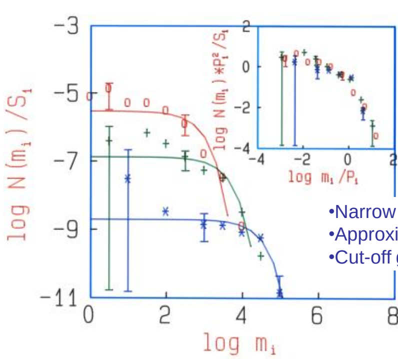
Time evolution: Smoluchowski Equations

$$\frac{dN(m_i)}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} K_{j,i-j} N(m_j) N(m_{i-j}) - \sum_{j=1}^{\infty} K_{i,j} N(m_i) N(m_j),$$

Scaling solutions

Cluster mass distribution

Diffusion-limited aggregation



- Narrow distribution
- Approximately constant
- Cut-off grows in time

Cluster mass distribution

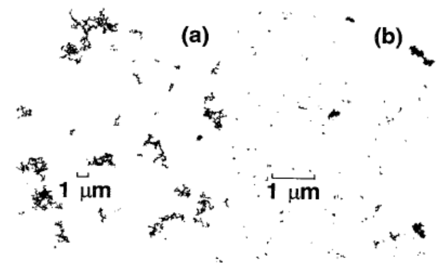
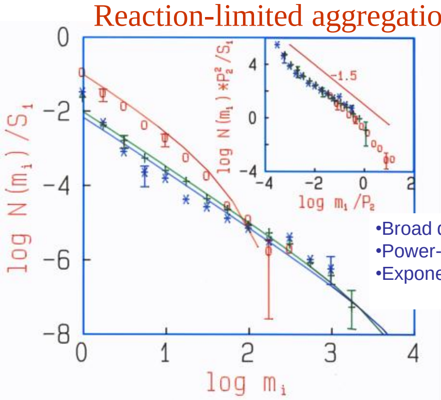


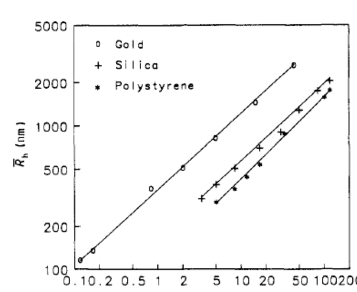
FIG. 1. Typical TEM images of clusters formed by (a) diffusion-limited aggregation and (b) reaction-limited aggregation. The aggregate's fractal dimensions and the cluster-mass distributions are clearly different for the two regimes.

Reaction-limited aggregation



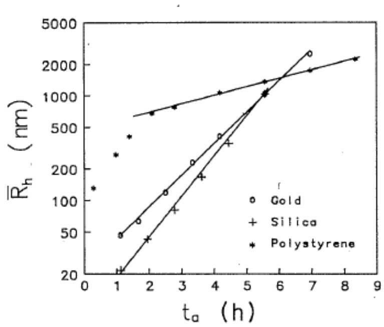
- Broad distribution
- Power-lay
- Exponential growth in time

Diffusion-limited aggregation



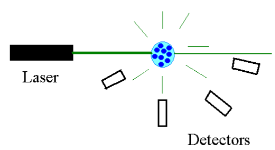
Linear growth in time

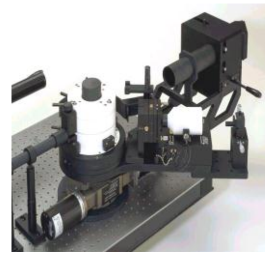
Reaction-limited aggregation



Exponential growth in time

Light Scattering





Static Scattering: Structure

Scattered field from single particle

$$E_m(q) = A_m e^{i\vec{q}\cdot\vec{r}_m} e^{-i\omega t}$$

Scattered intensity per particle — Phase factor — Frequency of light

Measure the scattered intensity from collection of particles

$$I(q) = \sum_{m,n} E_m E_n^* = \sum_{m,n} A_m A_n e^{i\vec{q}\cdot(\vec{r}_m - \vec{r}_n)} = P(q) S(q)$$

Form factor — Structure factor

•Measure *q* dependence of scattering
•Probes spatial Fourier Transform of density correlations

Scattering from fractals

$$I(q) \simeq N_q(R_q)\, m_q^2$$

$$= \frac{M_T}{m_q} m_q^2$$

$$\simeq M_T\, m_q$$

$$\simeq M_T\, R_q^{d_f}$$

$$= \frac{M_T}{q^{d_f}}$$

$$N(R_q) = \frac{M_T}{M_q}$$

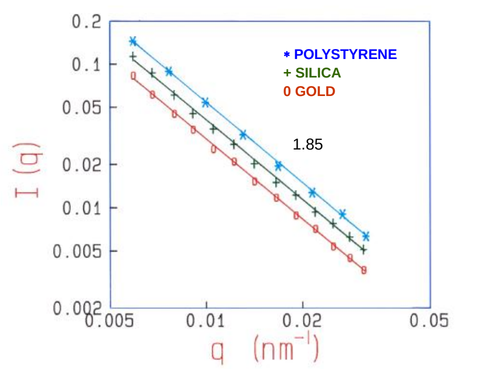
MASS CORRELATIONS:

$$I(q) = \sum_M N(M) I_M(q)$$

$$I_M(q) = A M^2 S(qR_g).$$

$$S(qR_g) = \begin{cases} 1 & \text{for } qR_g \ll 1 \\ (qR_g)^{-d_f} & \text{for } qR_g \gg 1. \end{cases}$$

