

## Introduction to Colloid Physics

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Boulder Summer School  
Soft Matter Physics

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## Dispersed particles

- Dispersed system
  - Particles in continuous fluid phase

Dispersed Particle	Dispersion
Solid	Colloid
Fluid	Emulsion
Gas	Foam

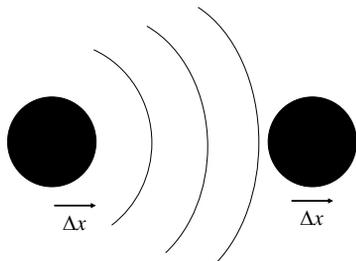
## Colloidal particles

- Colloidal particles are ubiquitous
- Biology
  - Viruses, macromolecules, organelles
  - Probe particles for bioassays
  - Quantum dots for fluorescent assays
  - Spores, bacteria
- Processing
  - Paints, coatings, materials control
  - Ceramics

## Colloidal particles

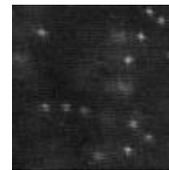
- Key  $\rightarrow$  control rheology
- Solid particles behave like continuous fluid
- Process solids, while flow like fluids
- *eg* Paints and coatings
  - Spread paint like a fluid
  - Solidify into a solid coating

## Continuous phase fluid



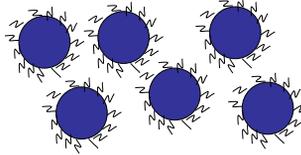
Hydrodynamic interactions

## Continuous phase fluid



- Thermalization with fluid
- Equilibrates particles
- Brownian motion

## Colloidal Particles

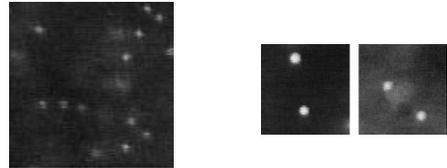


Stability:  
Short range repulsion  
Sometimes a slight charge

Colloid Particles are:

- Big
  - $a \sim 1$  micron
  - Can "see" them
- Slow
  - $\tau \sim a^2/D \sim$  ms to sec
  - Follow individual particle dynamics

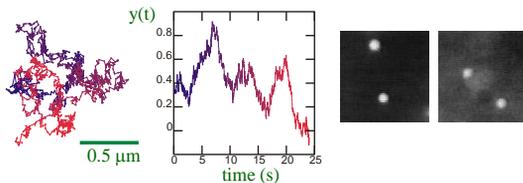
## Colloidal particles undergoing Brownian motion



Thermal motion ensures particles are  
always equilibrated with the fluid  
They can explore phase space

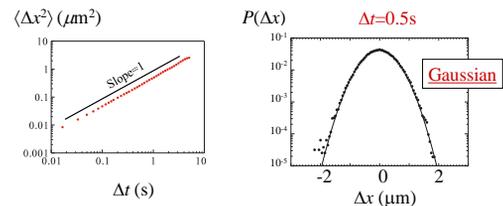
## Brownian Motion

(2  $\mu\text{m}$  particles, dilute sample)



## Diffusion

Mean square displacement: Displacement distribution function:



Leads to normal diffusion:  $\langle \Delta x^2 \rangle = 2Dt$   $D = \frac{k_B T}{6\pi\eta a}$  Particle size  $a$  viscosity  $\eta$

## Colloidal particles

- Ignore hydrodynamic interactions
  - Thermalize system
  - Important only for dynamics
  - No effect on static properties
- Consider just two-body interactions between particles

## Colloidal particles

- Properties set by particle density
- Concentration of particles low compared to normal material
- Typical solid:  $\sim 10^{27}$  atoms/  $\text{m}^3$  ( $1 / \text{nm}^3$ )
- Colloids:  $\sim 10^{18}$  particles/  $\text{m}^3$  ( $1 / \mu\text{m}^3$ )
- Latent heat of phase transitions too small to measure
- Very low pressure:  $\Pi = nk_B T$
- $\Pi \sim 4 \times 10^{-21} / 10^{-18} = 4 \times 10^{-3}$  Pa

## Soft Solids

Easily deformable → Low Elastic Constant:  $\frac{\text{Energy}}{\text{Volume}}$

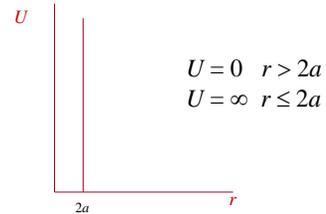
Hard Materials  $\frac{\text{eV}}{\text{\AA}^3}$  GPa

Soft Materials  $\frac{k_B T}{\mu\text{m}^3}$  1 Pa

Soft materials invariably have a larger length scale

## Colloidal Interactions

### Hard-sphere interactions



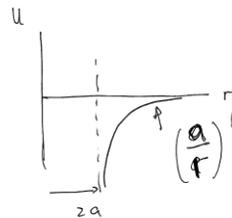
Only excluded volume

## Colloidal Interactions

- van der Waals interactions
- Dispersion interactions
  - Dipole-induced dipole interactions
- Depend on polarizability of material
  - Require different materials
  - Always present for particles in a fluid

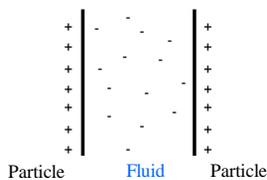
## van der Waals interactions

$$U_A = -\frac{A_{\text{pmp}}}{6} \left[ \frac{2a^2}{R^2 - 4a^2} + \frac{2a^2}{R^2} + \ln\left(\frac{R^2 - 4a^2}{R^2}\right) \right]$$



- Repulsive
- Short-ranged
- Dipole-dipole  $1/r^6$

## Stabilizing interactions



## Colloidal Interactions - Stabilization

- Screened Coulomb interaction

$$U_R = 2\pi\epsilon\psi_0^2 a(2a/R)\exp[-\kappa(R - 2a)]$$

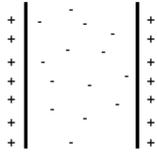
Surface potential

Inverse screening length

$$\kappa = (\epsilon k_B T / 2z^2 e^2 n_b)^{-1/2}$$

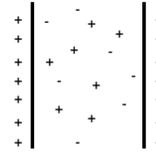
Ion density

### Stabilizing interactions



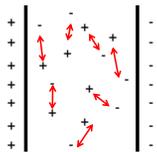
Disjoining pressure:  
Can't compress ions

### Destabilizing interactions



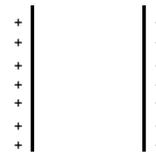
Disjoining pressure:  
Can't compress ions

### Destabilizing interactions



Counter ions can be neutralized

### Destabilizing interactions



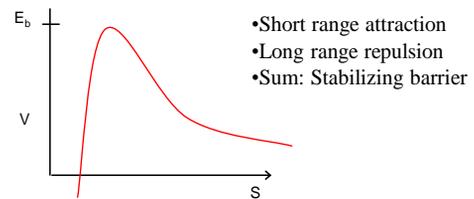
Counter ions escape

### Destabilizing interactions



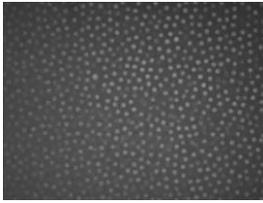
Attractive interaction  
Not symmetric with repulsive interaction

