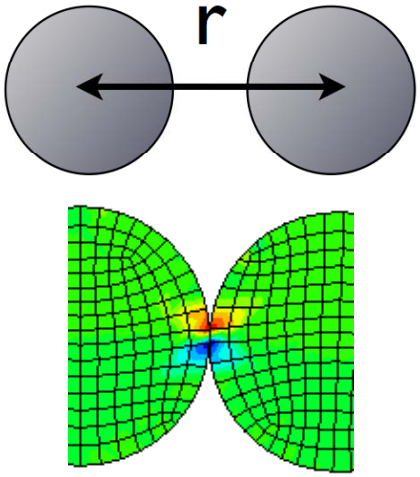
Reaction limited

$d_f \approx 2.0 - 2.2$

Microscopic mechanics of fractal gels

A. Krall and D. Weitz, *Phys. Rev. Lett.* 80, 778 (1998).
J. P. Pantina and E. M. Furst. *Phys. Rev. Lett.*, 94:138301 (2005).
J. P. Pantina and E. M. Furst, *Langmuir*, 22:5282–5288 (2006).

Interactions



Double layer
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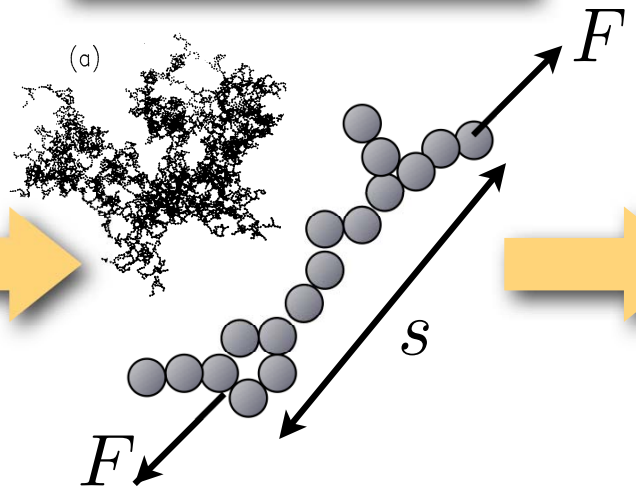
Micromechanics



Bending rigidity

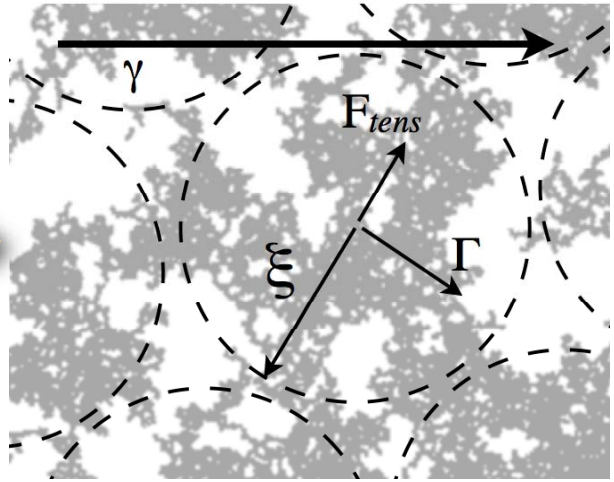
$$\kappa = \kappa_0 (a/s)^{\beta}$$

$$\beta = 2 + d_b \approx 3.1$$

Tensile rupture force F_{tens}

Critical bending moment M_c

Gel rheology



Elastic modulus

$$G_0 \sim \frac{\kappa(\xi)}{\xi} \sim \kappa_0 a^{\beta} \xi^{-1-\beta}$$

Yield stress

$$\sigma_y \sim F_{tens} \xi^{-2}$$

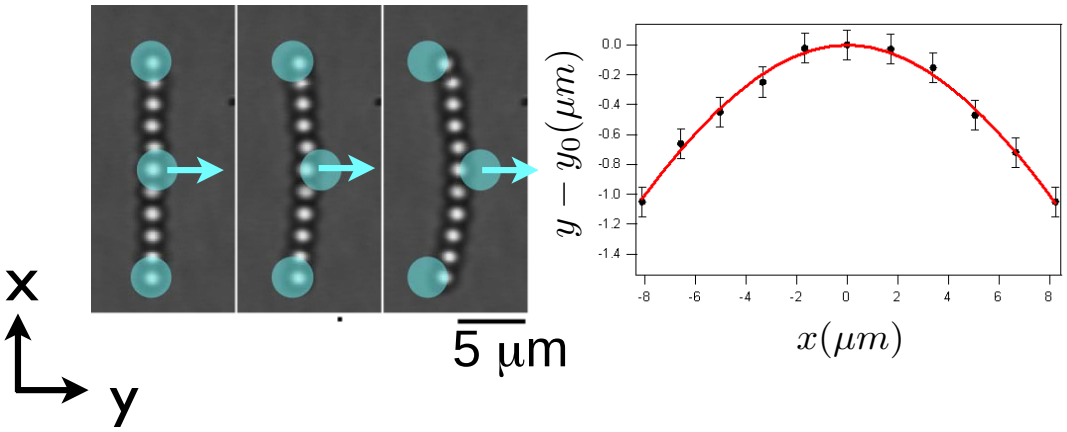
$$\sigma_y \sim \Gamma \xi^{-3}$$

Bending rigidity to fractal gel modulus

3-point bending geometry using laser tweezers

J. P. Pantina and E. M. Furst. *Phys. Rev. Lett.*, 94:138301 (2005).
J. P. Pantina and E. M. Furst, *Langmuir*, 22:5282–5288 (2006).

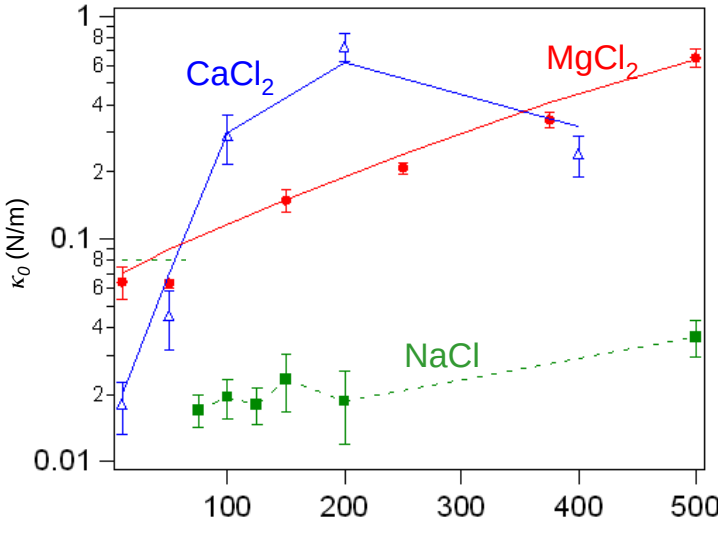
$$\kappa(L) = \kappa_0 \left(\frac{a}{L}\right)^3 = \frac{F_y}{y(L)} = \frac{3EI}{L^3}$$



$$G_0 \sim \frac{\kappa(\xi)}{\xi} \sim \kappa_0 a^\beta \xi^{-1-\beta}$$

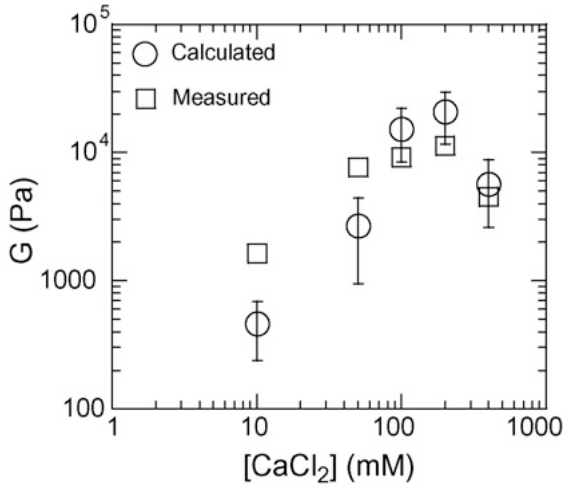
$$G_0 = \frac{\kappa_0}{a} \phi^{(3+d_b)/(3-d_f)}$$