DIFFUSION-LIMITED COLLOID AGGREGATION

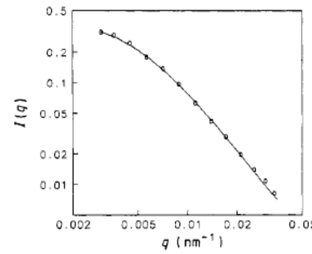


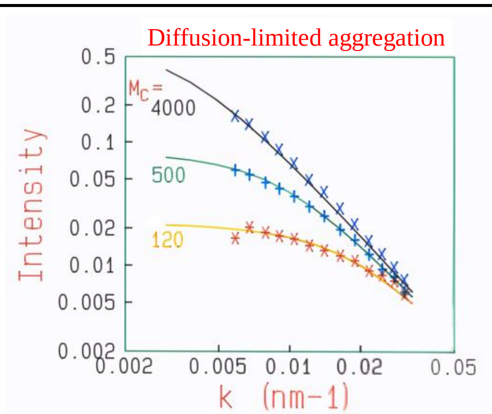
Fisher-Burford

$$S(qR_g) = \left(1 + \frac{1}{3}\frac{2}{d_f}(qR_g)^2\right)^{-d_f/2}$$

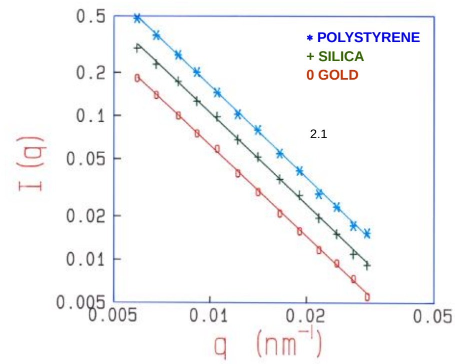
$$qR_g \ll 1 : \quad S(qR_g) = 1 - \frac{1}{3}(qR_g)^2$$

$$qR_g \gg 1 : \quad S(qR_g) \sim (qR_g)^{-d_f}$$

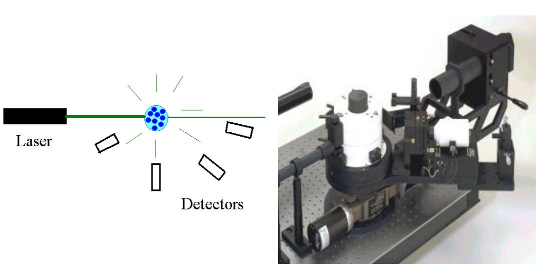




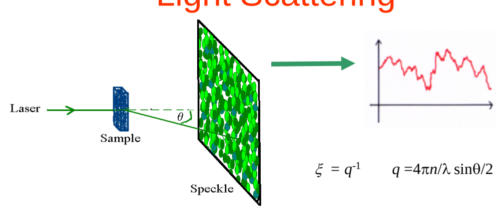
REACTION-LIMITED COLLOID AGGREGATION



Dynamic Light Scattering



Structure and Dyanmics: Light Scattering

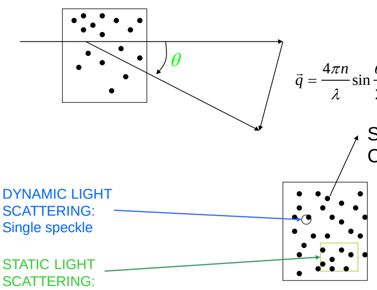


$\xi = q^{-1}$ $\quad q = 4\pi n/\lambda \sin\theta/2$

- SLS: $< I >$ vs. q ⟶ probe structure
- DLS: $< I(q,t)I(q,t+\tau) >$ ⟶ probe dynamics $f(q,\tau)$

Light Scattering

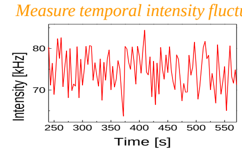
Probes characteristic sizes of colloidal particles



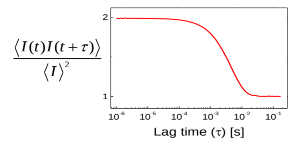
$$\vec{q} = \frac{4\pi n}{\lambda}\sin\frac{\theta}{2}$$

Dynamic Light Scattering

Measure temporal intensity fluctuations



Obtain an intensity autocorrelation function



Dynamic Light Scattering

Measure temporal correlation function of scattered light:
Intermediate structure factor

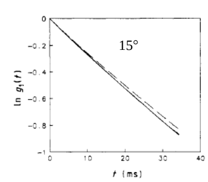
$$f(q,t) \sim \langle E(0)E(t)\rangle$$

$$\langle E(0)E(t)\rangle = \left\langle A^2 \sum_{m,n} e^{i\vec{q}\cdot\{\vec{r}_m(0)-\vec{r}_n(t)\}} \right\rangle$$ Time average over all particles

$$\sim e^{-q^2\langle \Delta r^2(t)\rangle}$$ Correlations only between the same particles
Cumulant expansion: $\Delta r^2(t) \sim Dt$

