Scaling Behavior of the Elastic Properties of Colloidal Gels

W.H. Shih, W.Y Shih, S.I. Kim, J. Liu, I.A. Akasay
Physical Review A, 42(8), 1990

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Cambridge, MA – July 26th, 2017
Colloidal (particulate) gels

Gels: relatively low volume fraction of particles with attractive interactions…

…and all dimensions < 1µm (so they undergo Brownian motion)

Sciortino, 2002, *Nat. Mat.* 1

Ferromagnetic particles (800um wide)


http://www2.mpip-mainz.mpg.de/~auhammer/research-colloids-colloids_in_polymeric_matrices.php
The (once) elusive nature of gelation

Gelation: Gel Point or Critical Gel

\[ t_c \]

\[ \eta \]

\[ G_\infty \]

\[ \text{Steady shear} \]

\[ \text{Solid} \]

\[ \text{Liquid} \]

\[ \text{Stress Relaxation} \]

\[ \log \eta, G_\infty \]

polydimethylsiloxane with balanced stoichiometry

SAOS across transition

- STOPPING THE REACTION AT TIME INDICATED

If reaction cannot be stopped then measurements should be at low mutation number:

\[ N_{mu} = \Delta t / \lambda_{mu} \]

\[ N'_{mu} = \frac{2\pi}{\omega G'} \frac{\partial G'}{\partial t} \]

\[ N''_{mu} = \frac{2\pi}{\omega G''} \frac{\partial G''}{\partial t} \]

Winter and Chambon, 1986, J. Rheol., 30(2)
Winter, 1987, Polymer Eng Sci, 27(22)
Mours and Winter, 1994, Rheo Acta, 33
The (once) elusive nature of gelation

**Gelation:**

- **Gel Point or Critical Gel**
- **Liquid**
- **Solid**
- **Steady shear**
- **Stress Relaxation**

**polydimethylsiloxane with balanced stoichiometry**

**SAOS across transition**

- **STOPPING THE REACTION AT TIME INDICATED**

\[ G' \sim G'' \sim \omega^n \]

\[ \tan \delta = \frac{G''}{G'} = \text{const} \]

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**References:**

Winter and Chambon, 1986, *J. Rheol.*, 30(2)
Winter, 99 NATO ASI Meeting, France, 2000
The (once) elusive nature of gelation

**Gelation:**
- Gel Point or Critical Gel

- Liquid
- Solid

- Steady shear \( \eta \)
- Stress Relaxation

- \( G_\infty \)

\( t_c \) REACTION TIME

- \( G' \) and \( G'' \) vs. REACTION TIME
- SAOS across transition

- STOPPING THE REACTION AT TIME INDICATED

\[ G' \sim G'' \sim \omega^n \]
\[ \tan \delta = \frac{G''}{G'} = \text{const} \]

Negi et al., 2014, *J Rheol*, 58(5)


Winter, 99 NATO ASI Meeting, France, 2000
Gelation as a critical phenomena

Percolation theory has been widely used to study the gelation

![Graphs showing percolation theory](a p = 0.2 b p = 0.59 c p = 0.8)

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Percolation of</th>
<th>Sites</th>
<th>Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triangular</td>
<td>1/2</td>
<td>2 sin((\pi/18))</td>
<td></td>
</tr>
<tr>
<td>Square</td>
<td>0.5927460</td>
<td>1/2</td>
<td></td>
</tr>
<tr>
<td>Honeycomb</td>
<td>0.6962</td>
<td>1 − 2 sin((\pi/18))</td>
<td></td>
</tr>
<tr>
<td>Face Centered Cubic</td>
<td>0.198</td>
<td>0.119</td>
<td></td>
</tr>
<tr>
<td>Body Centered Cubic</td>
<td>0.245</td>
<td>0.1803</td>
<td></td>
</tr>
<tr>
<td>Simple Cubic (1(^{st})nn)</td>
<td>0.31161</td>
<td>0.248814</td>
<td></td>
</tr>
<tr>
<td>Simple Cubic (2(^{nd})nn)</td>
<td>0.137</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>Simple Cubic (3(^{rd})nn)</td>
<td>0.097</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>Cayley Tree</td>
<td>1/(z − 1)</td>
<td>1/(z − 1)</td>
<td></td>
</tr>
</tbody>
</table>