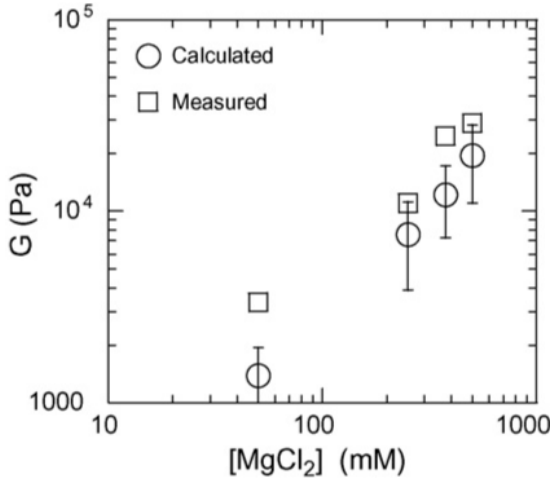
Single-bond bending rigidity (1.47μm PMMA)



Bulk rheology, PMMA gels

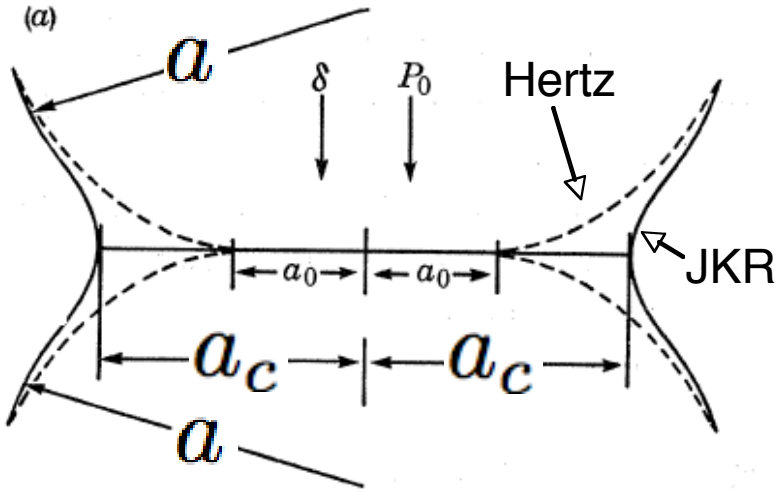
P. B. Laxton and J. C. Berg, *Coll. Surf. A* 301, 137 (2007).





Adhesion between elastic particles
JKR Theory

Johnson, Kendall and Roberts, Proc. R. Soc. London, Ser. A 324, 301 (1971).
Pantina and Furst, Phys. Rev. Lett. 94:138301, 2005.

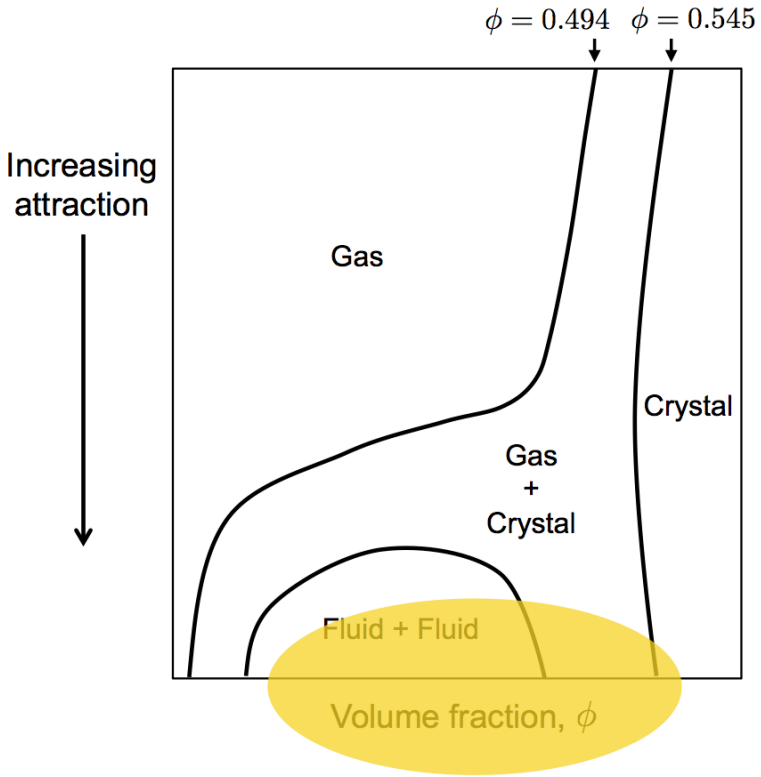


Single-bond rigidity:

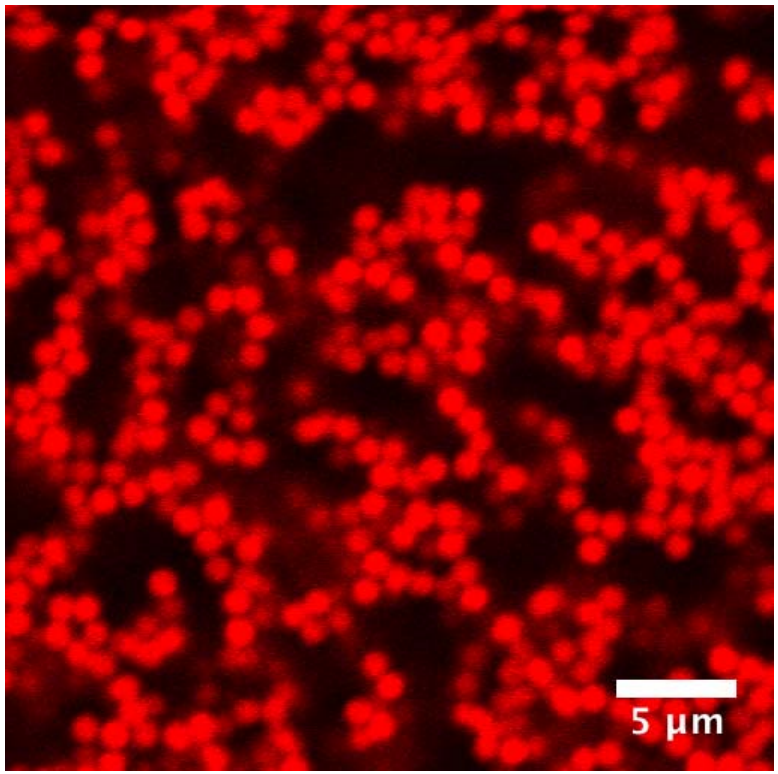
$$\kappa_0 = \frac{3\pi E}{4a^3}\left(\frac{3\pi a^2 W_{SL}}{2K}\right)^{4/3}$$

Relates mechanics to adhesion energy (particle interfacial phenomena)

"Cluster gels"
Lower attraction, higher density



- Ramakrishnan, S.; Chen, Y.-L.; Schweizer, K. S.; Zukoski, C. F. *Phys. Rev. E* 2004, 70, 40401.
- N. Koumakis, G. Petekidis, *Soft Matter* 7, 2456 (2011).
- P. J. Lu, et al., *Nature* 453, 499 (2008).