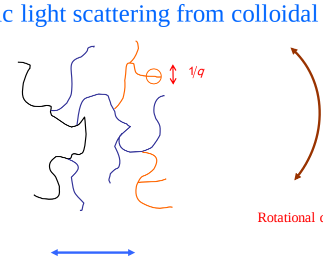
$$\sim e^{-q^2 Dt}$$ Physics: How to change the phase of the field by π
Each particle must move by $\sim\lambda$

Dynamic light scattering from colloidal clusters



Small angle → don't resolve internal motion

Dynamic light scattering from colloidal cluster



$$S(k,t) = \sum_l S_l(k) e^{-Dk^2 t}$$

Dynamic light scattering from colloidal cluster

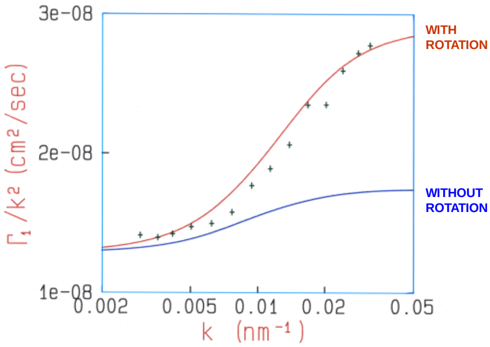
$$S(k,t) = \sum_l S_l(k) e^{-Dk^2 t} e^{-l(l+1)\Theta t} \, .$$

$$g_1(t) = \frac{1}{I(q)} \sum_M N(M) M^2 \exp(-q^2 Dt) \sum_{l=0}^{\infty} S_l(qR_g) \exp[-l(l+1)\Theta t].$$

$$g_1(t) = \frac{1}{I(q)} \sum_M N(M) M^2 S(qR_g) \exp(-q^2 D_{\text{eff}} t) \, .$$

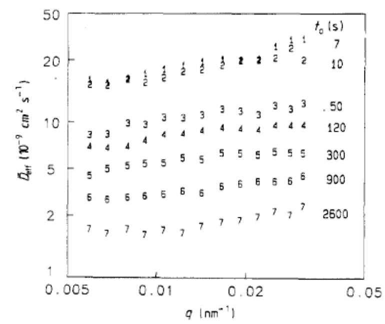
$$\bar{D}_{\text{eff}} = \frac{\sum_M N(M) M^2 S(qR_g) D_{\text{eff}}}{\sum_M N(M) M^2 S(qR_g)} \, .$$

Diffusion-limited colloid aggregation

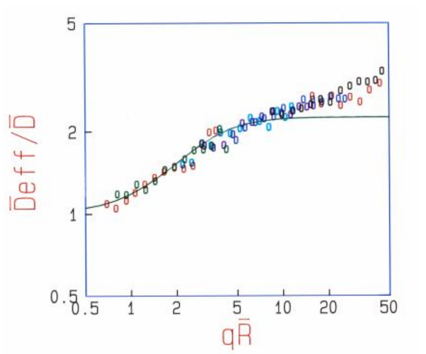


Dynamic light scattering from colloidal clusters

Time evolution

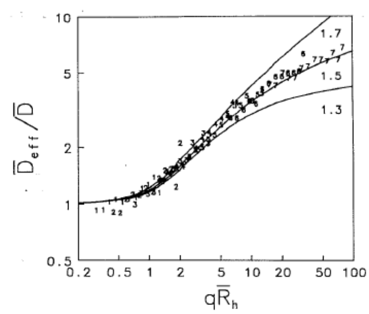


Diffusion-limited colloid aggregation



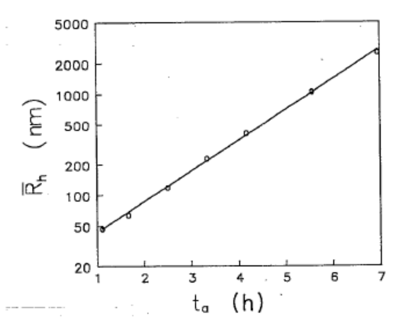
Effective diffusion coefficients for colloidal clusters

Power-law distribution

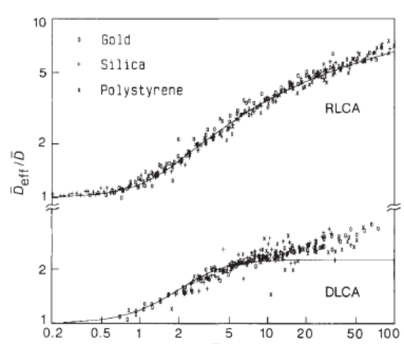


Dynamic light scattering from colloidal clusters

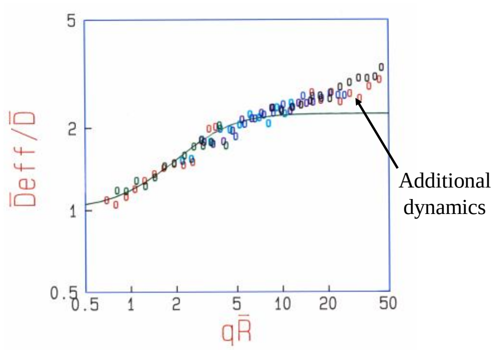
Time evolution → Exponential growth



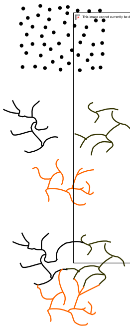
Universal Behavio



Diffusion-limited colloid aggregation



DIFFUSION-LIMITED GELATION



MASS	NUMBER	VOLUME FRACTION
M_0	N_0	Φ_0

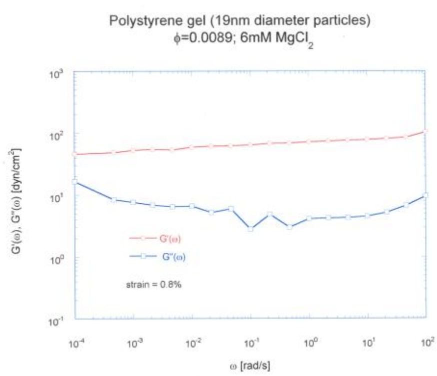
$$M_c \simeq \left(\frac{R_c}{a}\right)^{d_f}$$