### Colloidal interactions – stabilizing



$E_b > k_B T \rightarrow$  Colloid stable against aggregation

### Repulsive Spheres

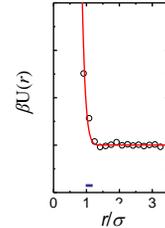


Repulsive interactions

### Repulsive Spheres

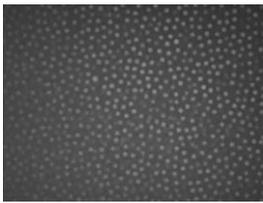
$$g(r) \propto \exp[-\beta u(r)] \quad \beta^{-1} \equiv k_B T$$

$$U = -k_B T \ln(g(r))$$

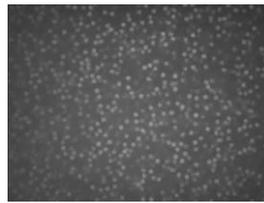


### Screen charges

No Salt



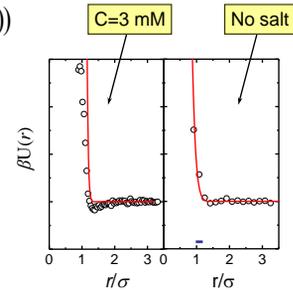
Salt



### Screen charges

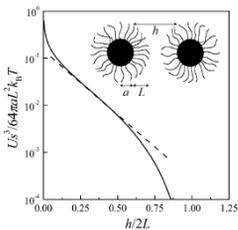
$$g(r) \propto \exp[-\beta u(r)]$$

$$U = -k_B T \ln(g(r))$$



### Steric Interactions

- Repulsive interaction
- Due to elasticity polymer brush
- Osmotic effect

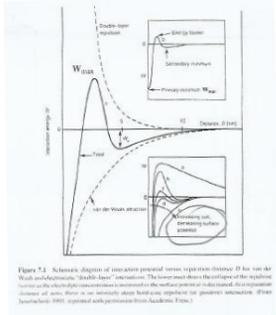


- Depends on thickness of brush
- Can be much less than  $a$
- Thin brush  $\rightarrow$  hard-sphere like

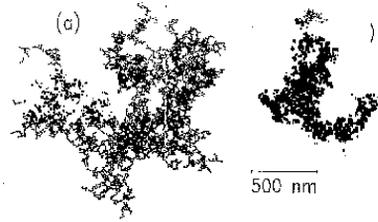
### Colloidal interactions – destabilizing

- Add electrolyte  $\rightarrow$  screen repulsion
- Reduce steric repulsion
- Always have van der Waals attraction
  - Colloids are inherently unstable
- Can also induce controlled attraction

## Colloidal Stability



## Colloidal Aggregation



Colloidal Gold

## COLLOIDAL GOLD

### TRADITIONAL COLLOID:

- FARADAY (1850's)
- ZSIGMONDY, SMOLUCHOWSKI (AGGREGATION)
- TURKEVITCH (TEM).
- MEDICAL, BIOPHYSICAL USES.
- SERS.

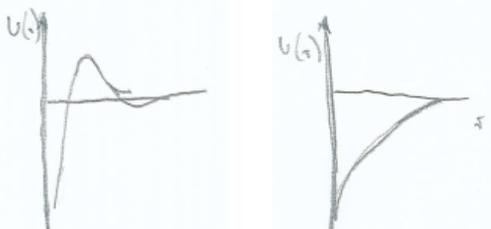
### PROPERTIES:

- OPTICAL ABSORPTION RESONANCE:  
WINE RED → BLUE (ON AGGREGATION)
- 75 Å RADIUS
- UNIFORM ( $\frac{\Delta\epsilon}{R} \sim 10\%$ )
- $\sim 10^{12} / cc \Rightarrow$  SEPARATION  $\sim 120$  RADII
- $D \sim 5 \times 10^{-7} cm^2 / sec$  (DIFFUSIVE MOTION)
- MASS  $\sim 10^{-17} gm \rightarrow \sim 10^{-18}$  U.S. \$
- 1 GAL. = 5¢ U.S. = PROFIT ON 1 GAL. GAS.

### AGGREGATION:

- STABILIZED BY CHARGED IONS ON SURFACE
- ADD NEUTRAL ORGANIC (PYRIDINE)
  - DISPLACE CHARGE
- FORM GOLD-GOLD BONDS,  $\gg kT$ 
  - IRREVERSIBLE
  - KINETIC
  - NON-EQUILIBRIUM

## Colloidal Stability



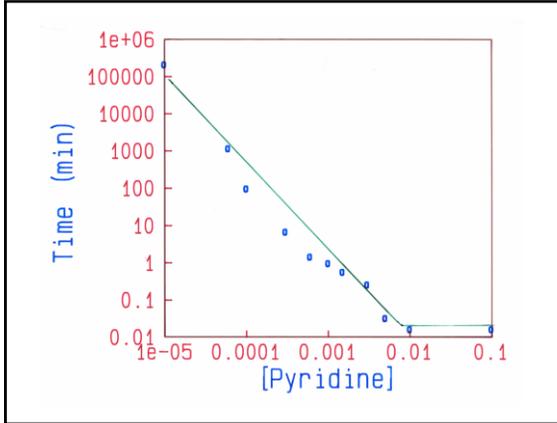
Partial Stability  
→ Many collisions to stick

No Stability  
→ Sticks every collision

## Effect of energy barrier

$$v \propto \exp \left\{ - \frac{U_{MAX}}{kT} \right\}$$

$$t_{U_{MAX}} \sim \frac{\tau^2}{D_0} \exp \left\{ - \frac{U_{MAX}}{kT} \right\}$$



**Dilute, stable suspension**

$$D = \frac{kT}{6\pi\eta R}$$

$R$   
 $\phi$

**Destabilize**

**Irreversible aggregation**

**Rate-limiting step: diffusion-induced collision**

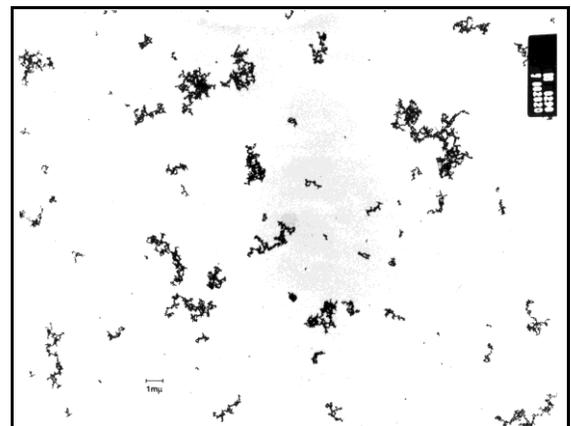
DIFFUSION-INDUCED COLLISIONS.  
HOW LONG DOES THIS TAKE?

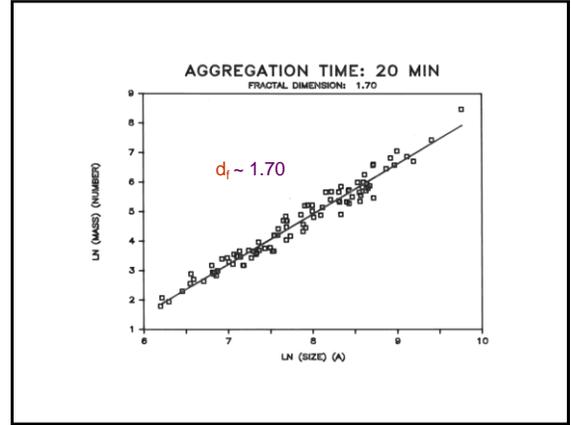
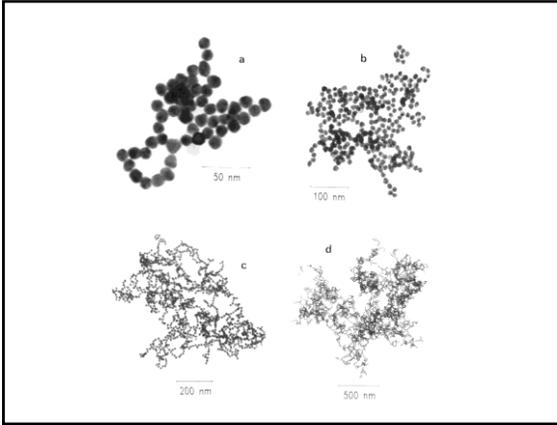
- DIFFUSION EQUATION
- SCALING

1.  $s \sim c^{-1/3}$   
 $\tau \sim \frac{s^2}{D} \sim \frac{1}{c^2 D}$  **WRONG!**