More weakly attractive $\sim 5 - 20 k_B T$

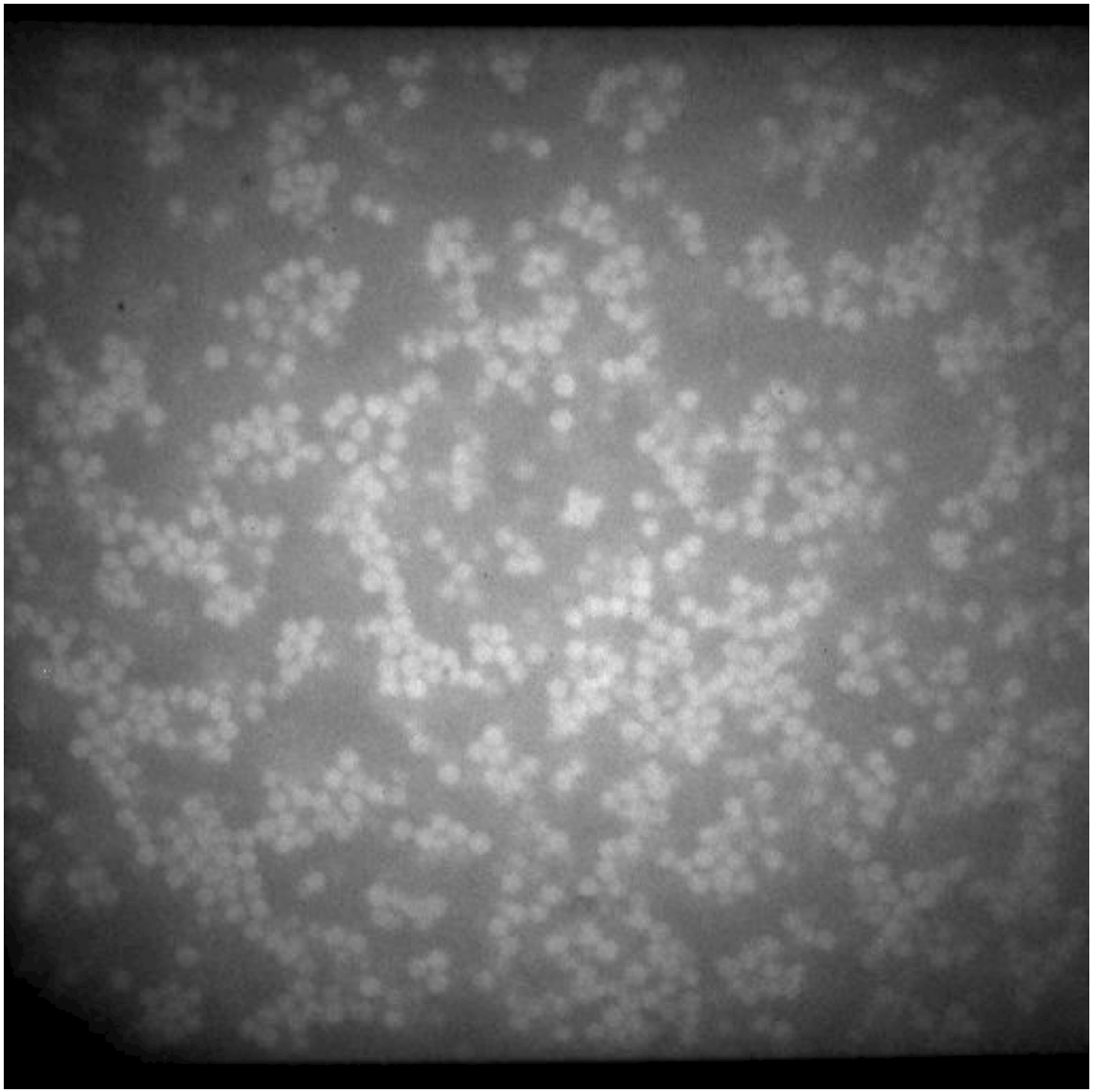
More concentrated $\phi \sim 0.1 - 0.4$

<u>Non-fractal</u> microstructure

Clusters – micromechanical units of depletion gels

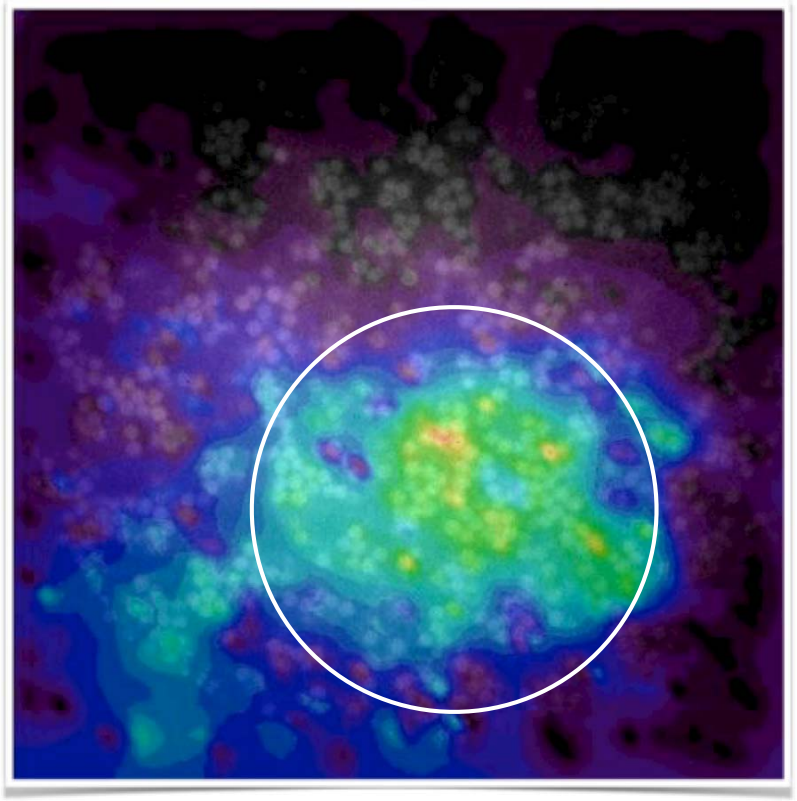
M. H. Lee and E. M. Furst, *Phys. Rev. E* 77, 041408 (2008).

Local strain propagation generated by forced probe



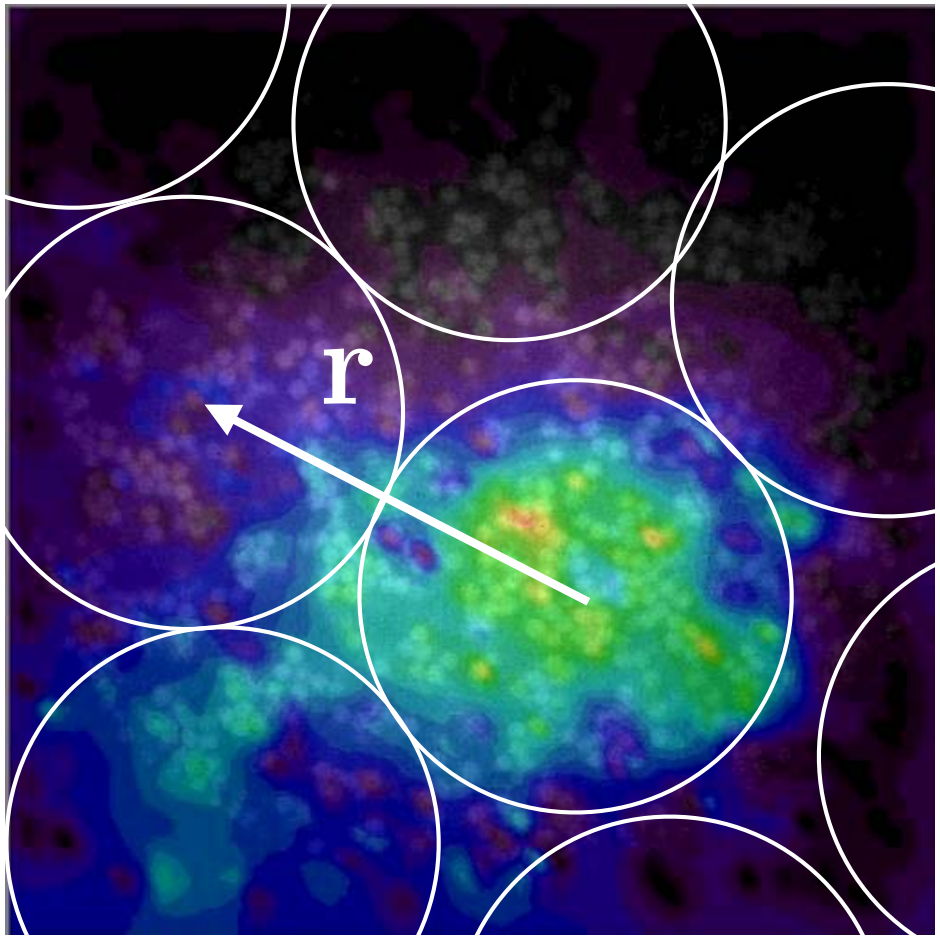
1.5µm PMMA, Φ= 0.22, Cp= 10mg/ml

Overlay of strain field with confocal image
1.5µm PMMA, Φ= 0.22, Cp= 10mg/ml



Cauchy-Born cluster model of gel modulus

Zaccone, A.; Wu, H.; Del Gado, E. *Phys. Rev. Lett.* 2009, 103, 208301.
Kobelev, V. & Schweizer, K. S. *J. Chem. Phys.* 2005, 123, 164902–164913
Ramakrishnan, S.; Chen, Y.-L.; Schweizer, K. S.; Zukoski, C. F. *Phys. Rev. E* 2004, 70, 40401.



