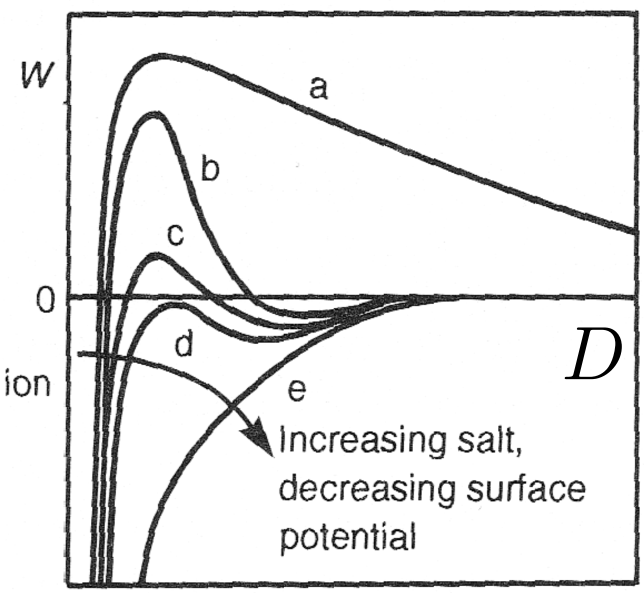
Colloidal flocculation

Flocculation

Reduced barrier



Israelachvili, *Intermolecular and Surface Forces*, 3rd ed., Academic Press, New York, 2007.

Double layer and vdw interactions (DLVO, 1941 & 1948)

$$U_{\mathrm{e}} \approx 64 k_B T a n_\infty \gamma^2 \kappa^{-2} e^{-\kappa D}$$

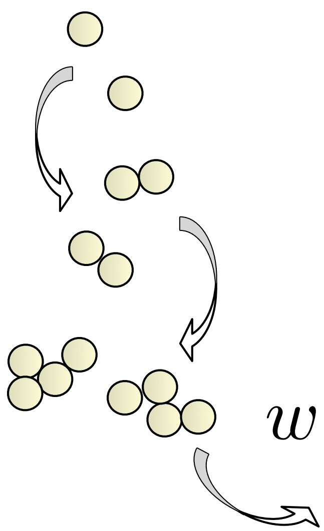
$$U_{\mathrm{vdw}} \approx \frac{a A_H}{12D} \qquad D \ll a$$

Critical counter-ion concentration for flocculation:

$$n_{\mathrm{crit}} = \frac{49.6}{z^6 l_b^3}\left[\frac{k_B T}{A_H}\right] \tanh^4\left(\frac{e z \psi_s}{4 k_B T}\right)$$

$l_b = e^2/4\pi\varepsilon\varepsilon_0 k_B T$ Bjerrum length

Doublet formation



Stability ratio

Fuchs, 1934

$$w = 2a \int_{2a}^{\infty} \frac{U/k_B T}{r^2 G(r)} dr$$

$$w = J_0/J$$

Doublet formation

$$t_p = \frac{\pi \mu a^3 w}{\phi k_B T}$$

Doublet formation times

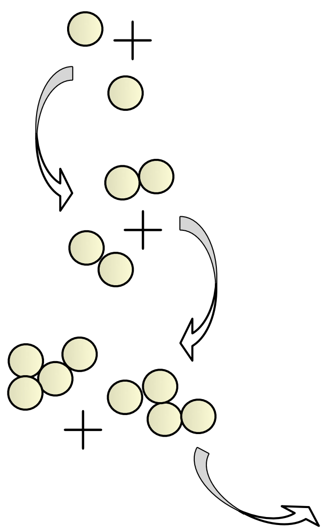
$$w = 1$$

t_p	$\phi = 10^{-5}$	$\phi = 10^{-1}$
$a = 0.1 \mu m$	70s	7ms
$a = 1.0 \mu m$	20h	7s

W. B. Russel, D. A. Saville, and W. R. Schowalter, Colloidal Dispersions (Cambridge University Press, New York, 1989).

Flocculation kinetics

Smoluchowski, 1917



Particle flux

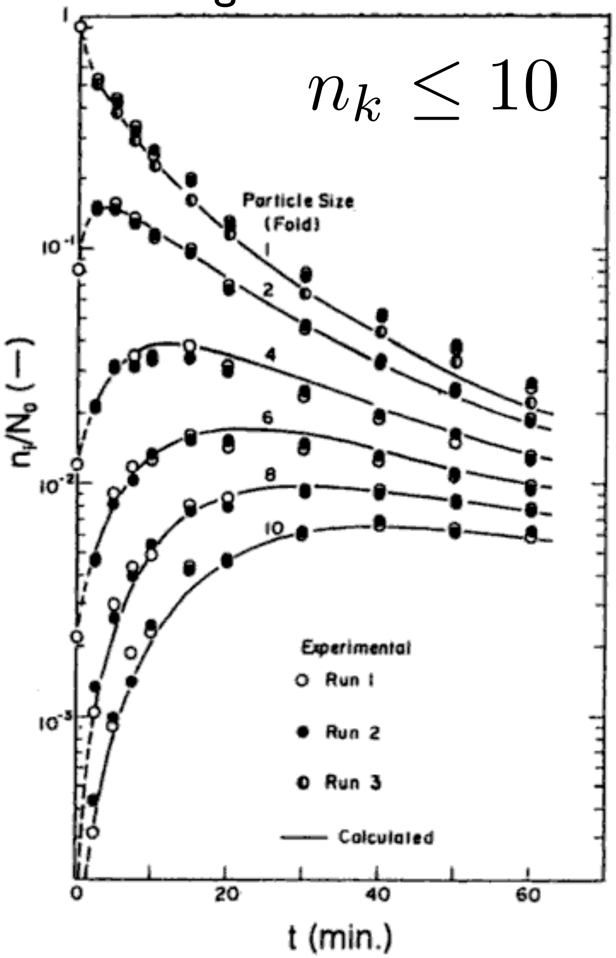
$$J_{ij} = \frac{2k_BT}{3\mu}(a_i + a_j)\left(\frac{1}{a_i} + \frac{1}{a_j}\right)\frac{n_i n_j}{w_{ij}}$$