Volume:  $s a^2$   
contour length:  $s = \# \text{ steps} \times \text{step length}$   
 $= \left(\frac{R}{a}\right)^2 a$   
 $= \frac{R^2}{a}$

Volume:  $R^3 a$   
time:  $\frac{R^2}{D}$   
Volume/time =  $Da$   
Volume required =  $\frac{1}{c}$   
 $t = \frac{1}{c a D}$   
Rd:  $\tau^{-1} = c a D$





**FRACTAL:**

- SELF-SIMILAR
- NO CHARACTERISTIC LENGTH SCALE

$$M \sim R^{d_f}$$

$d_f$ : FRACTAL DIMENSION  
NON-INTEGRAL

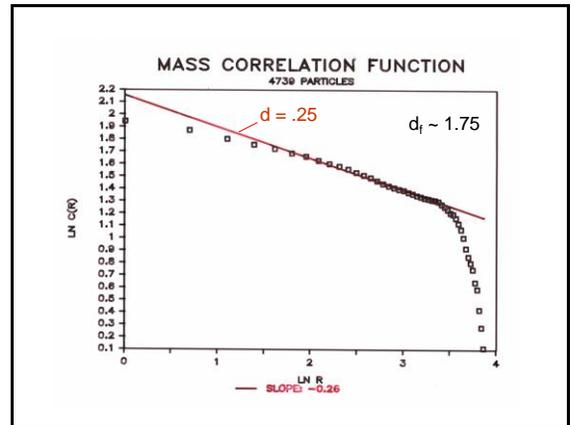
**DENSITY: DECREASES WITH SIZE**

$$\rho = \frac{M}{V} = \frac{L^{d_f}}{L^d} = L^{d_f-d}$$

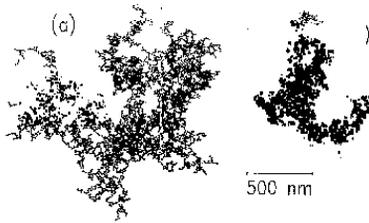
**MASS CORRELATIONS:**

3d:  $c(r) \sim \frac{1}{r^{3-d_f}}$

2d:  $c(r) \sim \frac{1}{r^{2-d_f}}$

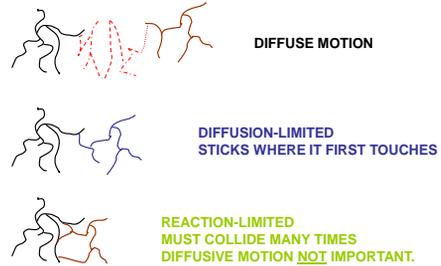


## Colloidal Aggregation



Colloidal Gold

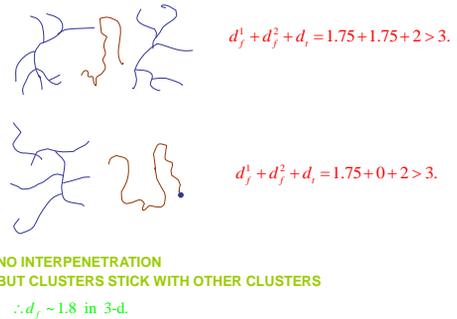
## DIFFUSION – REACTION – LIMITED AGGREGATION



## DIMENSIONS:

- d: Euclidean dimension of space  
 $d = 3$  real space  
 $d = 2$  surface
- $d_f$ : Fractal dimension  
 Amount of volume occupied by a space filling object is  $M \sim R^{d_f}$
- $d_t$ : Trajectory dimension  
 Fractal dimension of trajectory  
 Random walk:  $d_t = 2$   
 Ballistic motion:  $d_t = 1$   
 No motion:  $d_t = 0$

## DIFFUSION-LIMITED CLUSTER AGGREGATION

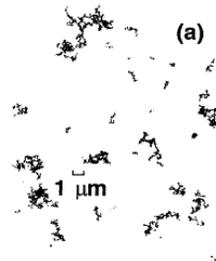


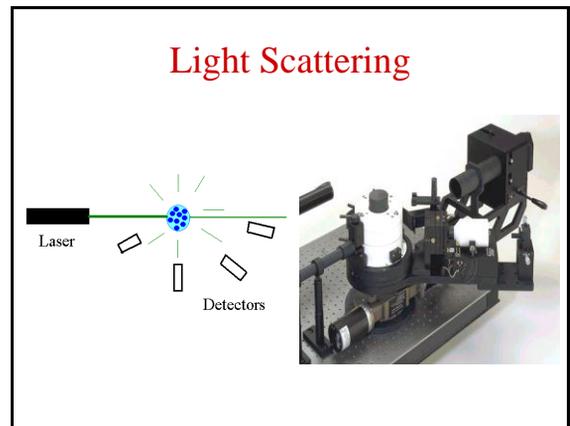
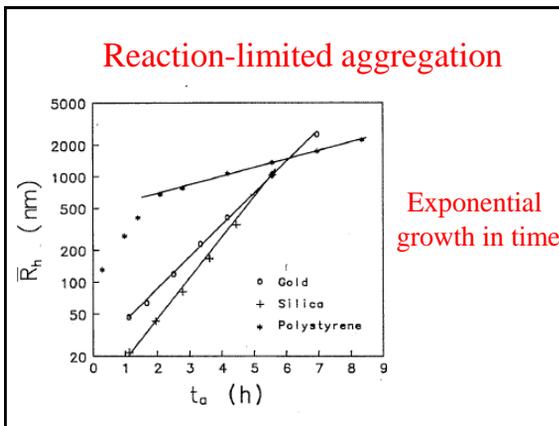
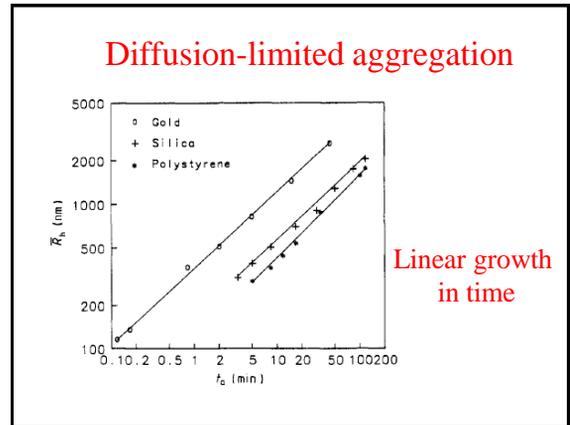
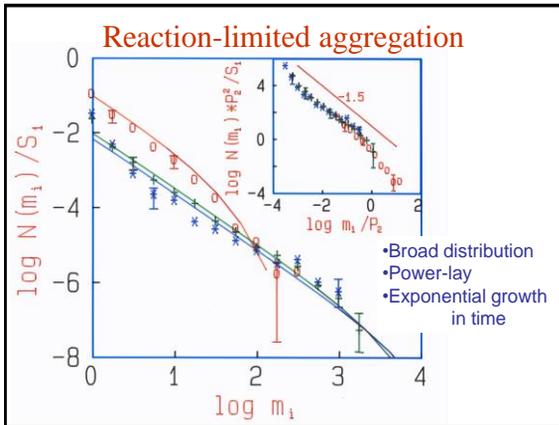
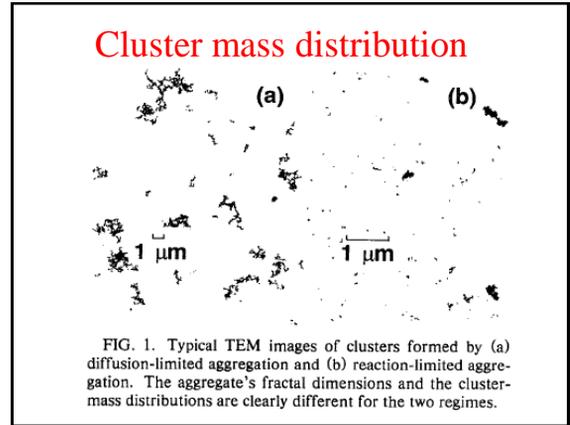
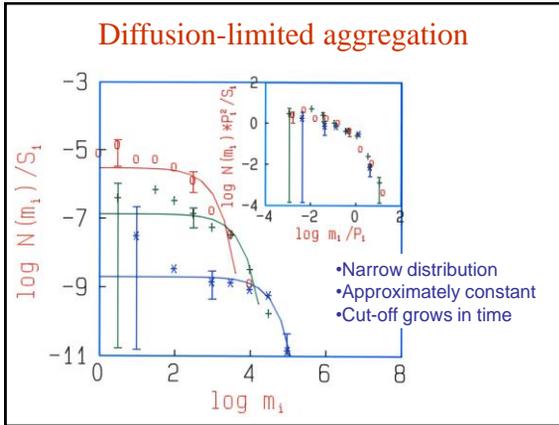
## Time evolution: Smoluchowski Equations