$$G' = 4 n_e \kappa \left\langle r^2 \right\rangle$$

number density of elastic bonds × *bond stiffness* × *weighted cluster separation*

$$\left\langle r^2 \right\rangle = (1/3) \int (r_x r_y + r_y r_z + r_x r_z) P(\mathbf{r}) d\mathbf{r}$$

Distribution of cluster-cluster contacts $P(\mathbf{r})$

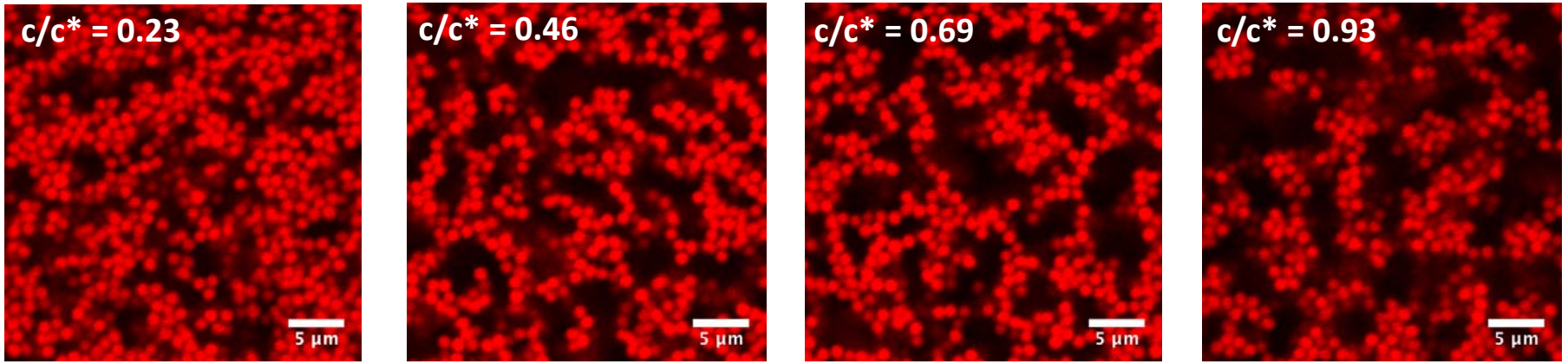
$$n_e = \frac{1}{2} n_c z_c$$

number density of clusters × *average cluster contacts*

A new model depletion gel

Hsiao, L. C.; Solomon, M. J.; Whitaker, K. A.; Furst, E. M., *J. Rheology* 2014, 58, 1485–1504.

PHSA-PMMA in cyclohexane/cyclohexyl bromide (ϕ = 0.2)



PHSA stabilized polymethyl methacrylate (2a = 2.7 µm)

37%/63% (w/w) cyclohexane/cyclohexyl bromide

$$\frac{n_p}{n_s} = 1.03 \qquad \frac{\rho_p - \rho_s}{\rho_p} = 10.2\%$$

Polystyrene depletant

M_w = 900,000 Da

R_g = 32 ± 2 nm

c* = 10.8 mg/mL

Balance requirements for

Colloid interactions

Microstructure imaging

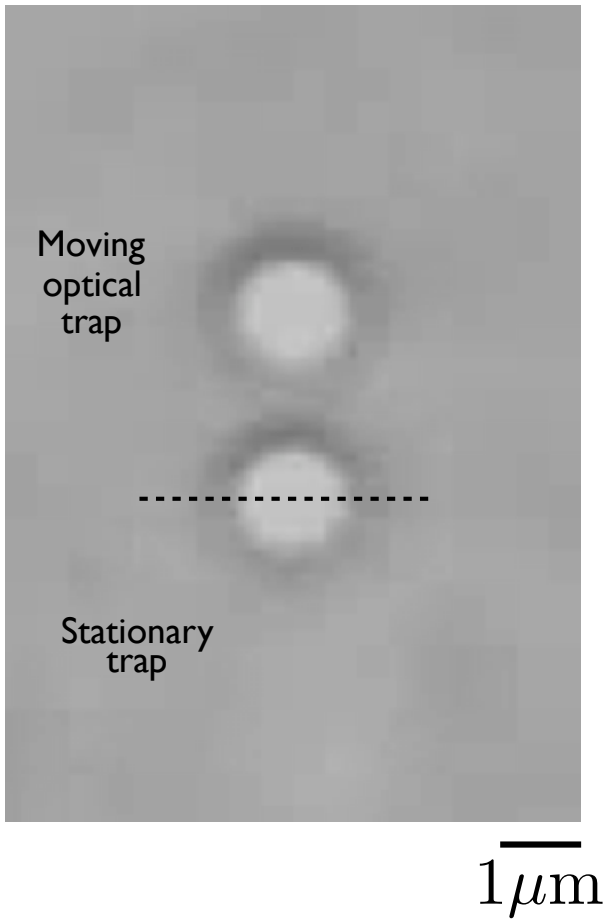
Bulk rheology

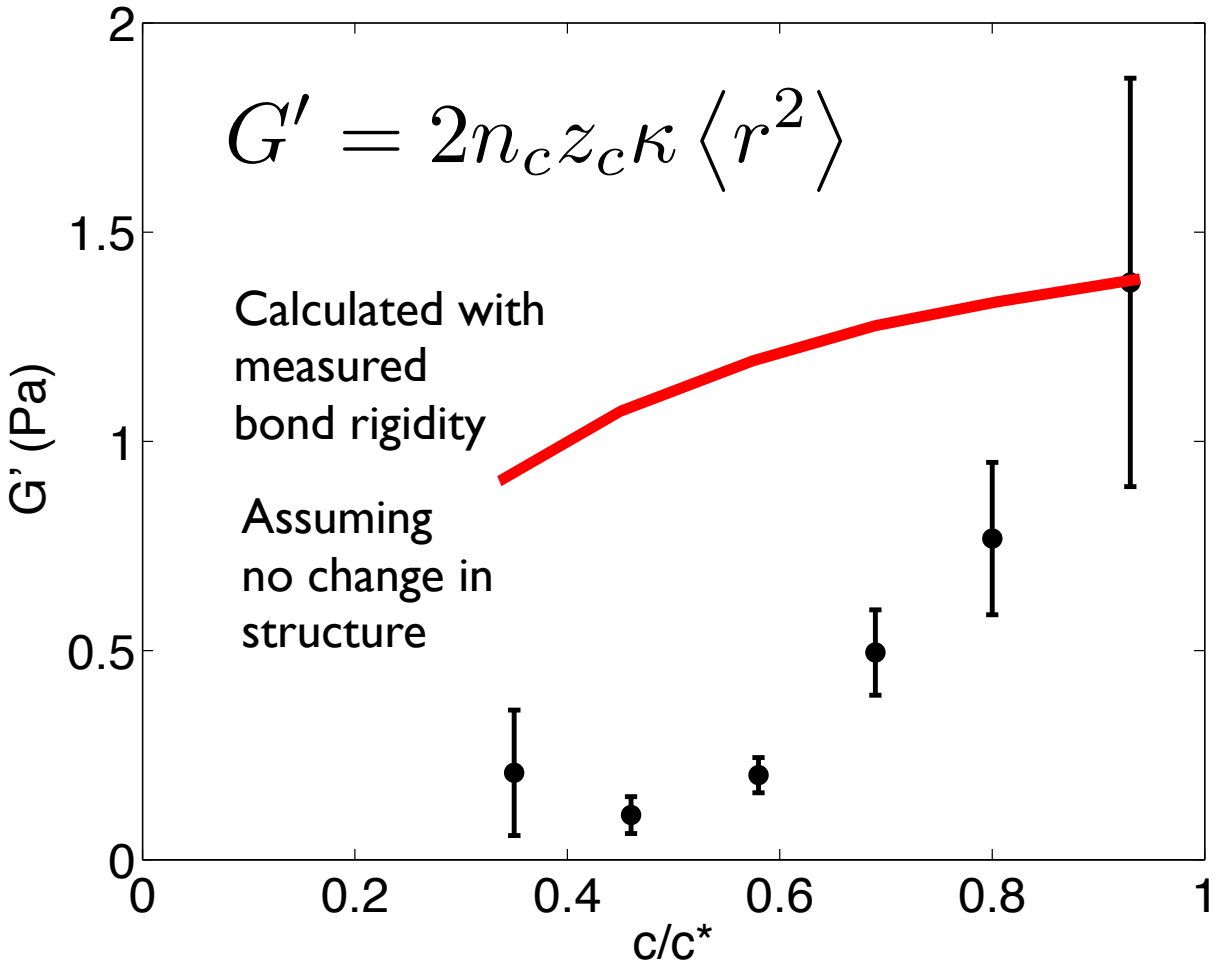
Depletion gel modulus and bond rigidity

Whitaker, K.A. & Furst, E. M. *J. Rheology* 60, 517–529 (2016).
Swan, J.W., Shindel, M. & Furst, E. M. *Phys. Rev. Lett.* 109, 198302 (2012).