$$N_c = \frac{N_o}{M_c} = N_0\left(\frac{R_c}{a}\right)^{-d_f}$$

$$\phi_c = \frac{V_c}{V} N_c = \frac{R_c^3}{V} N_0 \left(\frac{R_c}{a}\right)^{-d_f} = \phi_0 \left(\frac{R_c}{a}\right)^{3-d_f}$$

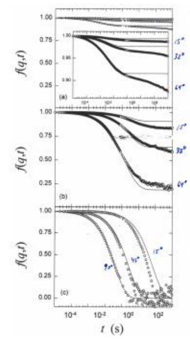
$$\phi_g = \phi_c = 1$$

$$R_c = a\phi_0^{1/3-d_f} \sim \phi.$$



DYNAMIC LIGHT SCATTERING FROM COLLOIDAL GEL

BOUYANCY-MATCHED POLYSTYRENE ***a* = 9.5 nm**



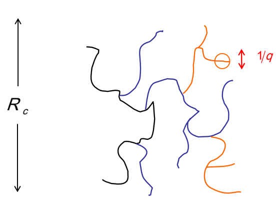
ϕ_0

5.0×10^{-3}

1.5×10^{-3}

1.7×10^{-4}

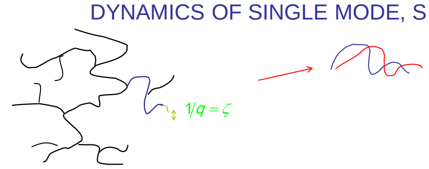
DYNAMICS OF A FRACTAL COLLOIDAL GEL



- CONSIDER BLOB OF SIZE $1/q = R_q$
- MOTION DUE TO FLUCTUATIONS OF ALL OTHER CONNECTED BLOBS
  - INDEPENDENT MODES
  - OVERDAMPED

LARGER BLOBS: LARGER DISPLACEMENT
SLOWER TIMESCALES

DYNAMICS OF SINGLE MODE, S



CONSTRAINED BROWNIAN MOTION $\left\langle \Delta r_\zeta^2(t) \right\rangle_s = \frac{kT}{k(s)n(s)}\left[1 - e^{-t/\tau(s)}\right]$

1. SPRING CONSTANT: SIZE DEPENDENT

$$k(s) = k_0\left(\frac{s}{a}\right)^{-\beta}$$

SINGLE PARTICLE SPRING CONSTANT

KANTOR-WEBMAN
$\beta = 2 + d_B$ → "BOND" DIMENSION

2. TIME CONSTANT: VISCOUS DAMPING

$$\tau(s) = \frac{6\pi\eta s}{k(s)}$$

3. MAXIMUM AMPLITUDE:

$$\delta_m^2 = \frac{kT}{k(s)n(s)}$$

kT / NORMAL MODE
n(s): DENSITY OF LOCAL MODES

$$n(s) = N_c\left(\frac{a}{s}\right)^{d_f}$$

DISPLACEMENT OF REGION OF SIZE $\xi = \frac{1}{q}$

- SUM CONTRIBUTIONS OF ALL SIZES, S $\frac{dn(s)}{ds}$
- USE DENSITY OF MODES

$$\left\langle \Delta r_\xi^2(t) \right\rangle = 2d_f kt \int_\xi^{R_c} \frac{ds}{sk(s)} \left[1 - e^{-t/\tau(s)}\right]$$

- CAN BE DONE ANALYTICALLY
- FUNCTIONAL FORM IS:

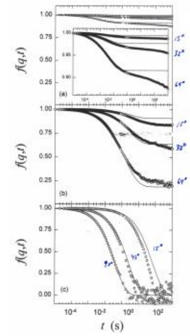
$$\boxed{\left\langle \Delta r_\xi^2(t) \right\rangle = \delta^2 \left[1 - e^{-(t/\tau)^P}\right]}$$

→INITIAL DECAY: STRETCHED EXPONENTIAL
→DECAYS TO A PLATEAU: δ^2

$$f(q,t) = \exp\left\{-q^2 \langle \Delta r^2_{\xi=\frac{1}{q}}(t) \rangle\right\}$$