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i=1,j=k-i}^{k-1} J_{ij} - \sum_{i=1}^{\infty} J_{ki}$$

$$n_k(t) = n_0 \frac{(t/t_p)^{k-1}}{(1+t/t_p)^{k+1}}$$

$$t_p = 3\mu w / 4 n_0 k_B T$$

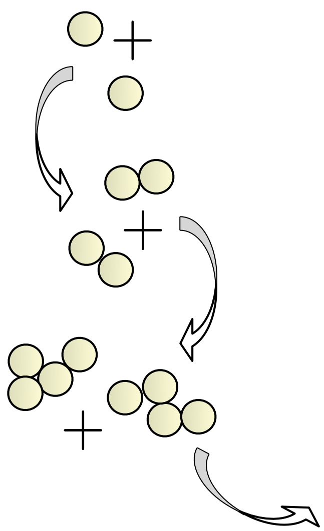
Polystyrene latex flocculation using Coulter counter

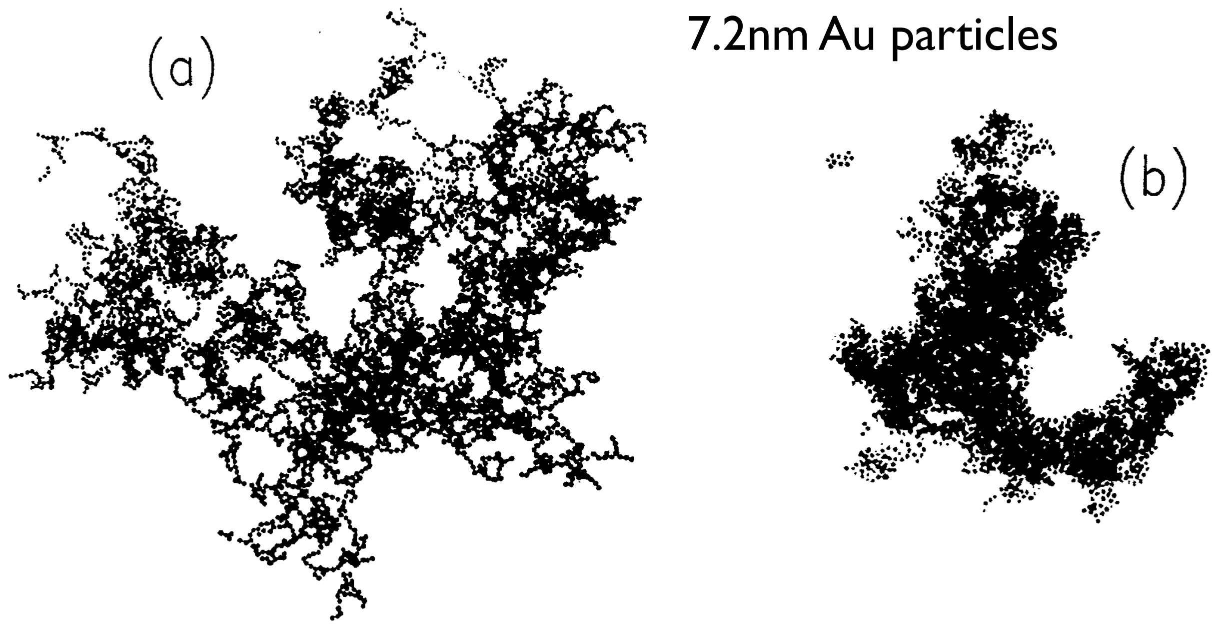


Higashitani & Matsuno, 1979.

Floc structure

$\xi \sim ak^{d_f}$ $\quad d_f$ Fractal dimension





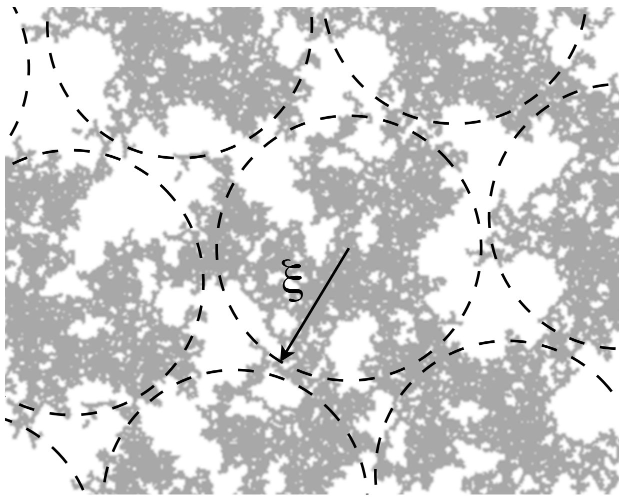
Diffusion limited
$d_f \approx 1.7 - 1.8$

Reaction limited
$d_f \approx 2.0 - 2.2$

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).