PHSA-PMMA in cyclohexane/cyclohexyl bromide ($\phi = 0.2$)

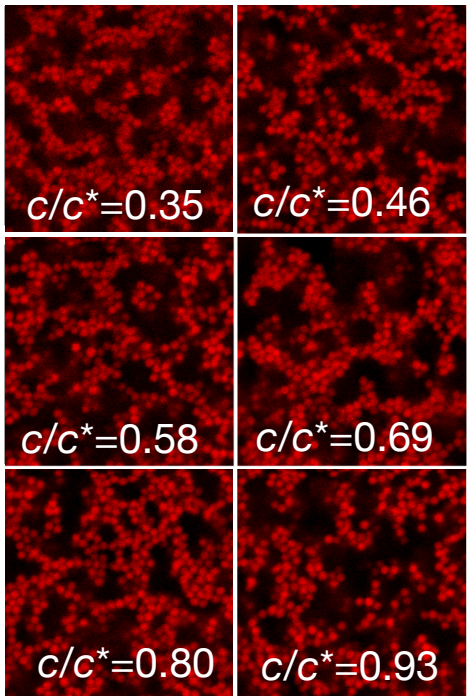
Bond rupture – laser tweezers





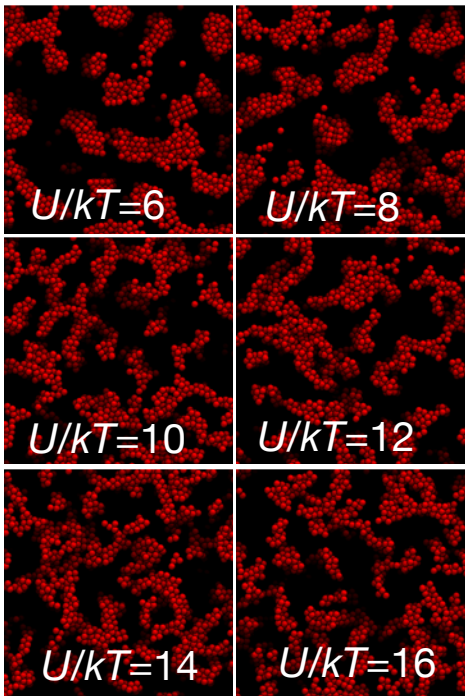
Gel structure correlation length

Confocal



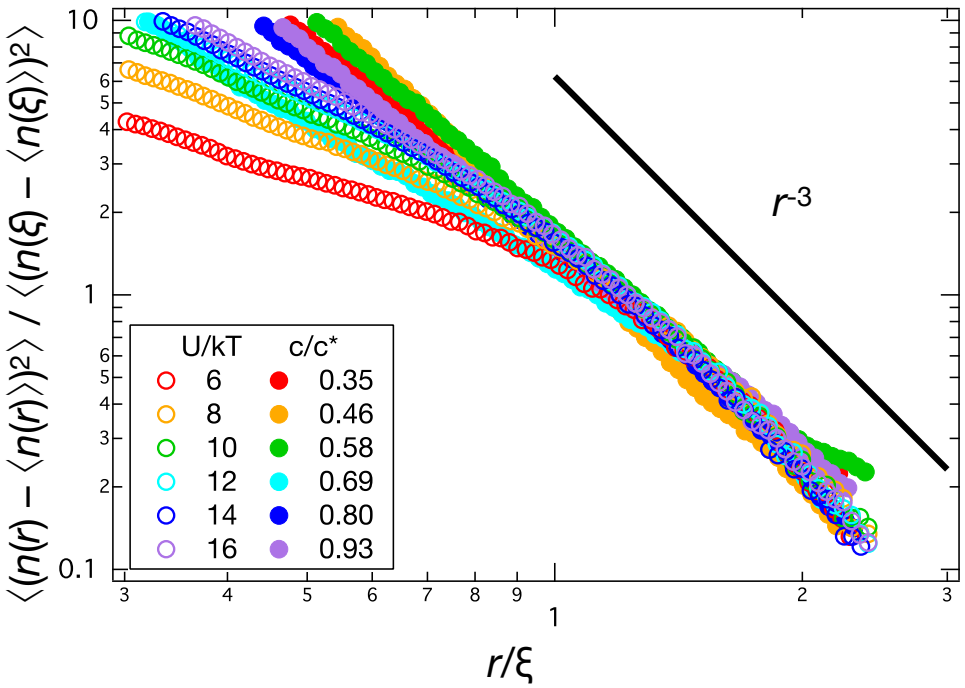
Whitaker, Hsiao, Solomon & Furst

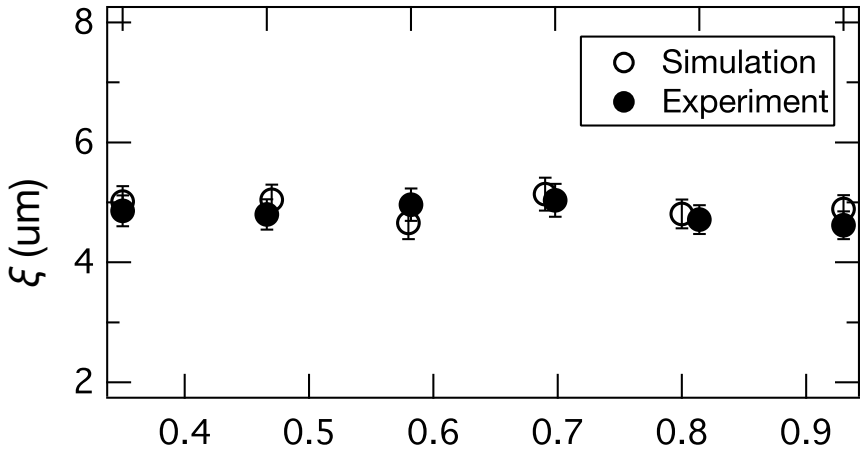