DYNAMIC LIGHT SCATTERING FROM COLLOIDAL GEL

BOUYANCY-MATCHED POLYSTYRENE ***a = 9.5 nm***



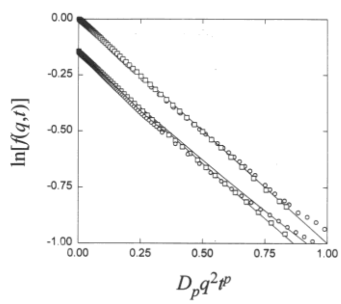
ϕ_0

5.0×10^{-3}

1.5×10^{-3}

1.7×10^{-4}

SCALING STRETCHED EXPONENTIAL



$P = 0.66$

ELASTIC MODULUS OF GEL

DETERMINED DIRECTLY BY δ^2
↳ SET BY AVERAGE CLUSTER SIZE

ϕ_0 DEPENDENCE

$\sim \delta^2 \rightarrow \delta^2 k(R_c) \simeq kT$

$$G(\phi_0) = \frac{k(R_c)}{R_c} = k_0 a^\beta R_c^{-1-\beta}$$

$$\Rightarrow \frac{\delta^2}{R_c} \sim \tau$$

BUT $R_c \sim \phi_0^{\frac{1}{d_f - 3}}$

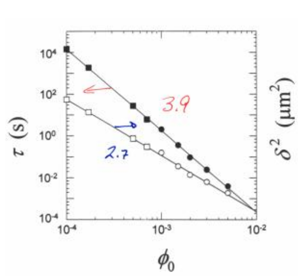
$$G(\phi_0) \sim \phi_0^{\frac{-(1+\beta)}{d_f - 3}} \sim \phi_0^{3.7}$$

EXPERIMENT: 3.9

→ MEASURE MODULUS OPTICALLY!

VOLUME FRACTION DEPENDENCE

LIGHT SCATTERING PROBE OF MODULUS



$G \simeq \frac{k_c}{R_c}$

BUT $\tau_c \sim \frac{R_c}{k_c}$

$G \sim \phi^{3.9}$

R_c ONLY LENGTH IN PROBLEM

Foams & Emulsions

EMULSION: UNUSUAL SOLID

- MADE COMPLETELY FROM FLUIDS
- MUST BE "HELD TOGETHER" BY OSMOTIC PRESSURE
  - → PURELY REPULSIVE INTERACTION BETWEEN SPHERES
  - → NO FRICTION
  - → "PACKING"

QUESTIONS:

WHAT IS OSMOTIC PRESSURE?

WHAT IS ELASTIC MODULUS?

SCALE SET BY $\frac{\gamma}{a} \sim 10^4\,\mathrm{Pa}$

vs. $\frac{kT}{a^3} \sim 10^{-3}\,\mathrm{Pa}$

FOR $1\ \mu m$ drop

"PHASE BEHAVIOR"

UNIFORM SPHERES IN A FLUID → DISORDERED

→EQUATION OF STATE

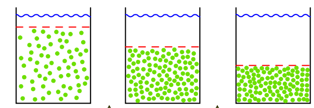
OSMOTIC PRESSURE Π vs ϕ DROPLET VOLUME FRACTION

ENTROPIC

$nk_BT \sim \leq 10^{-1}$ dynes/cm^2

SURFACE TENSION

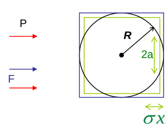
$\frac{\sigma}{R} \sim 10^5$ dynes/cm^2

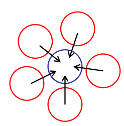


$\phi < 0.58$ $\phi > 0.63$

→ SPHERES MUST DEFORM

OSMOTIC PRESSURE





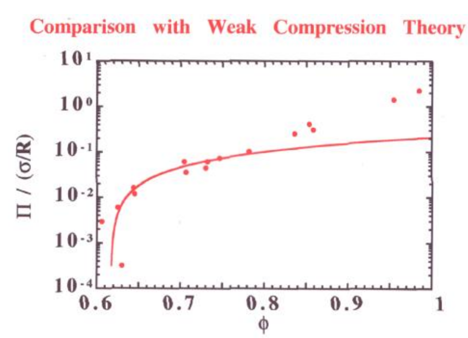
$$R^2 = a^2 + (R - \delta x)^2$$

$$a^2 \simeq R\delta x$$

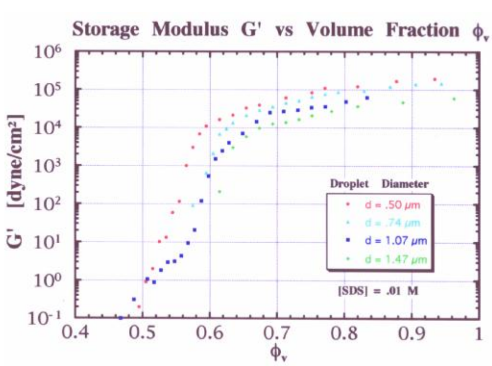
$$\Delta v \sim R^2 \delta x$$ ← HARMONIC SPRING

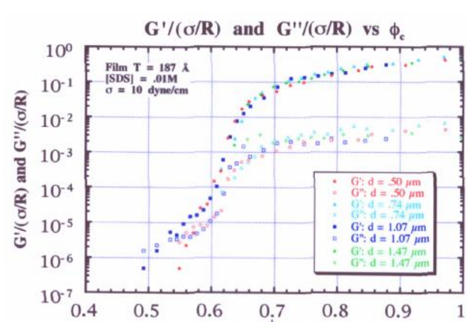
$$\Pi \simeq \frac{\sigma}{R}\frac{a^2}{R^2} \simeq \frac{\sigma}{R}\frac{R\delta x}{R^2}$$

$$\boxed{\Pi \simeq \frac{\sigma}{R}\frac{\Delta v}{v} \simeq \frac{\sigma}{R}(\phi - \phi_c)}$$