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

Scaling solutions

## Cluster mass distribution





## 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

$$I(q) \approx N_g(R_g) m_g^2$$

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

$$\approx M_T m_g$$

$$\approx M_T R_g^{d_f}$$

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



$$N(R_g) = \frac{M_T}{M_g}$$

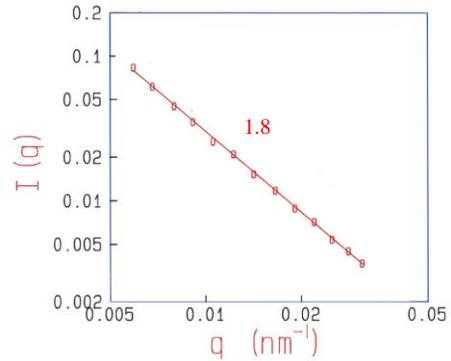
MASS CORRELATIONS:

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

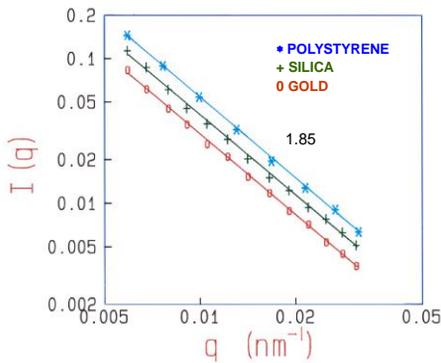
$$I_M(q) = A M^2 S(q R_g)$$

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

## Static scattering from diffusion-limited aggregates



## DIFFUSION-LIMITED COLLOID AGGREGATION

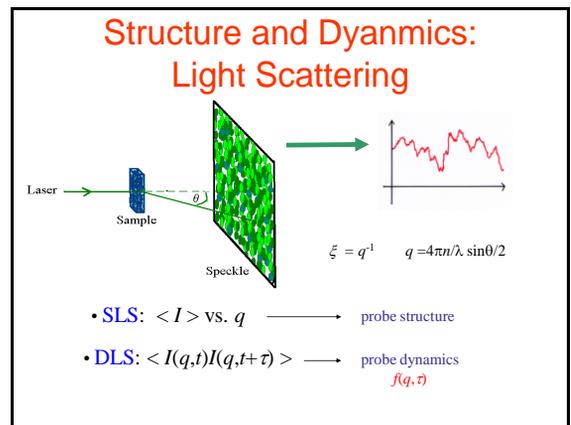
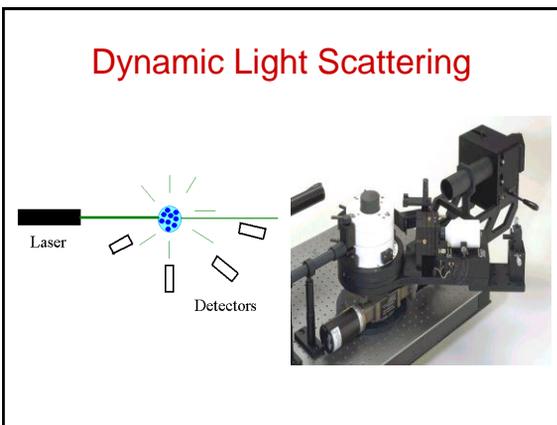
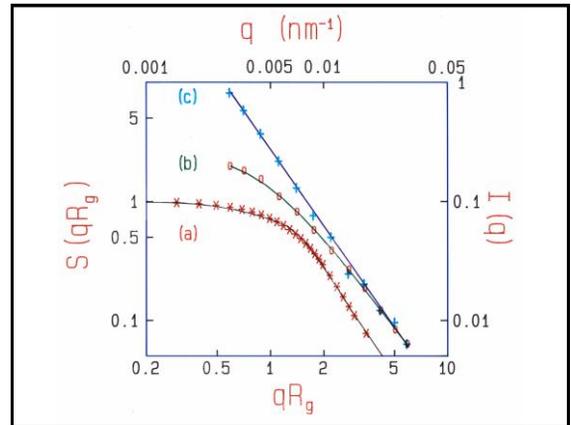
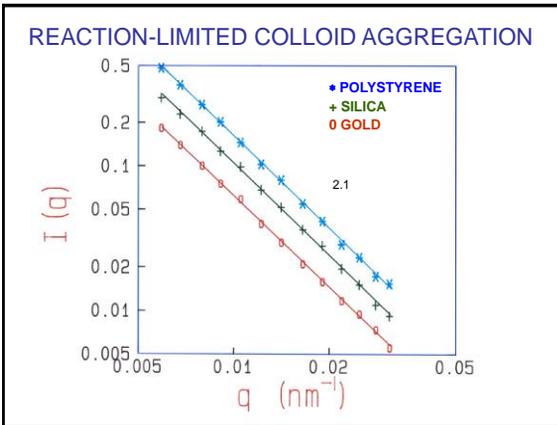
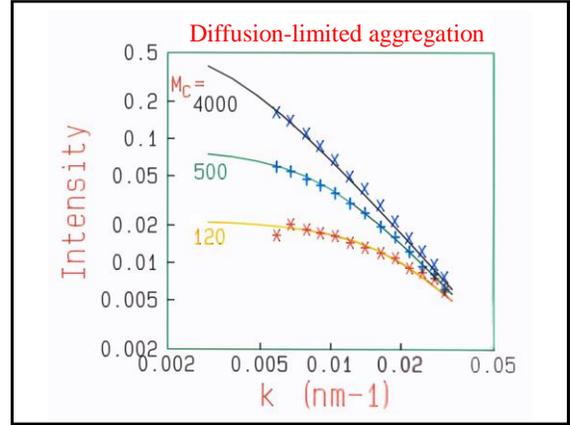
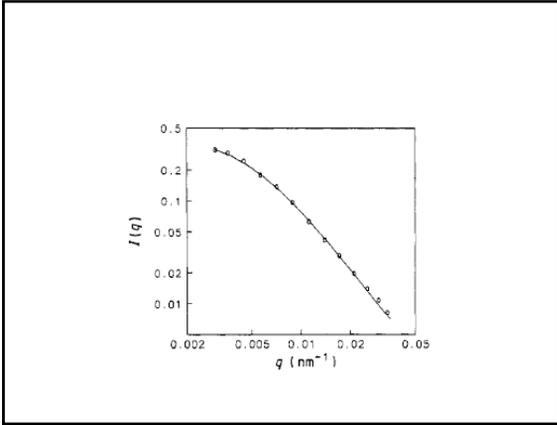