Simulation



Swan and Varga

Number density fluctuation

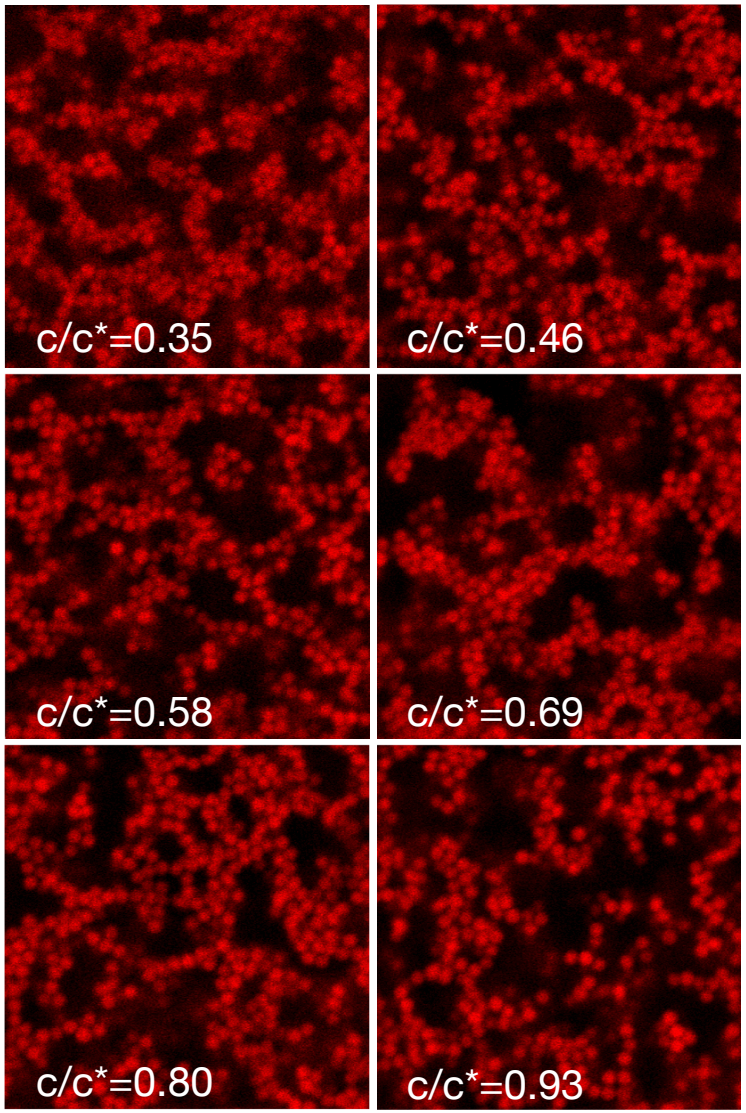




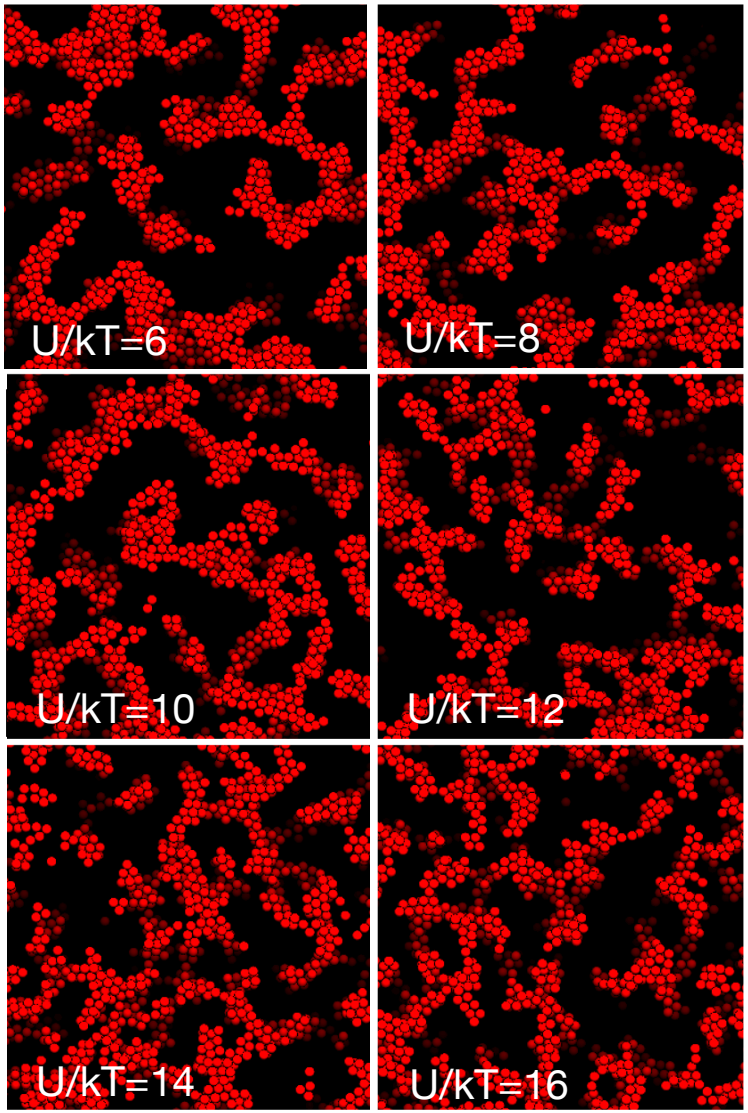
Also observed by Ramakrishnan et al. for 90nm silica in decalin, PS depletant

Ramakrishnan, S.; Chen, Y.-L.; Schweizer, K. S.; Zukoski, C. F. *Phys. Rev. E* 2004, 70, 40401.