Percolation

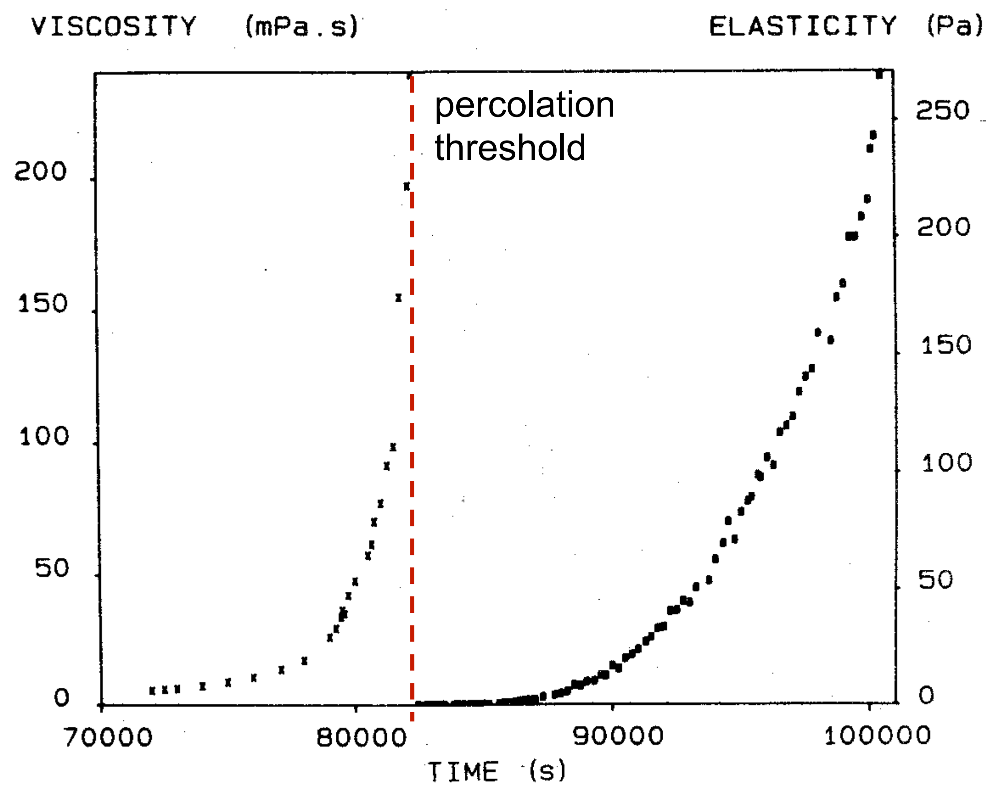
Flocs close-packed:



$$\phi_k \approx \phi_{\rm rcp} = 0.64$$

$$\phi_k = \phi_{\rm rcp} k^{1-3/d_f}$$

$$\xi = a(\phi_{\rm rcp}/\phi)^{1/(3-d_f)}$$



Gauthier-Manuel et al., *J. Phys*. **48**:869, 1987.

Gel rheology

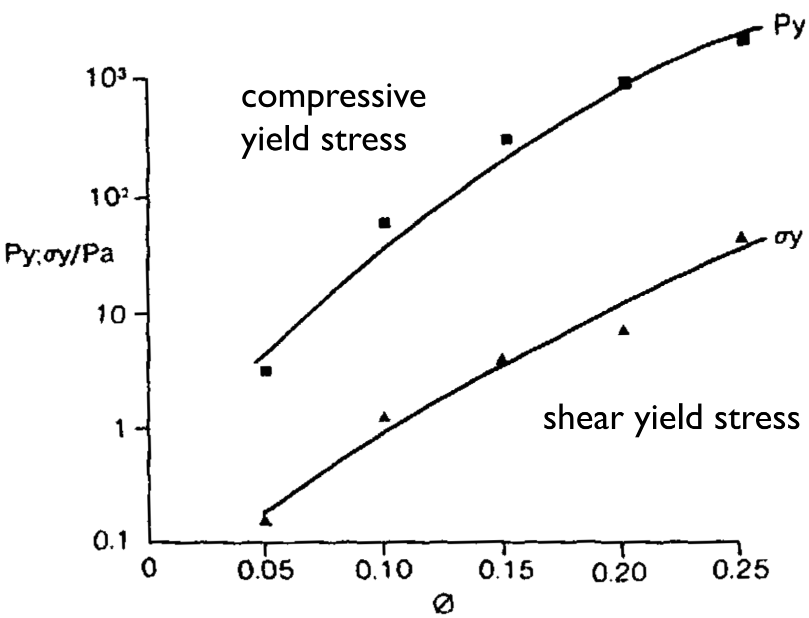
Gel rheology

- Elastic modulus, yield stress, yield strain
- Model and "real" systems:
  - polystyrene latices in water
    flocculated (salts) or with non-adsorbing polymer
  - poly(methyl methacrylate) in organic solvents
    with non-adsorbing polymer – "depletion" gels
  - "organophilic" silica in organic solvents
    with non-adsorbing polymer or "thermoreversible"
  - mineral suspensions
    typically aqueous, flocculated by addition of salts

Gel rheology — flocculated polystyrene latices

Buscall, R. et al. "The rheology of strongly-flocculated suspensions." J. Non-Newtonian Fluid Mech. 24, 183–202 (1987).