## Fisher-Burford

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

$$q R_g \ll 1 : S(q R_g) = 1 - \frac{1}{2} (q R_g)^2$$

$$q R_g \gg 1 : S(q R_g) \sim (q R_g)^{-d_f}$$



## Light Scattering

Probes characteristic sizes of colloidal particles

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

Speckle:  
Coherence area

DYNAMIC LIGHT SCATTERING:  
Single speckle

STATIC LIGHT SCATTERING:  
Many speckles

## 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  $\pi$   
Each particle must move by  $\sim \lambda$

## Dynamic light scattering from colloidal clusters

Small angle  $\rightarrow$  don't resolve internal motion

## Dynamic light scattering from colloidal cluster

Translational diffusion

Rotational diffusion

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

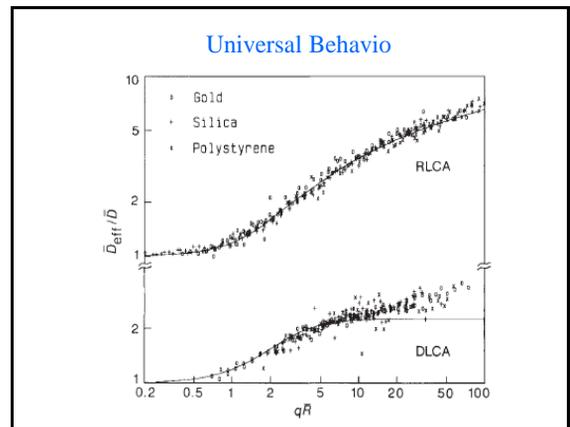
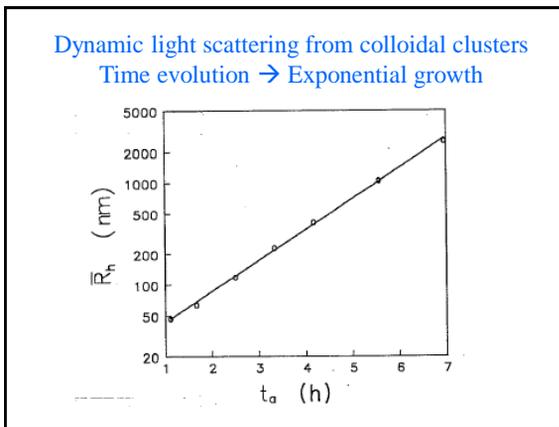
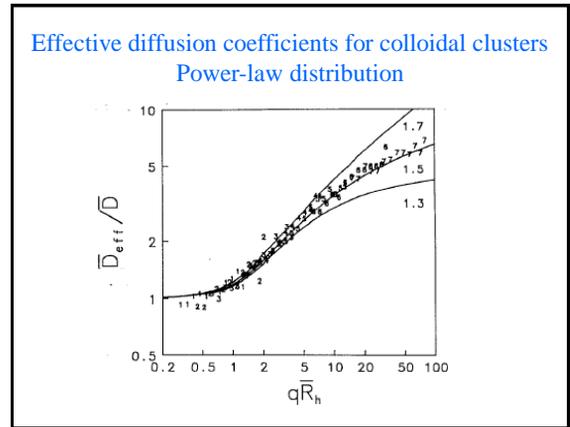
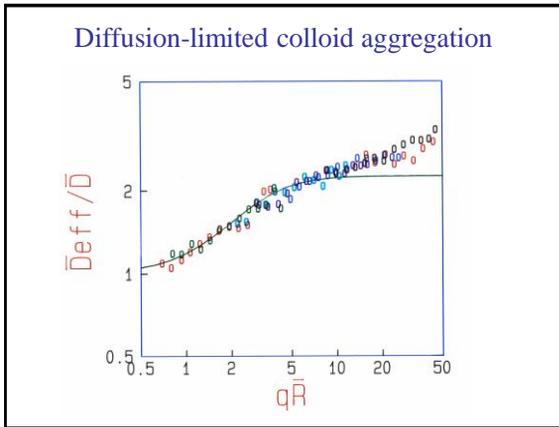
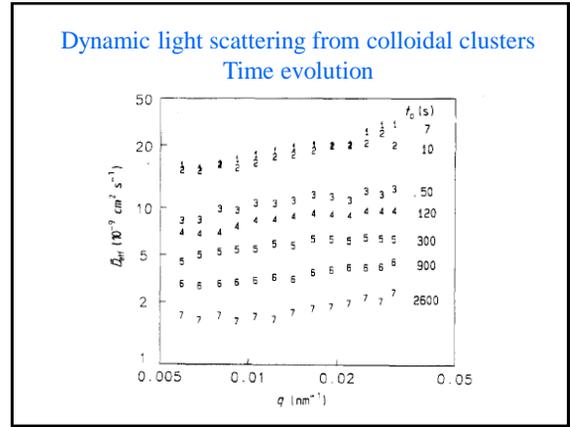
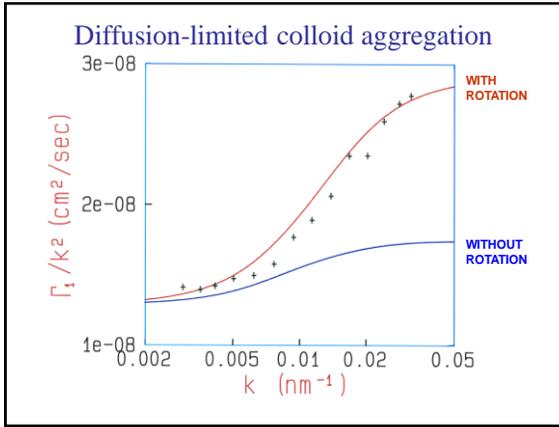
## Dynamic light scattering from colloidal cluster

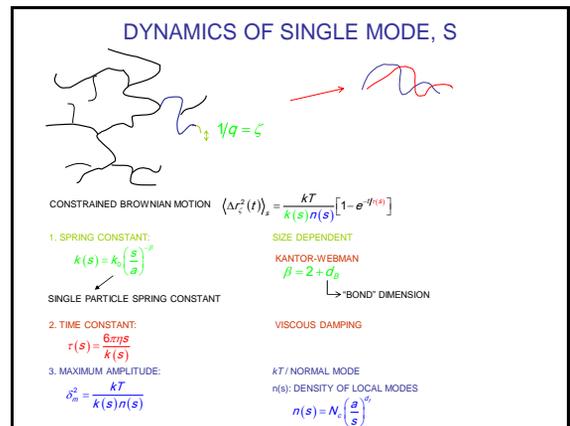
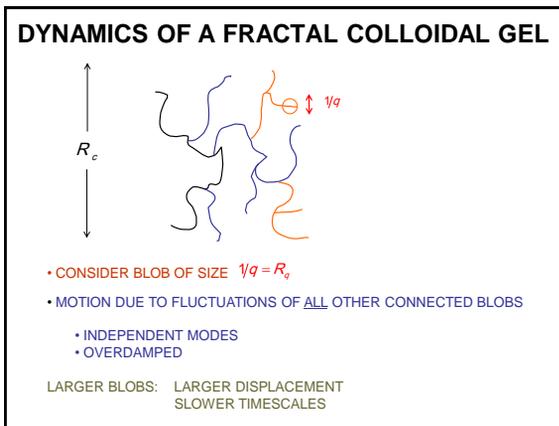
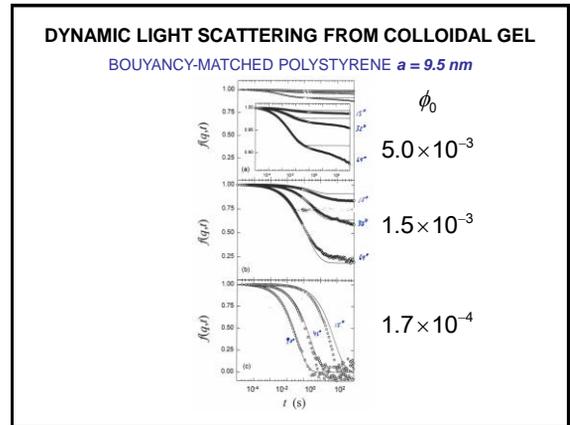
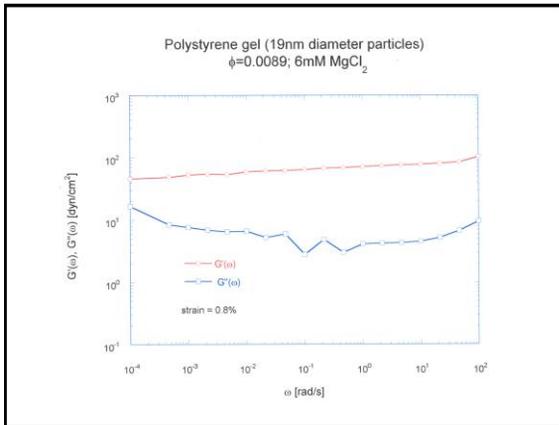
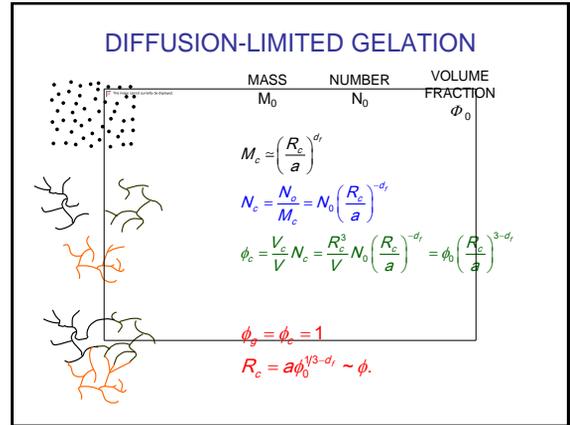
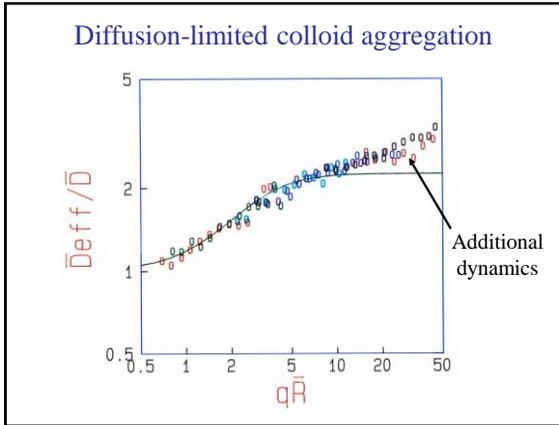
$$S(k, t) = \sum_l S_l(k) e^{-Dk^2 t} e^{-l(l+1)\Theta t}$$