Universal Scaling of Static Properties

<table>
<thead>
<tr>
<th>Prob of being in (\infty) cluster</th>
<th>Gel fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_\infty \sim (p - p_c)^\beta)</td>
<td>(f_g \propto</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Correlation length</th>
<th>Typical cluster size</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\xi \sim</td>
<td>p - p_c</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mean n. sites (mass) cluster</th>
<th>Weight ave mol weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S \sim</td>
<td>p - p_c</td>
</tr>
</tbody>
</table>

Other examples: magnetization, vapor-liquid critical point
Dynamic scaling at the gel point

\[ G(t) = St^{-n} \quad \text{for} \quad \lambda_0 < t < \infty \]

\[ \lambda_{\text{max}} \propto \begin{cases} (p_c - p)^{-\alpha_-} & \text{for sol, } p < p_c \\ (p - p_c)^{-\alpha_+} & \text{for gel, } p > p_c \end{cases} \]

The exponents are not independent:

\[ n = \frac{z}{z + s} \]

\[ \alpha = s + z, \]

\[ s = (1 - n)\alpha; \quad z = n\alpha \]

BUT values are NOT UNIVERSAL (no unique results for each theory)

Winter and Mours, 1997, Adv Polymer Sci, 134
Additional scaling: *dynamic exponent* $\kappa$

\[
\left( \frac{1}{G'} \frac{\partial G'}{\partial p} \right)_{\omega} \propto \left( \frac{1}{G''} \frac{\partial G''}{\partial p} \right)_{\omega} \propto \omega^{-\kappa} \quad \text{for } p \text{ near } p_c
\]
Colloidal aggregates as fractals

Confocal images of opaque PAAm gel reveal self-similarity

\[ M(bL) = b^{df} M(L) \]

\(df\) (or \(D, Df,\) etc.) is the fractal dimension, integer only for “regular” Euclidean spaces.

Fractals and Percolation, Figure 8
2D Sierpinski gasket. Generation and self-similarity

Fractals and Percolation, Figure 9
Lattice composed of Sierpinski gasket cells of size \(\xi\)

Strelniker, Havlin, Bunde, 2008
Tokita, 2016, Gels, 2(2)
Today focus far from gelation threshold

“Far” from gelation, percolation scaling does no longer hold.

- Gel made of closely packed blobs/flocs that are fractal
- Fractal dimension ($D$) depends on aggregation kinetics (e.g., DLA: diffusion limited aggregation $D \approx 1.8$, RLA: reaction limited aggregation $D \approx 2$)

\[ \phi = \frac{\text{number of sites occupied by particles}}{\text{total number of sites taken by floc}} \approx \frac{(\xi/a)^D}{(\xi/a)^d} \approx \left( \frac{\xi}{a} \right)^{(D-d)} \]

\[ \xi \sim \phi^{1/(D-d)} = \frac{1}{\phi^{(d-D)}} \]

a: dimension of particles
d: Euclidean dimension

De Gennes, 1979, *Scaling concepts in polymer physics*


Inter- and intra-flocs links as springs

- inter-flock links, treated as: \( K_l \)
- backbone that sustain the stress, modeled as: (intra-floc links) 

The backbone has its own fractal dimension:
\[ x < D \]
\[ N_{bb} \sim \xi^x \]

It is possible to combine the single springs to obtain an estimate of overall elastic constant of the floc.
Elastic constant of a linear chain of springs

Elastic energy of the chain:

\[ H = \frac{G}{2} \sum_{i=1}^{N} \delta \phi_i^2 + \frac{Q}{2a^2} \sum_{i=1}^{N} \delta b_i^2. \]

- change in the angle between two bonds
- change in length of bonds

\( G \) and \( Q \) are “local elastic constants” (there is an extra length squared in the dimension though!)

Minimization of functional:

\[ W = H - \vec{F} \cdot (\vec{R}_N' - \vec{R}_N) \]

Leads to expression for changes in angles and bonds length that can be substituted into the elastic energy

\[ H = \frac{F^2 N S_1}{2G} + \frac{F^2 a L_1}{2Q}. \]

Which yields the expression of elastic constant (when elongation is negligible):

\[ k = \frac{G}{NS_1^2} \]

\[ \vec{F} \cdot (\vec{R}_N' - \vec{R}_N) \]

displacement due to elongation

\[ = (\vec{F} \times \vec{z}) \cdot \sum_{i=1}^{N} \delta \phi_i \sum_{j>i}^{N} \vec{b}_j + \frac{\vec{F}}{a} \cdot \sum_{i=1}^{N} \vec{b}_i \delta b_i, \]

displacement due to rotation in the plane with arm given by distance to the end point \( N \) (plus use of identity for scalar triple product...)