Polystyrene latex in salt solutions



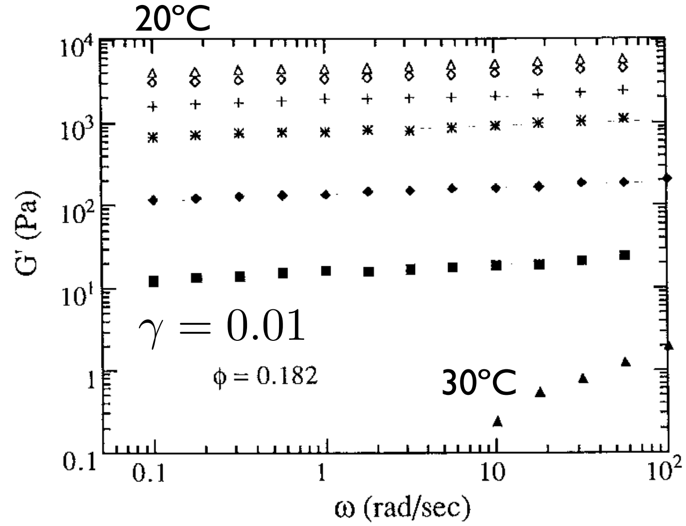
$$P_y \propto G \propto \phi^x$$

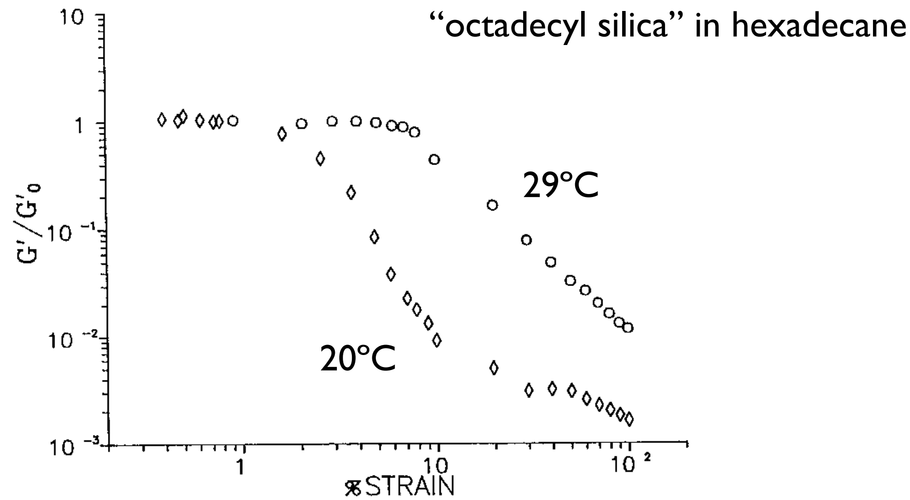
$$x \sim 4.0 - 5.0$$

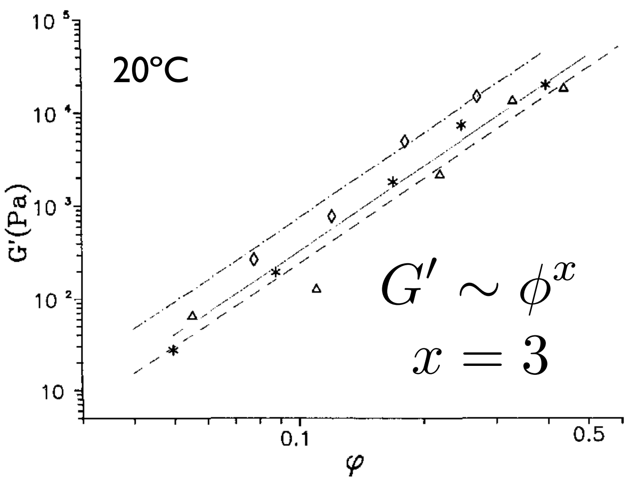
Compression — dewatering and filtration

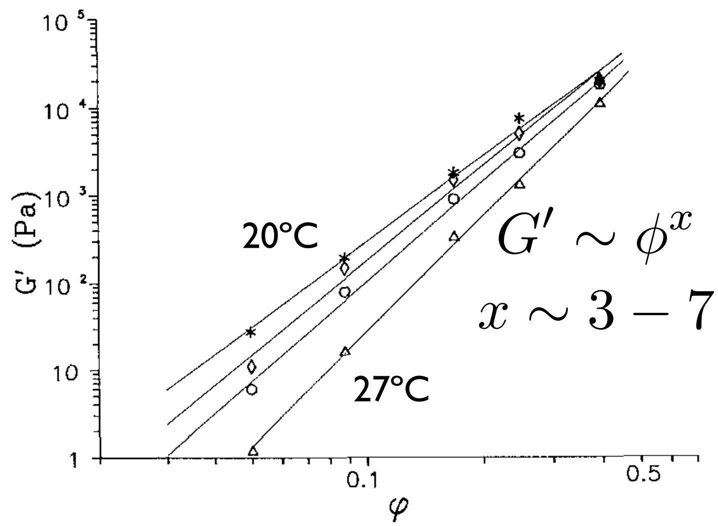
Gel rheology — Stöber organo-silica

Chen, M. & Russel, W. B. "Characteristics of flocculated silica dispersions." J Colloid Interface Sci. 141, 564–577 (1991).