I.D. clusters and their connections…



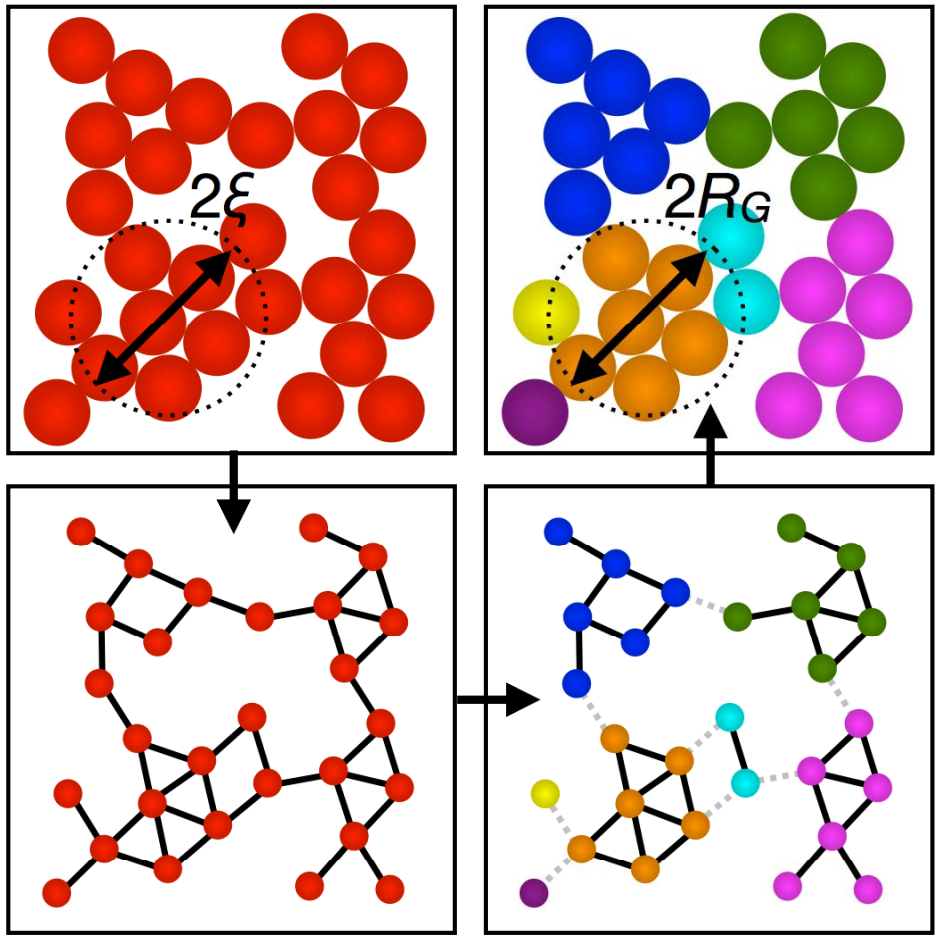
Whitaker, Hsiao, Solomon & Furst

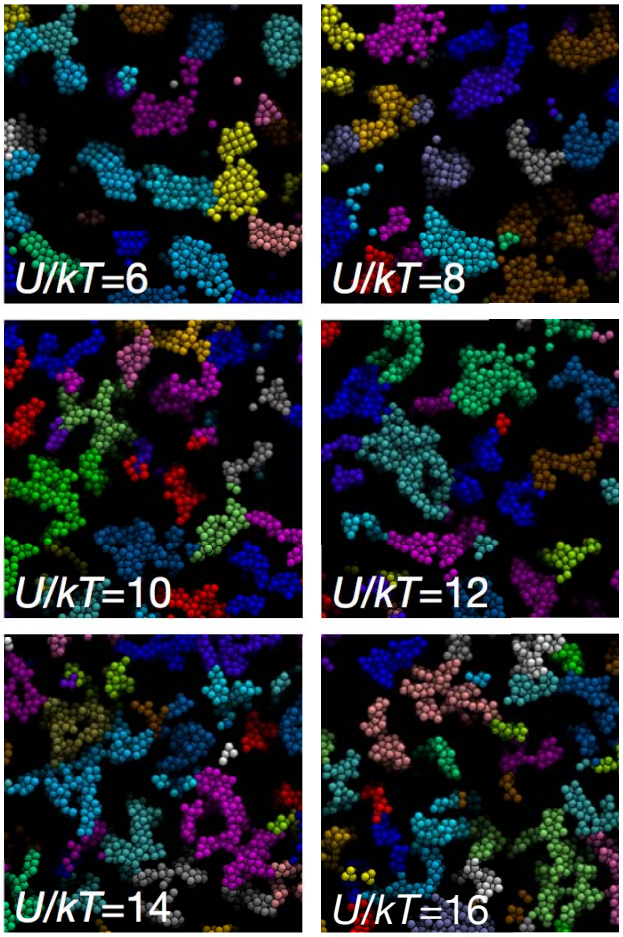


Swan and Varga

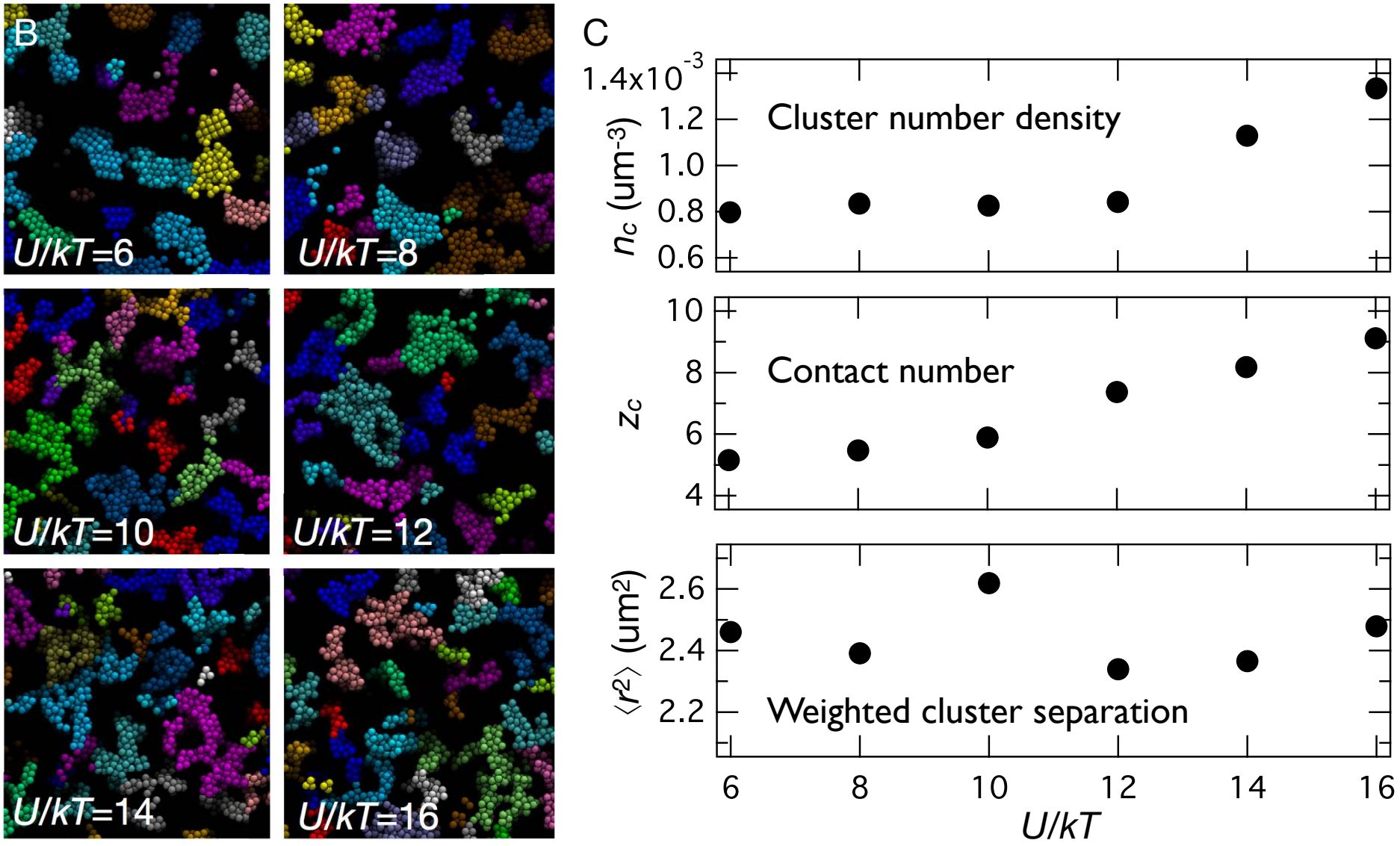
l-balanced graph partition

S. Zhong, J. Ghosh, Proceedings of the 2003 SIAM International Conference on Data Mining pp. 71–82 (2003).
J. P. Hespanha, An Efficient Matlab Algorithm for Graph Partitioning (2004).