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

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

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





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

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

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

- CAN BE DONE ANALYTICALLY
- FUNCTIONAL FORM IS:

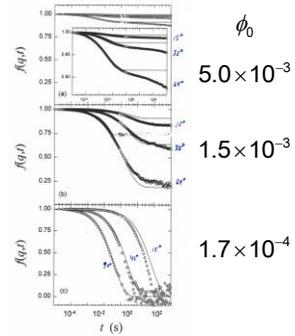
$$\langle \Delta r_\xi^2(t) \rangle = \delta^2 [1 - e^{-(t/\tau)^\beta}]$$

- INITIAL DECAY: STRETCHED EXPONENTIAL
- DECAYS TO A PLATEAU:  $\delta^2$

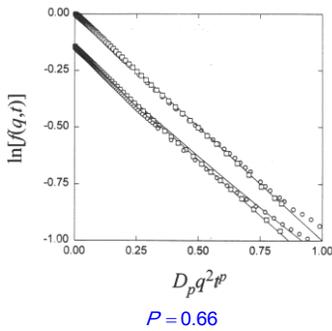
$$f(q,t) = \exp \left\{ -q^2 \langle \Delta r_{\xi=\frac{1}{q}}^2(t) \rangle \right\}$$

### DYNAMIC LIGHT SCATTERING FROM COLLOIDAL GEL

BOUANCY-MATCHED POLYSTYRENE  $a = 9.5 \text{ nm}$



### SCALING STRETCHED EXPONENTIAL



### ELASTIC MODULUS OF GEL

DETERMINED DIRECTLY BY  $\delta^2$   
 $\hookrightarrow$  SET BY AVERAGE CLUSTER SIZE

$\phi_0$  DEPENDENCE

$$G(\phi_0) = \frac{k(R_c)}{R_c} = k_0 a^\beta R_c^{-1-\beta} \sim \delta^2$$

$$\delta^2 k(R_c) = kT$$

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

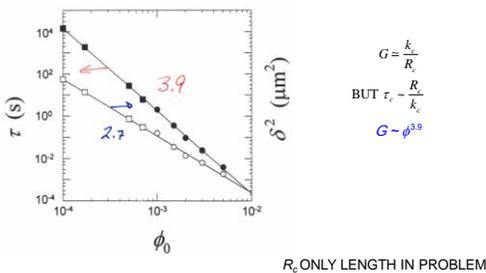
BUT  $R_c \sim \phi_0^{-\frac{1}{d-3}}$

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

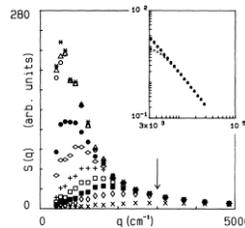
EXPERIMENT: 3.9

$\rightarrow$  MEASURE MODULUS OPTICALLY!

### VOLUME FRACTION DEPENDENCE LIGHT SCATTERING PROBE OF MODULUS



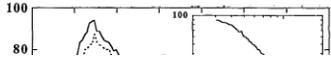
### Hints of equilibrium behavior



SALS from aggregating colloids

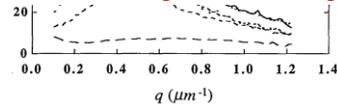
Carpineti & Giglio, PRL 68, 3327 (1992)

### Hints of equilibrium behavior



#### Real-space simulations:

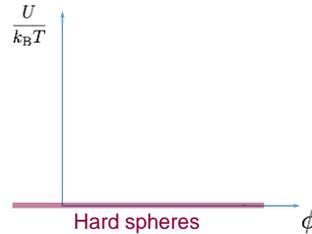
- Diffusion & aggregation of particles
- “Diffusion hole” → spinodal decomposition



Similar behavior for sticky emulsions

Bibette *et al.*, PRL 69, 981 (1992)

### State diagram for colloidal particles



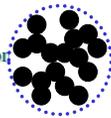
### State diagram for colloidal particles



### Carbon Black in Oil

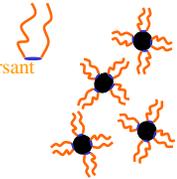
#### Problem:

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



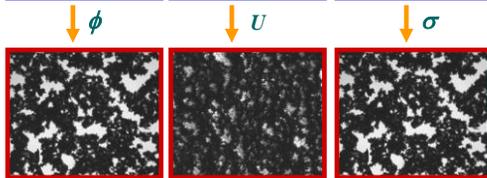
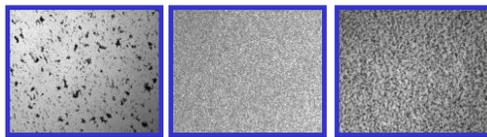
#### Solution:

- Add additive package – primarily dispersant
- Disperse soot particles

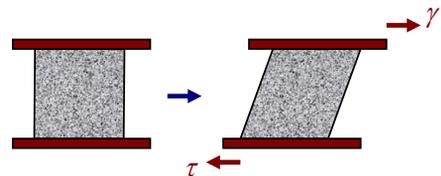


### Gelation of Attractive Particles

#### Carbon Black in Oil

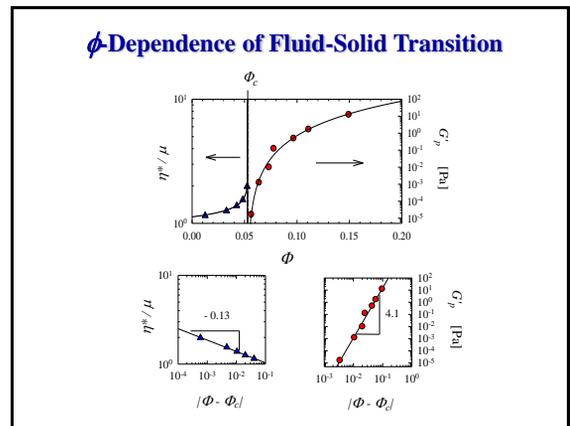
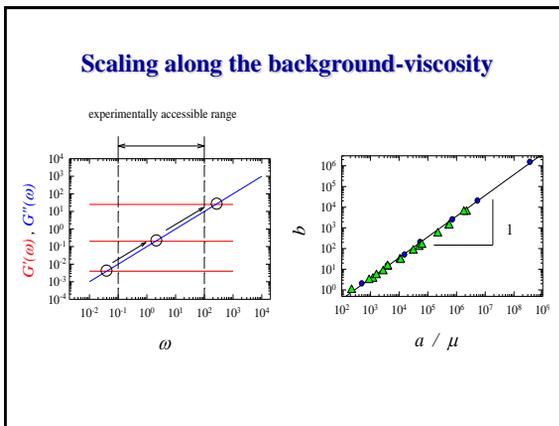
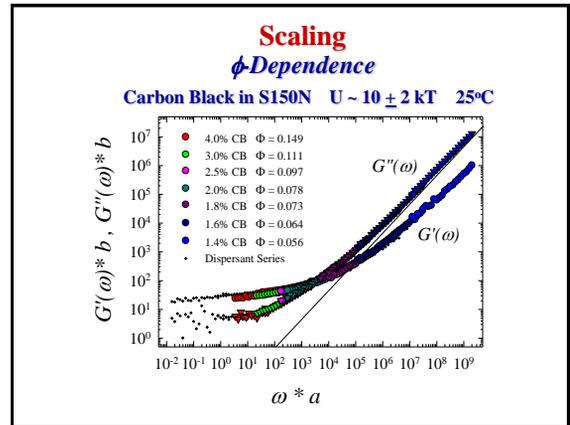
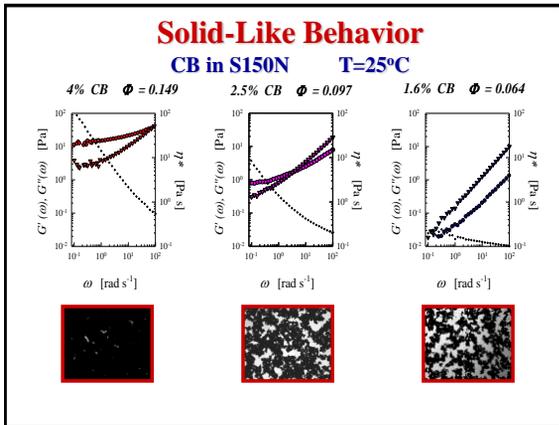
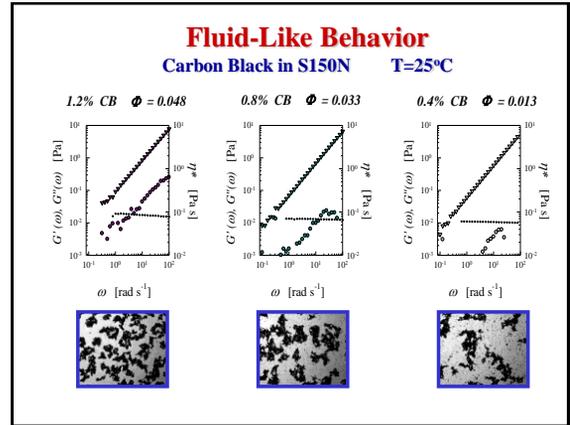
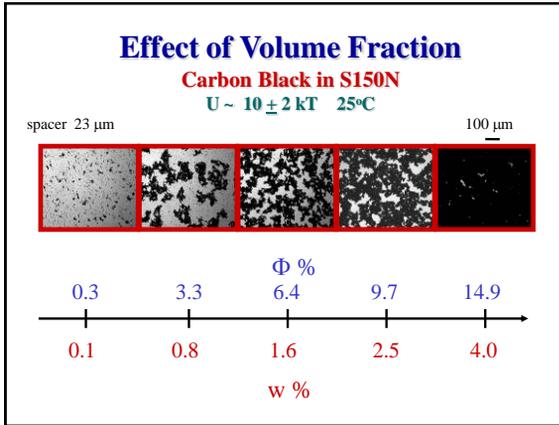


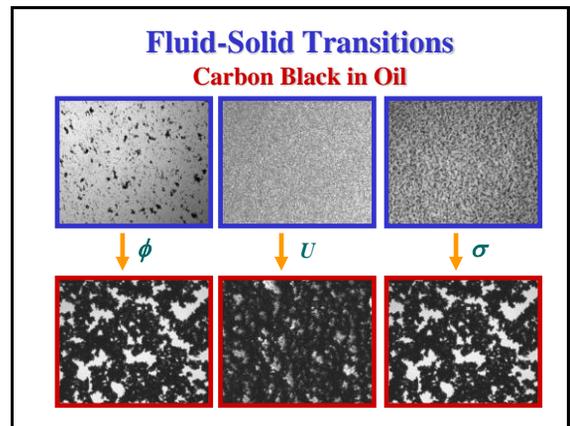
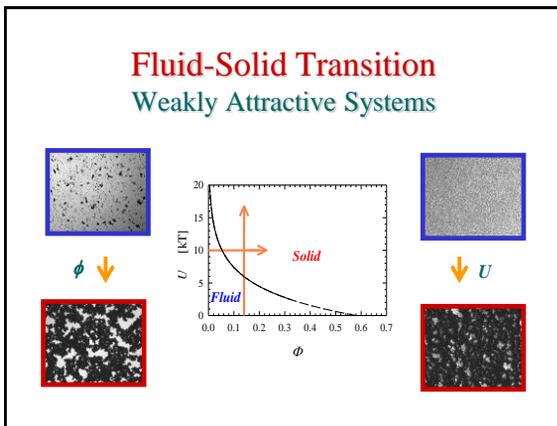
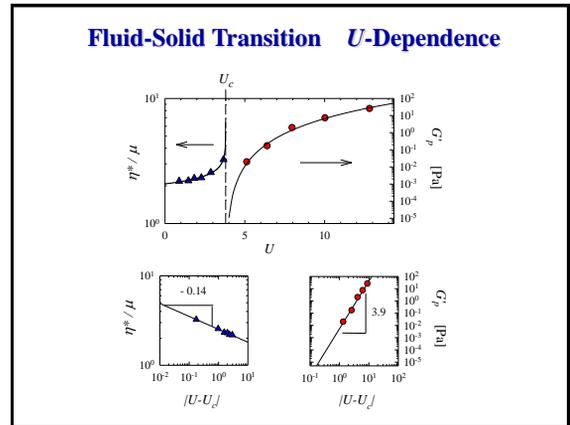
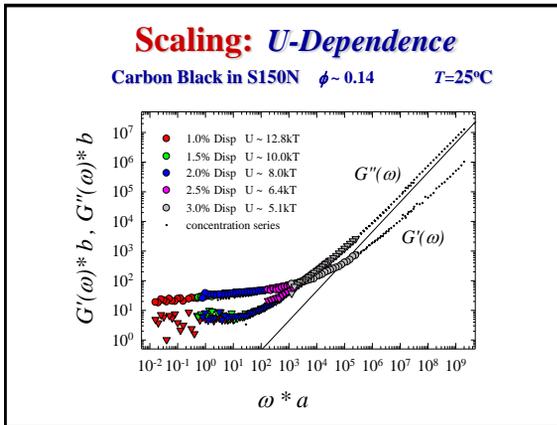
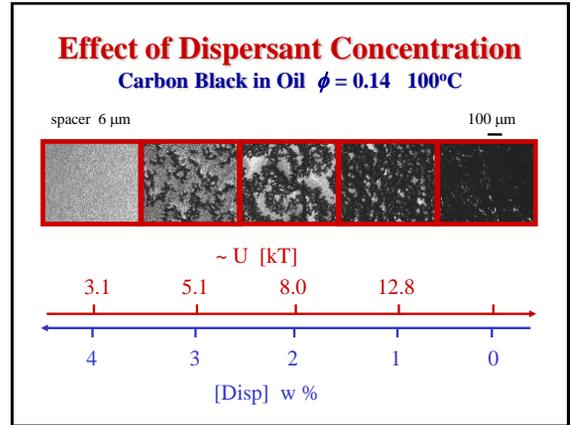
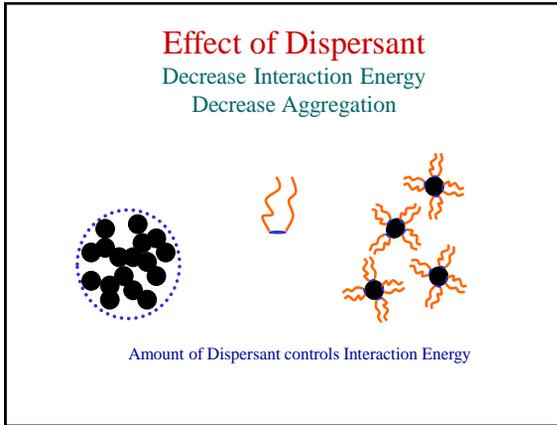
### Viscoelasticity of Soft Materials