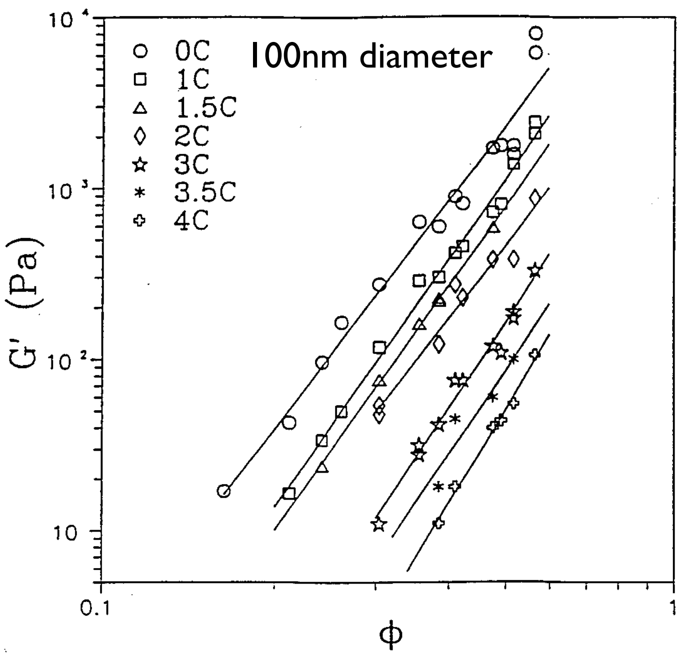
Gel rheology — Stöber organo-silica

Rueb, C. J. & Zukoski, C. F., "Viscoelastic properties of colloidal gels." J. Rheol. 41, 197–218 (1997).

"octadecyl silica" in decalin

$$G' \sim \phi^x$$

$$x = 4.4 - 5.6$$



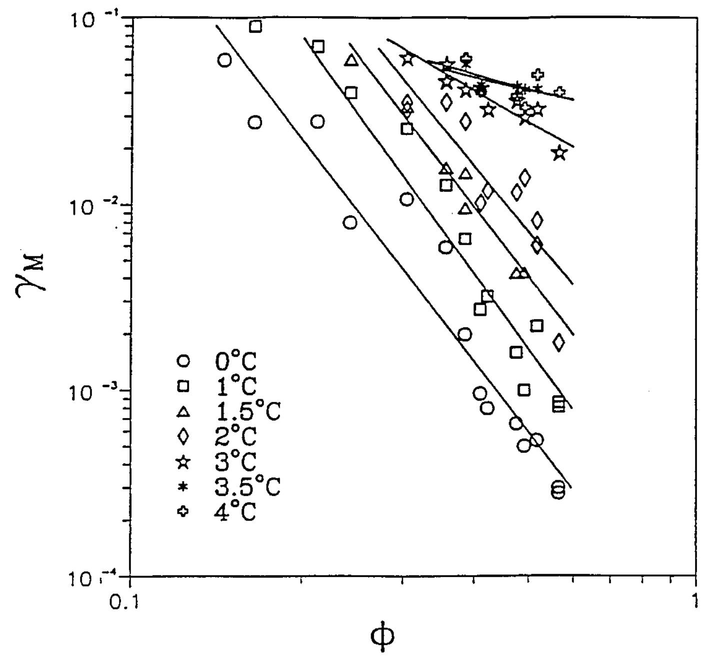


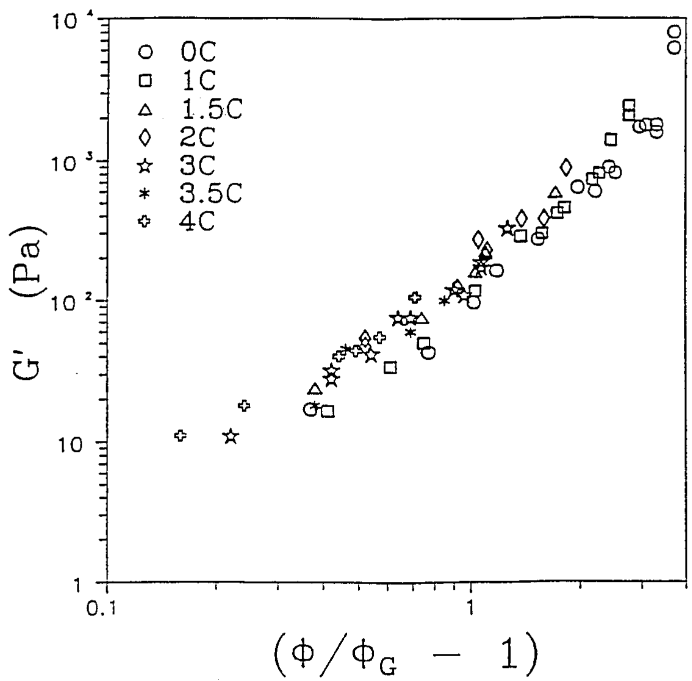
TABLE II. Power-law exponents for gel mechanical properties.