Kantor and Webman, 1984, PRL, 52(21)
Elastic constant of one floc...

Shih et. al, 1990, Phys Rev A, 42(8)

- backbone bonds singly connected (red bonds)
- backbone bonds multiply connected

Inter-flock links, treated as: $K_l$

Backbone that sustain the stress, modeled as: (intra-floc links)

The backbone has its own fractal dimension:

$x < D$

$N_{bb} \sim \xi^x$

It is possible to combine the single springs to obtain an estimate of overall elastic constant of the floc

$k = G/NS_1^2$

$K_\xi = \frac{K_0}{N_{bb}\xi^2} \sim \frac{K_0}{\xi(x+2)}$
...and elastic constant at scale $L$

If we linearly scale up the system to $L$:

$$K \sim \left( \frac{L}{\xi} \right)^{d-2} K_\xi$$

Similar to connection between resistivity and resistance of a conductor:

$$R = \rho \frac{l}{A} = \rho \frac{L}{L^{d-1}} = \rho L^{2-d}$$

Since the resistivity is independent of $L$:

$$R \sim L^{2-d}$$

Which means that the conductance:

(analogous of elastic constant)

$$G = \frac{1}{R} \sim L^{d-2}$$

If we apply this argument to the elastic constant:

$$K \sim L^{d-2} \quad K_\xi \sim \xi^{d-2}$$

And the ratio gives us the formula above
Strong- and weak-link regimes

**Strong-link regime**
- Strong interflloc links/springs
- Weak backbone links/springs

**Weak-link regime**
- Weak interflloc links/springs
- Strong backbone links/springs
Strong- and weak-link regimes: elastic constant

**Strong-link regime**
- Strong interflloc links/springs
- Weak backbone links/springs

\[ K \sim \left( \frac{L}{\xi} \right)^{d-2} K_\xi \]

\[ K \sim \varphi^{(d+x)/(d-D)} \]

\[ \xi \sim \varphi^{1/(D-d)} \]

**Weak-link regime**
- Weak interflloc links/springs
- Strong backbone links/springs

\[ K \sim \left( \frac{L}{\xi} \right)^{d-2} K_\ell \]

\[ K \sim \varphi^{(d-2)/(d-D)} \]

*In the strong-link regime the elastic constant grows more rapidly with volume fraction*
Strong- and weak-link regimes: limit of linearity

**Strong-link regime**
- Strong interflloc links/springs
- Weak backbone links/springs

**Weak-link regime**
- Weak interflloc links/springs
- Strong backbone links/springs

\[ F_\xi = K_\xi (\Delta L)_\xi = \frac{K_0}{\xi^{2+x}} \frac{\Delta L}{L/\xi} \]

\[ (\Delta L)_\xi \sim \frac{\Delta L}{L} \xi \]

\[ \gamma_0 = \frac{\Delta L}{L} \sim \xi^{1+x} \sim \varphi^{-(1+x)/(d-D)} \]

\[ F_\xi = K_\ell (\Delta L)_\xi \sim \xi \]

\[ \gamma_0 \sim \xi^{-1} \sim \varphi^{1/(d-D)} \]

*In the strong-link regime the limit of linearity decreases with vol fraction!*
Experimental results on boehmite alumina powders

\[ G'_0 \sim \begin{cases} \varphi^{4.1} & \text{for Catapal gels} \\ \varphi^{4.2} & \text{for Dispal gels} \end{cases} \]

\[ \gamma_0 \sim \begin{cases} \varphi^{-2.1} & \text{for Catapal gels} \\ \varphi^{-2.3} & \text{for Dispal gels} \end{cases} \]

- **Storage modulus** $G'_0$ vs. particle volume fraction $\phi$:
  - Slope $\sim 4.1$

- **Light scattering** $I(q)$ vs. $q$ (\(10^{-3} \text{ Å}^{-1}\)):
  - Slope $\sim -2.04$
Elasticity and yielding of a calcite paste: scaling laws in a dense colloidal suspension

Teresa Liberto, Marie Le Merrer, Catherine Barentin, Maurizio Bellotto and Jean Colombani

Elasticity and yielding of calcite paste:

Rheology of gel networks
combining experimental, computational and theoretical insights
Lyon, France, 21-23 June 2017