T.G. Mason and D.A. Weitz, *Phys. Rev. Lett.*, **75**, 2051-2054 (1995)





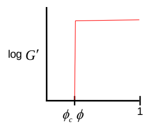
BEHAVIOR AT LOW ϕ

OSMOTIC PRESSURE: $\Pi \sim \frac{\sigma}{R}(\phi - \phi_c)$

- LINEAR IN VOLUME CHANGE
- LINEAR IN DEFORMATION

MODULUS $G' \sim \phi \frac{d\Pi}{d\phi} \sim \frac{\sigma}{R}\phi(\phi > \phi_c)$

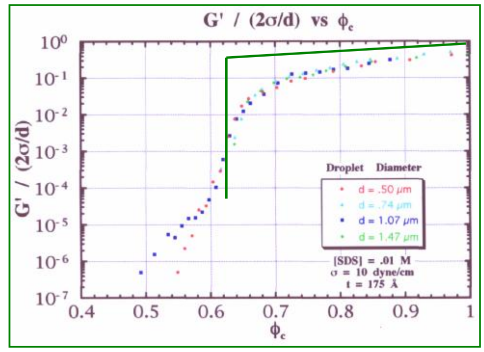
- WEAK DEPENDENCE ON ϕ
- AT ϕ_c: INCREASE VERY SUDDENLY



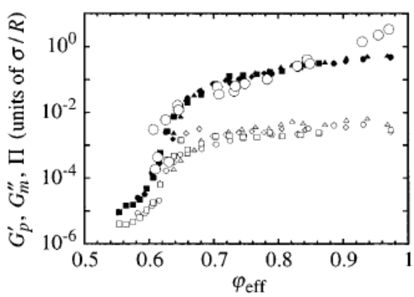
BEHAVIOR LIKE HARMONIC OSCILLATOR (SPRING)

G' → LIKE SPRING CONST
MAGNITUDE IS INDEPENDENT OF DEFORMATION

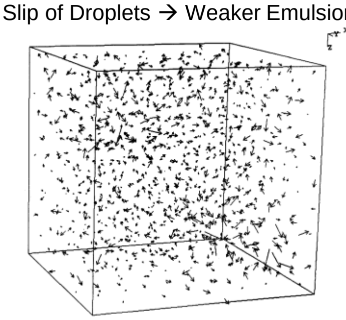
Predicted Behavior for Modulus



Osmotic pressure is equal to shear modulus



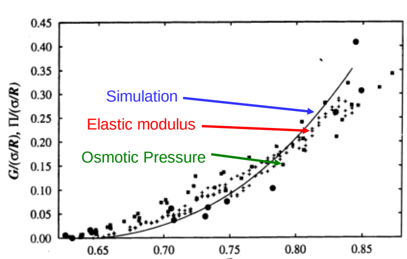
Computer Simulation:
Shows Droplet Motion in not Affine
Slip of Droplets → Weaker Emulsion



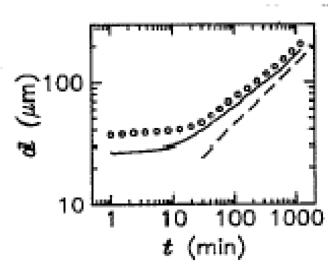
M.-D. LaCasse *et al*, *Phys. Rev. Lett.*, **76**, 3448-3451 (1996)

Comparison of
Computer Simulation, Elastic Modulus, Osmotic Pressure

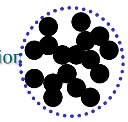
Osmotic Pressure = Elastic Modulus



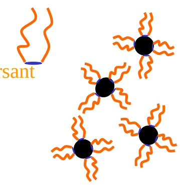
Evolution of Bubble Size in Foam



Carbon Black in Oil



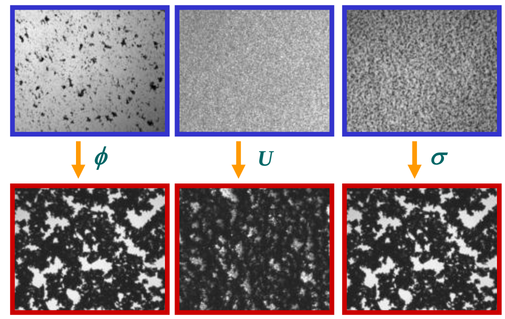
Problem:
- Large Effective Particle Volume Fraction
- Due to aggregate formation
- Difficult to control viscosity



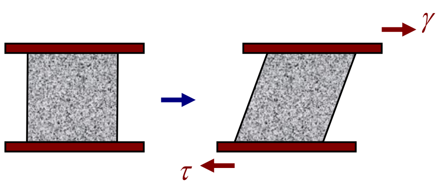
Solution:
- Add additive package – primarily dispersant
- Disperse soot particles

Gelation of Attractive Particles

Carbon Black in Oil



Viscoelasticity of Soft Materials



Solid: $\tau = G\gamma$

Fluid: $\tau = \eta\dot{\gamma}$

$$\gamma = \gamma_0 e^{i\omega t} \longrightarrow \tau = \left[G'(\omega) + iG''(\omega)\right]\gamma$$