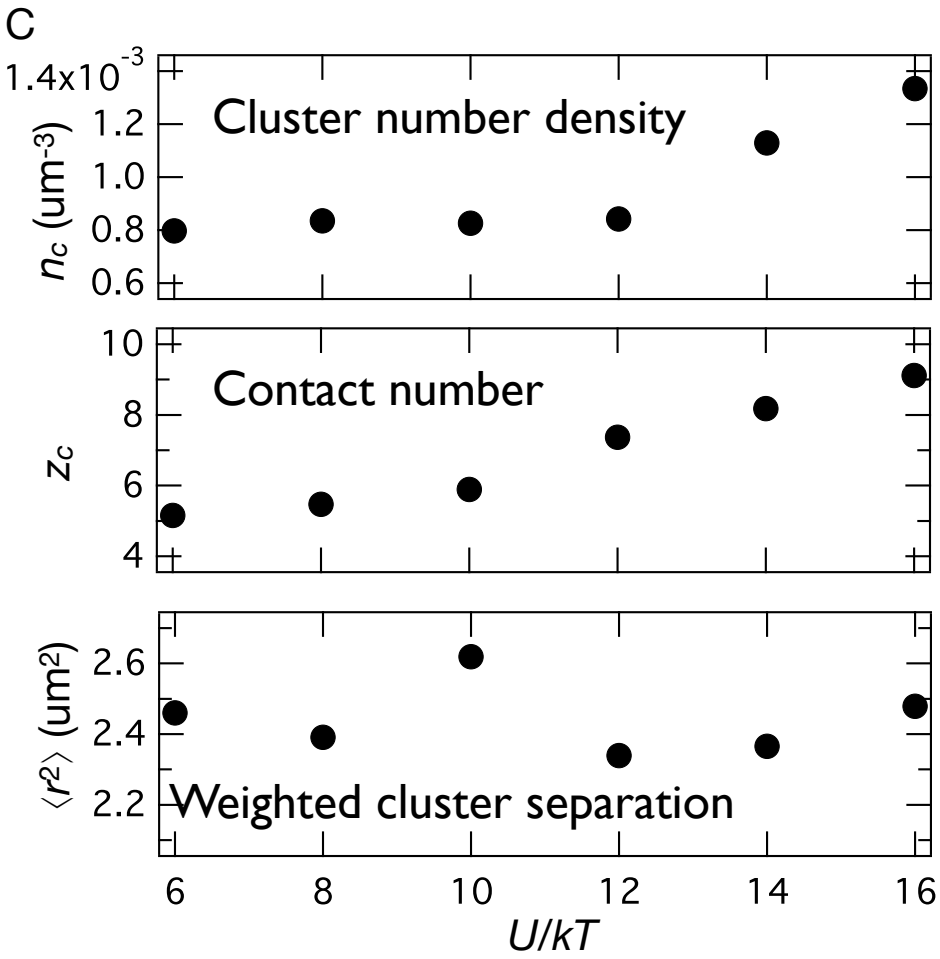


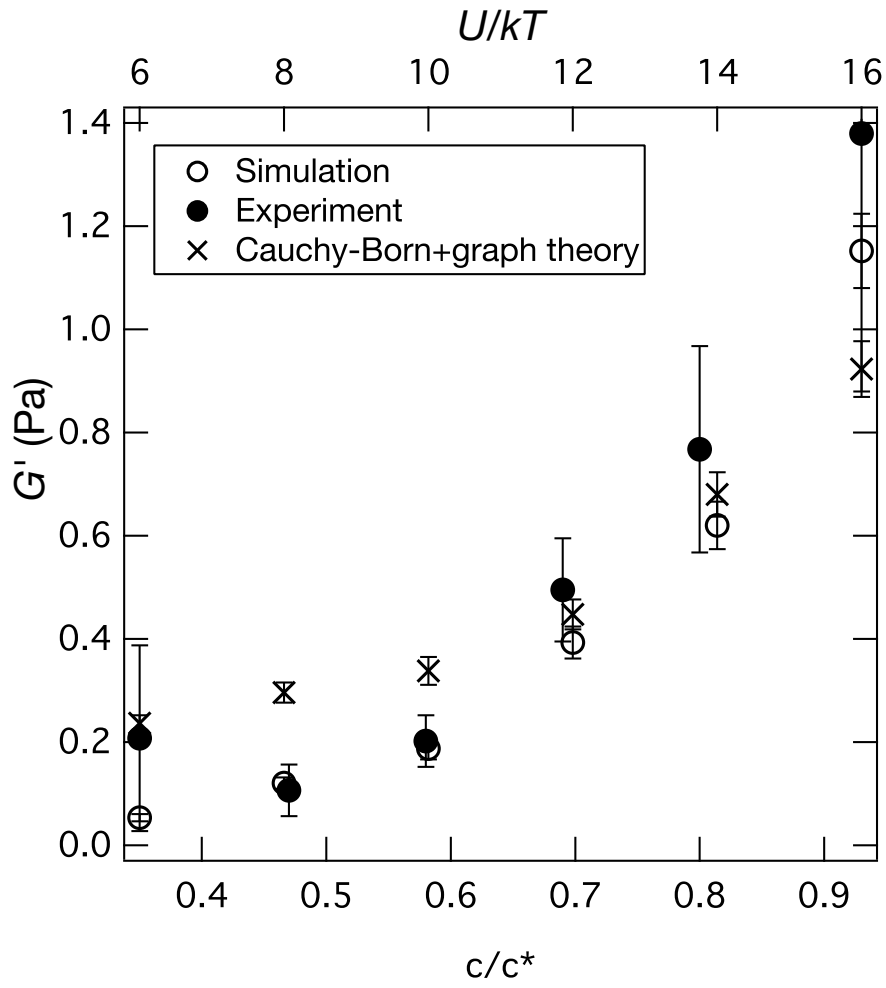
Cluster gel structure



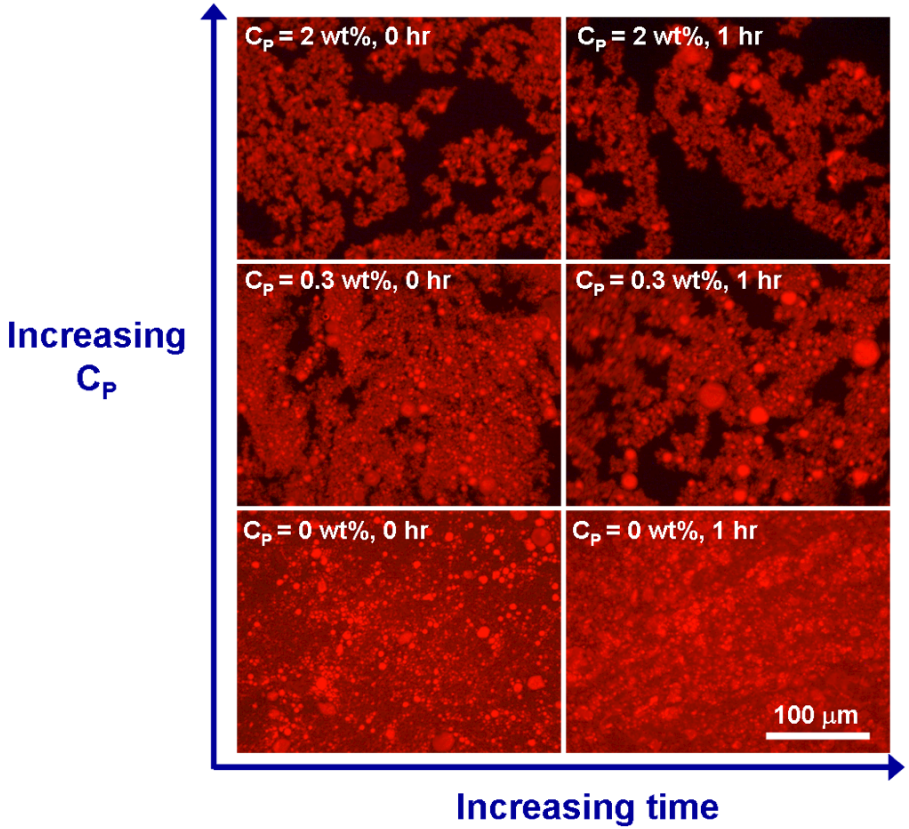
Cluster gel elasticity

$$G' = 2n_c z_c \kappa \left\langle r^2 \right\rangle$$





Colloid-polymer systems in industry



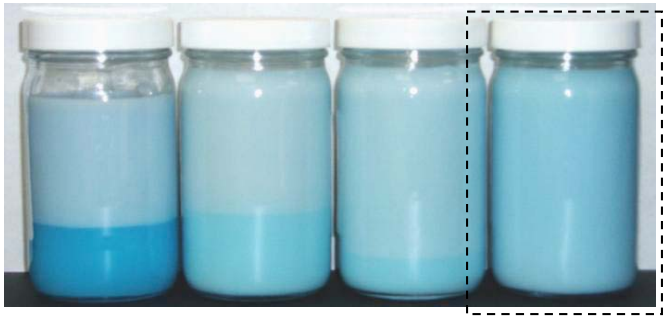
Surfactant vesicle suspension

2a=100nm-50μm ditallowethylester dimethyl ammonium chloride (DDAC), polymer: polyDADMAC (MW=14.5kDa), solvent: water

φ=0.3, $R_g/<R>$=0.09

J. Y. Huh, M. L. Lynch, and E. M. Furst. *Phys. Rev. E*, 76:051409, 2007.
J. Y. Huh, M. L. Lynch and E. M. Furst, *Ind. Eng. Chem. Res.* 50, 78-84, 2011.

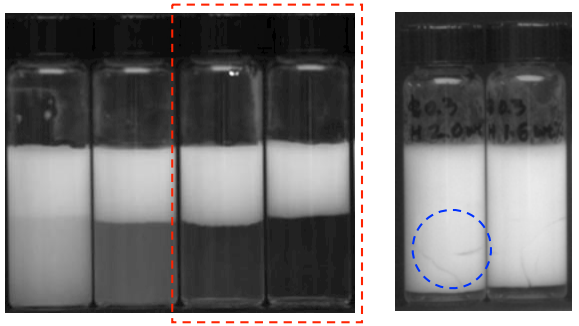
Phase separation



Stable, homogeneous dispersion

Thickening / gelation

Consolidation / sedimentation



SUMMARY

- Gels: rheology-structure-interactions
- Rheology of "dense" depletion gels – clusters
- An experimental system—bond mechanics, structure, rheology

Hsiao, L. C.; Solomon, M. J.; Whitaker, K. A.; Furst, E. M., *J. Rheology*, 58, 1485–1504 (2014).
Whitaker, K. A. & Furst, E. M. *J. Rheology* 60, 517–529 (2016).

Dr. Kathryn Whitaker, *Dow*
Prof. Lilian Hsiao, *NCSU*
Michael Solomon, *University of Michigan*
Dr. Zsigmond Varga and Jim Swan, *MIT*

Special thanks: Emanuela Del Gado, Jan Vermant

NSF CBET–1235955
International Fine Particles Research Institute (IFPRI)