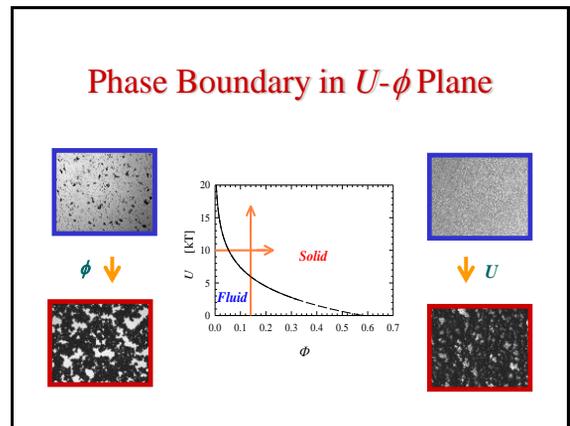
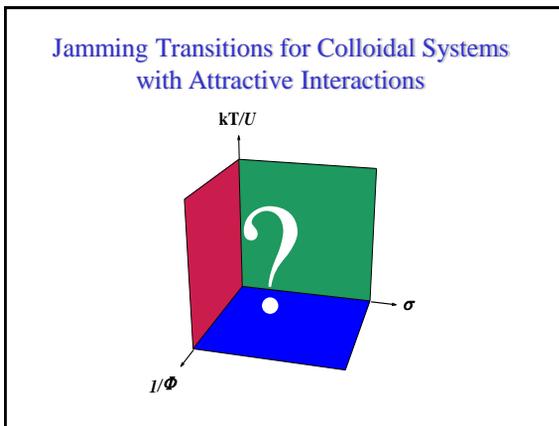
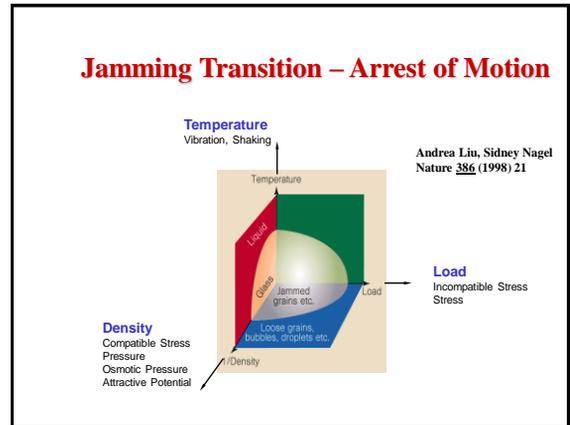
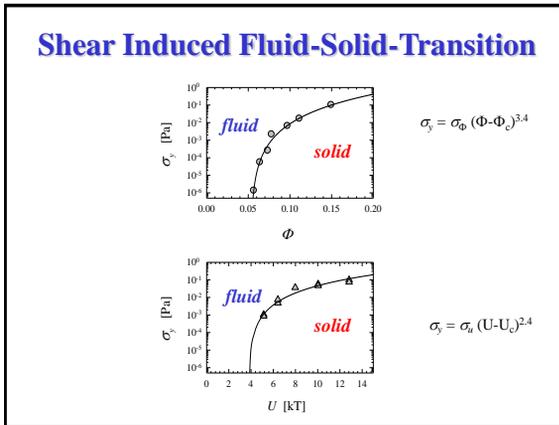
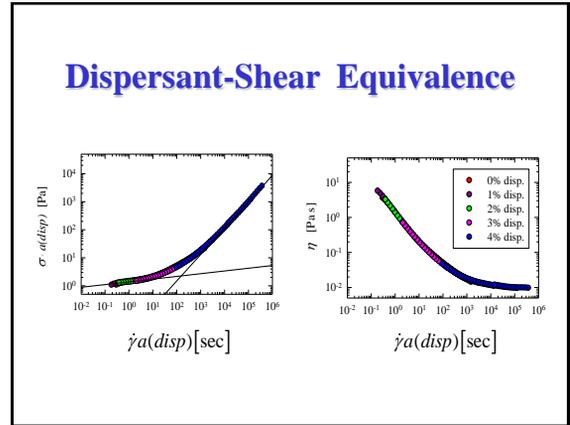
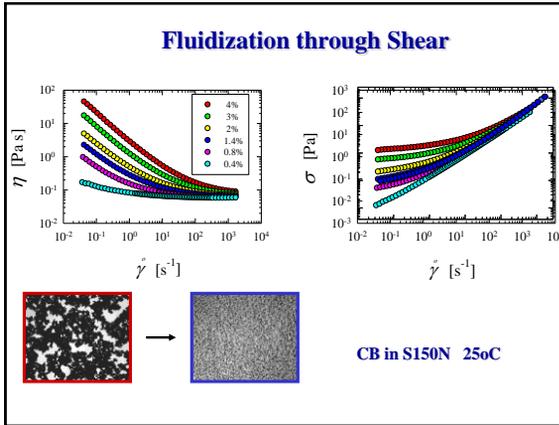


$$\begin{aligned} \text{Solid: } \tau &= G\gamma & \gamma &= \gamma_0 e^{i\omega t} \\ \text{Fluid: } \tau &= \eta\dot{\gamma} & \longrightarrow & \tau = [G'(\omega) + iG''(\omega)]\dot{\gamma} \end{aligned}$$

Elastic
Viscous

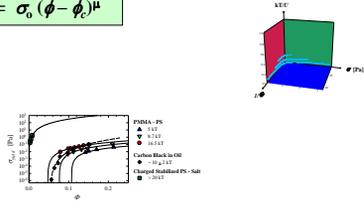






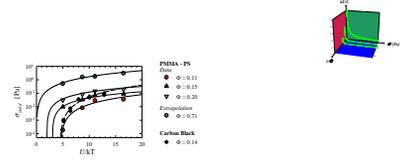
### Yield Stress as Phase Boundary

$$\sigma_y = \sigma_0 (\phi - \phi_c)^\mu$$

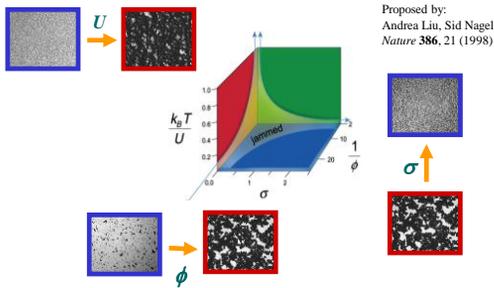


### Phase Boundary in $U - \sigma$ Plane $\phi = \text{const.}$

$$\sigma_y = \sigma_0 (U - U_c)^\nu$$



### Jamming Phase Diagram for Attractive Systems



Completely new way to look at viscosity of soot in oil