Temp	0 °C	1 °C	1.5 °C	2 °C	3 °C	3.5 °C	4 °C
x^a	4.4	4.8	4.7	4.4	5.1	5.0	5.6
t^b	−4.0	−4.2	−3.9	−3.7	−1.8	−0.8	−0.7

[a] Power-law exponent relating G'_∞ to volume fraction: $G'_\infty \sim \phi^x$. Uncertainties in x are ±0.4.
[b] Power-law exponent relating γ_M to volume fraction: $\gamma_M \sim \phi^t$. Uncertainties in t are ±0.2.

Gel rheology — Stöber organo-silica

Rueb, C. J. & Zukoski, C. F., Viscoelastic properties of colloidal gels. J. Rheol. 41, 197–218 (1997).

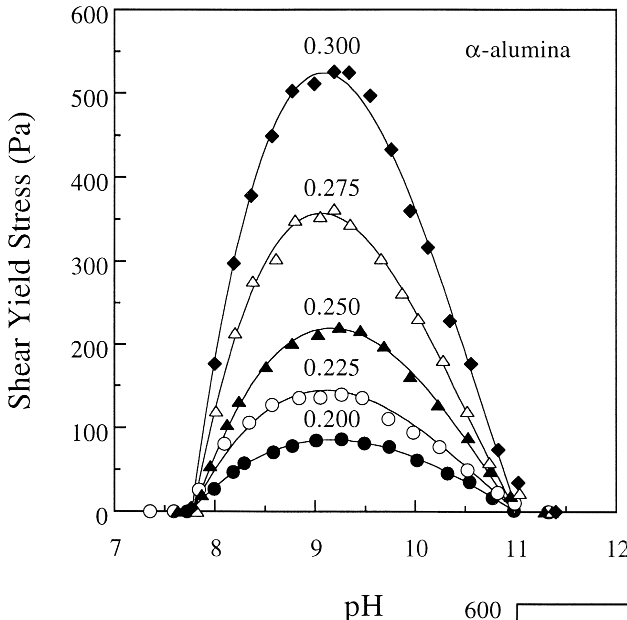


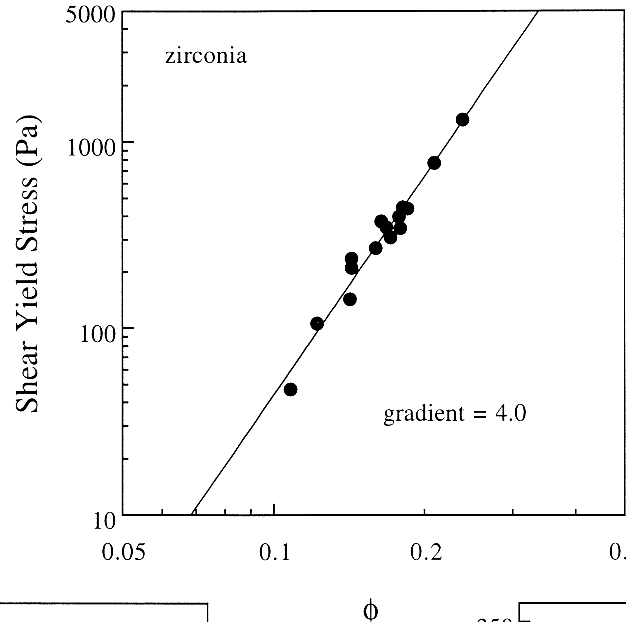
$$G' \sim (\phi/\phi_G - 1)^p$$

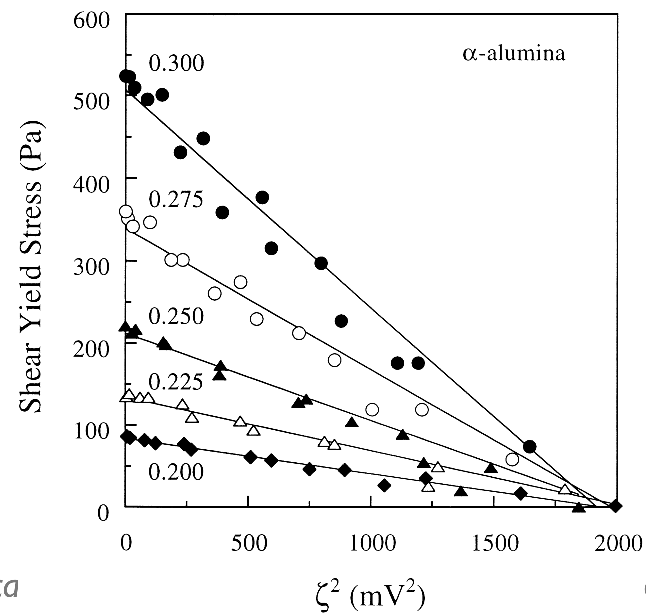
$$p = 2.0 \pm 0.3$$

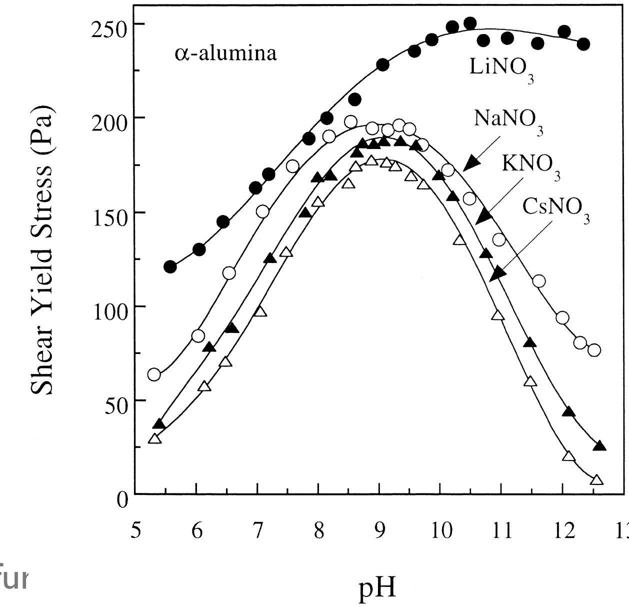