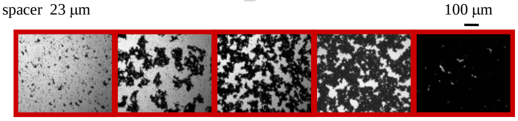
Elastic　　Viscous

Effect of Volume Fraction

Carbon Black in S150N

U ~ 10 ± 2 kT　25°C

spacer 23 µm　　100 µm



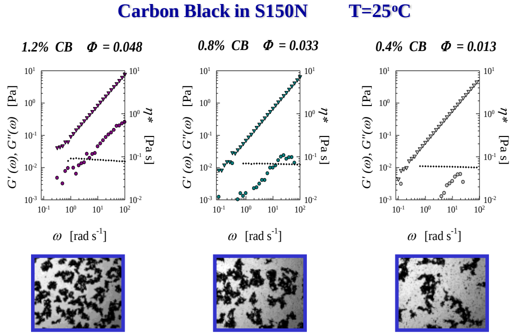
Φ %

0.3	3.3	6.4	9.7	14.9
0.1	0.8	1.6	2.5	4.0

w %

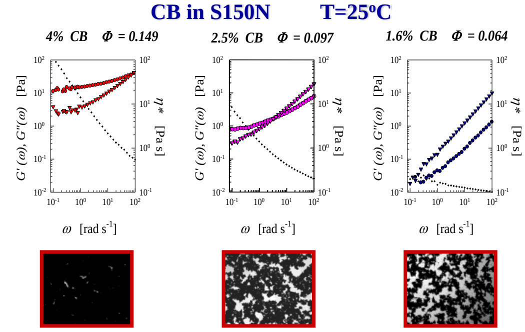
Fluid-Like Behavior

Carbon Black in S150N　　T=25°C

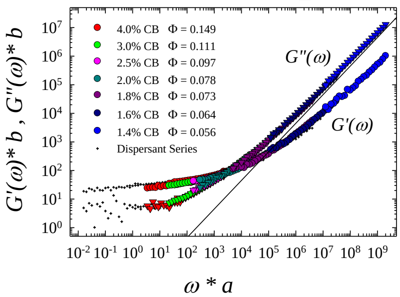


Solid-Like Behavior

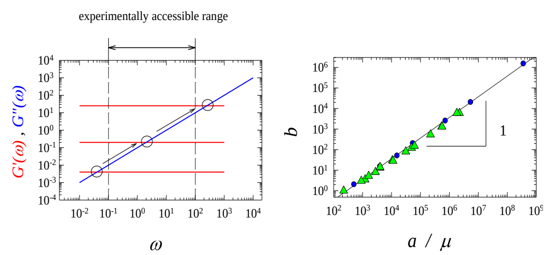
CB in S150N　　T=25°C



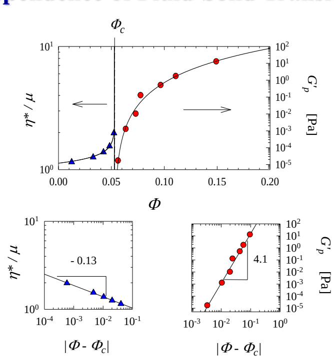
Scaling
ϕ-Dependence
Carbon Black in S150N U ~ 10 ± 2 kT 25°C



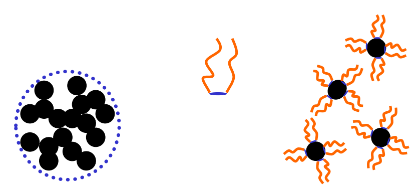
Scaling along the background-viscosity



ϕ-Dependence of Fluid-Solid Transition

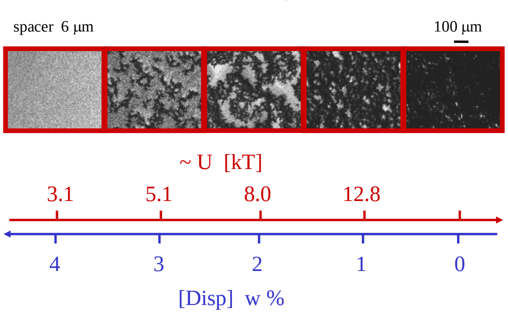


Effect of Dispersant
Decrease Interaction Energy
Decrease Aggregation

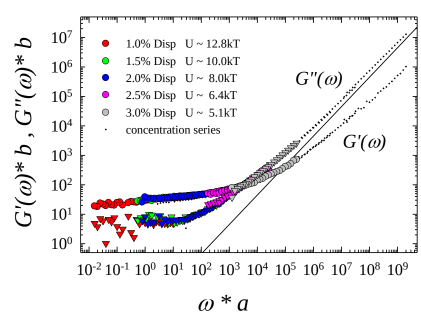


Amount of Dispersant controls Interaction Energy

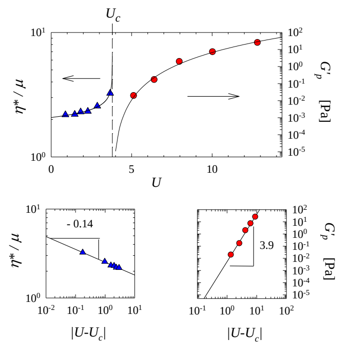
Effect of Dispersant Concentration
Carbon Black in Oil ϕ = 0.14 100°C