Mineral suspensions

Johnson, S. B., Franks, G.V, Scales, P. J. & Healy, T. W. “Surface chemistry–rheology relationships in concentrated mineral suspensions.” Int. J. Miner. Process. 58, 267–304 (1999); Buscall, R., Ettelaie, R. & Healy, T. W. , “Yield stress and contact forces in coagulated oxide dispersions.” J. Chem Soc. Faraday Trans 93, 4009–4015 (1997).



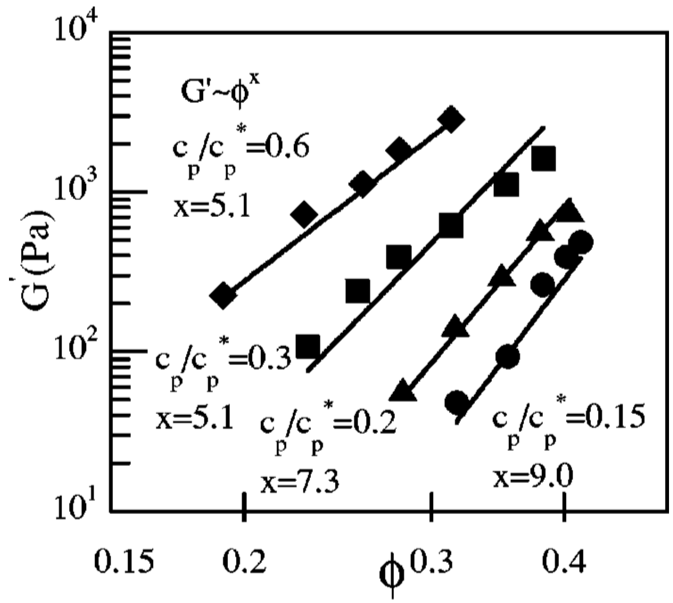




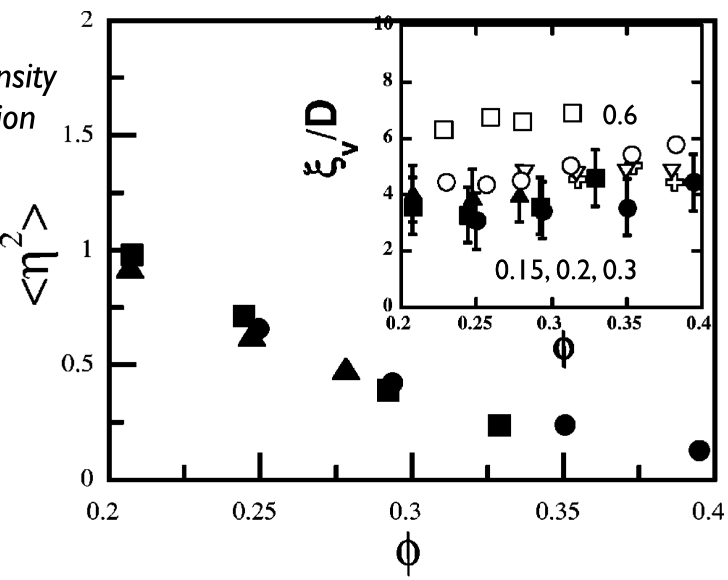


Depletion gel — silica, non-adsorbing polymer

H. K. Chan, et al., Phys. Rev. E, 85, 041403 (2012).
N. Koumakis, et al., Soft Matter, 7, 2456-2470 (2011).
S. Ramakrishnan, et al., Phys. Rev. E, 70, 040401 (2004).