Scaling: *U-Dependence*
Carbon Black in S150N ϕ ~ 0.14 *T*=25°C

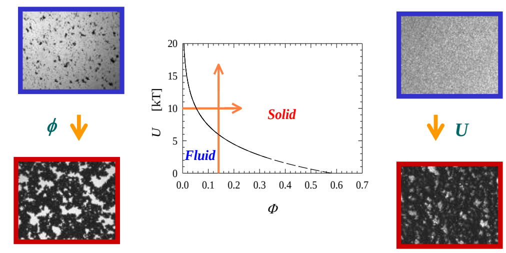


Fluid-Solid Transition *U*-Dependence



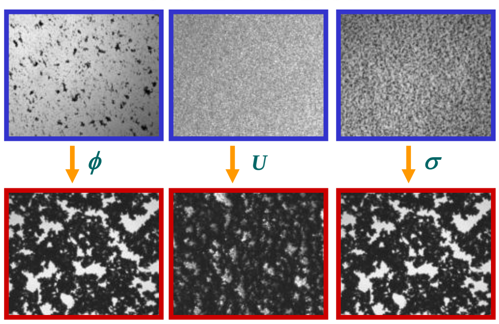
Fluid-Solid Transition

Weakly Attractive Systems

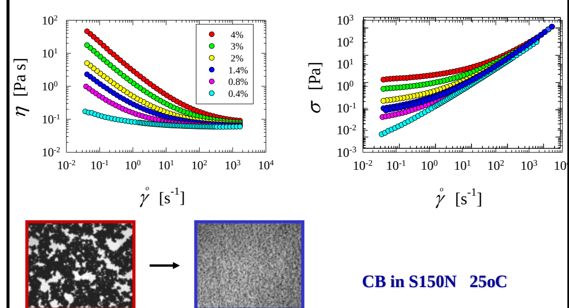


Fluid-Solid Transitions

Carbon Black in Oil

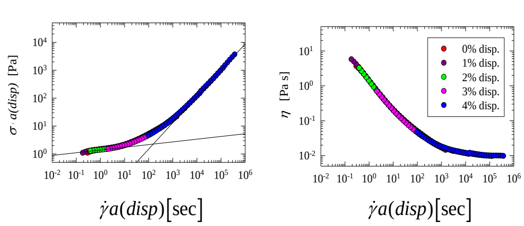


Fluidization through Shear

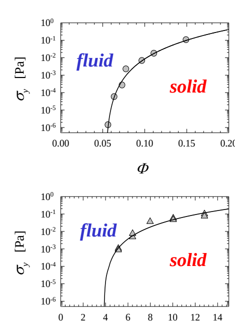


CB in S150N 25oC

Dispersant-Shear Equivalence



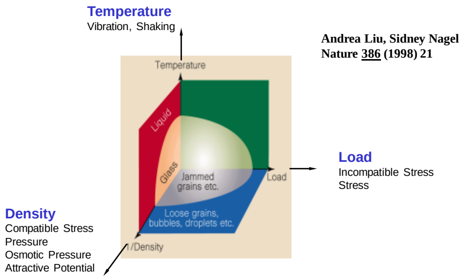
Shear Induced Fluid-Solid-Transition



$\sigma_y = \sigma_\Phi\,(\Phi-\Phi_c)^{3.4}$

$\sigma_y = \sigma_u\,(U-U_c)^{2.4}$

Jamming Transition – Arrest of Motion



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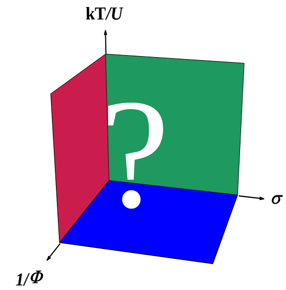
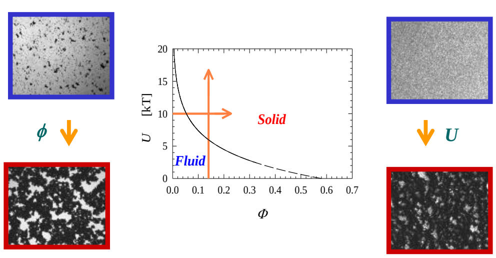
Jamming Transitions for Colloidal Systems with Attractive Interactions

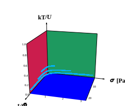


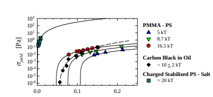
Phase Boundary in U-ϕ Plane



Yield Stress as Phase Boundary

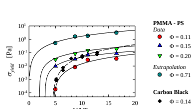
$\sigma_y = \sigma_o (\phi - \phi_c)^{\mu}$

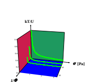




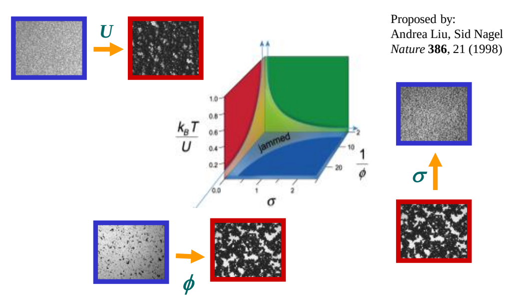
Phase Boundary in $U - \sigma$ Plane
ϕ = const.

$\sigma_y = \sigma_o (U - U_c)^{\nu}$





Jamming Phase Diagram for Attractive Systems



Proposed by:
Andrea Liu, Sid Nagel
Nature **386**, 21 (1998)

Completely new way to look at viscosity of soot in oil