max density fluctuation

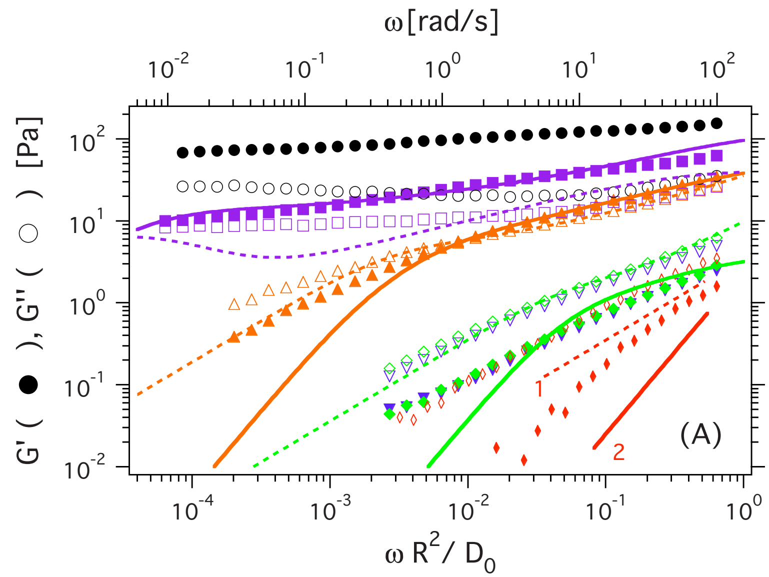


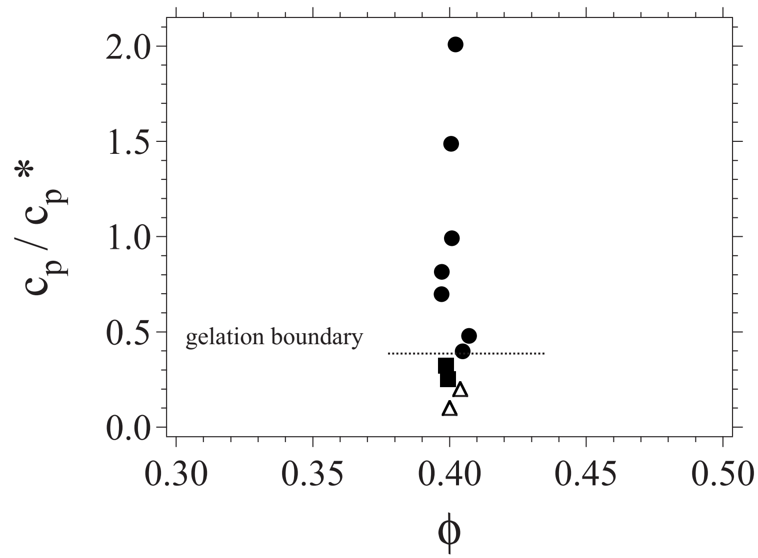
Cluster size
(solid symbols)

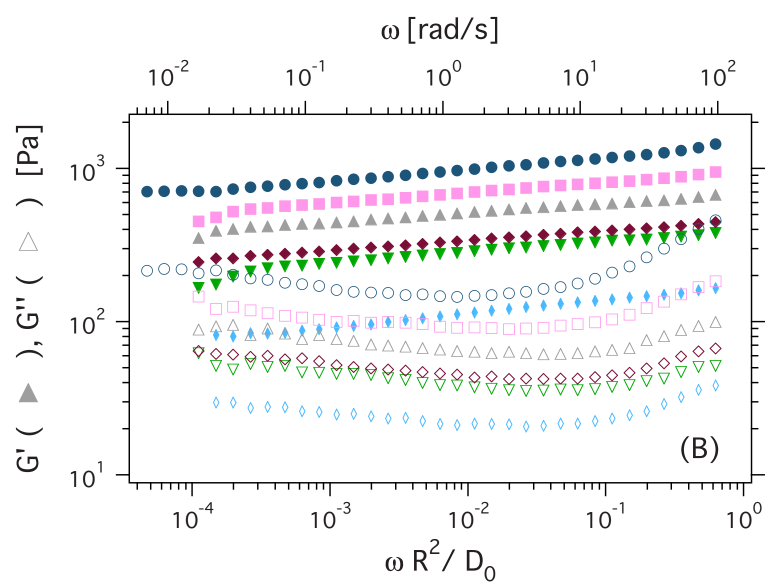
weak function of volume fraction, polymer conc.

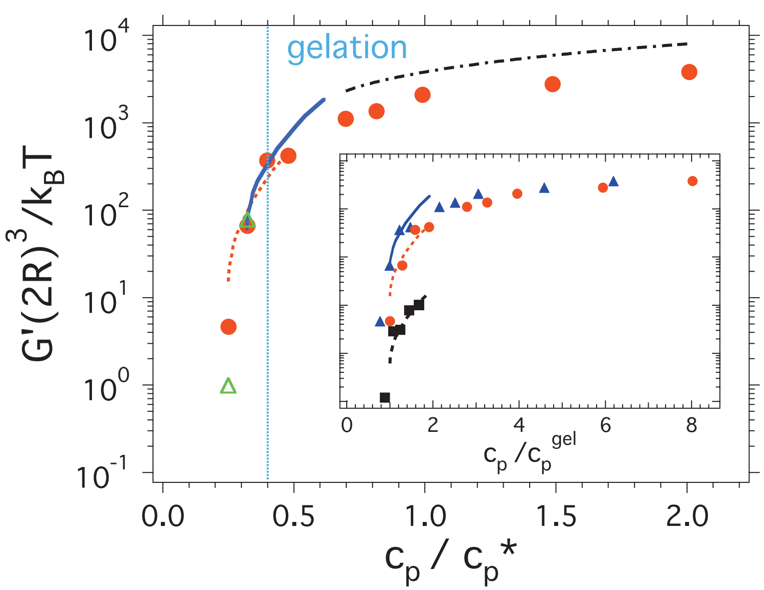
Colloid-polymer mixtures

Laurati, M. et al. Structure, dynamics, and rheology of colloid-polymer mixtures: From liquids to gels. J. Chem. Phys. 130, 134907 (2009).









Gel rheology — challenges

- Poor reproducibility
- Sensitivity to method of preparation
- Sensitivity to shear history (thixotropic)
- Limited range of linear viscoelastic response
- Slip in rheometers
- Sedimentation