Glasses and Gels

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Boulder summer school 7/5/06

• General introduction
• Experimental techniques
• Colloidal glasses
• Colloid Aggregation
• Colloidal gels

http://www.deas.harvard.edu/projects/weitzlab

Colloidal particles

• Good model system
  – Control size, shape
  – Control strength, range of interactions
• Statistical properties of phase behavior
• Model for complex fluid systems
• Equilibrium properties
• Non-equilibrium properties (often dominate)
Colloidal Particles

Stability:
- Short range repulsion
- Sometimes a slight charge

Colloid Particles are:
- Big
  - $a \approx 1$ micron
  - Can “see” them
- Slow
  - $\tau \approx a^2/D \approx \text{ms to sec}$
  - Follow individual particle dynamics

Colloidal particles undergoing Brownian motion

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

Easily deformable → Low Elastic Constant:

Elastic Constant: → Pressure \[
\begin{array}{ccc}
\text{Force} & \frac{\text{Force}}{\text{Area}} & \frac{\text{Energy}}{\text{Volume}} \\
\end{array}
\]

Atoms: \[\frac{eV}{\AA^3} \sim \text{GPa}\]

Colloids: \[\frac{k_BT}{\mu m^3} \sim \text{Pa}\]

Colloidal interactions – stabilizing

- REPULSION: Coulomb; Steric
- ATTRACTION: van der Waals; Chemical

- Short range attraction
- Long range repulsion
- Sum: Stabilizing barrier

\[E_b > k_BT \rightarrow \text{Colloid stable against aggregation}\]

OTHER POSSIBLE REPULSIVE INTERACTIONS
Hard Spheres: Only Volume Exclusion

Volume Fraction Controls Phase Behavior

Increase $\phi$ => Decrease Temperature

$$F = U^0 - TS$$

Hard Sphere Liquid - Crystal Coexistence

Maximum packing $\phi_{RCP} \approx 0.63$

Maximum packing $\phi_{HCP} = 0.74$

Hard Sphere Phase Diagram
Colloidal interactions – destabilizing

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

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Controlled Attraction of Colloidal Particles

Depletion attraction

Polystyrene polymer, $R_g=37$ nm + PMMA spheres, $r_c=350$ nm

T. Dinsmore
Phase diagram for attractive colloids

State diagram for colloidal particles

Fractal gels
Strong attractions
low \( \phi \)
Network formation

Weakly attractive “gels” at intermediate volume fractions

Nonequilibrium solid states

Equilibrium

Hard spheres

Glasses
Weak attractions
high \( \phi \)
Local caging

\( \phi \approx 10^{-3} \)

\( \phi \approx 0.6 \)
Jamming Transitions for Colloidal Systems with Attractive Interactions

\[ \frac{kT}{U} \]

\[ \frac{1}{\phi} \]

\[ \sigma \]

Jamming Transition – Arrest of Motion

Andrea Liu, Sidney Nagel
Nature 386 (1998) 21
Jamming Phase Diagram for Attractive Systems

Proposed by:
Andrea Liu, Sid Nagel


Experimental Techniques

- Light scattering
  - Static light scattering
  - Dynamic light scattering
  - Ultra-small angle dynamic light scattering
  - Diffusing-wave spectroscopy
- Microscopy
- Rheology
**Static Light Scattering**

X-ray scattering from gold aggregates  
Model $g(r)$

P. Dimon, SofK Sinha

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**Static Scattering: Structure**

Scattered field from single particle

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

Scattered intensity per particle  
Phase factor  
Frequency of light

Measure the scattered intensity from collection of particles

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

Form factor  
Structure factor

- Measure $q$ dependence of scattering
- Probes spatial Fourier Transform of density correlations
Experimental Techniques

- Light scattering
  - Static light scattering
  - Dynamic light scattering
  - Ultra-small angle dynamic light scattering
  - Diffusing-wave spectroscopy
- Microscopy
- Rheology

Dynamic Light Scattering

Laser

Detectors
Structure and Dynamics: 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

\[ \bar{q} = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \]

Speckle: Coherence area

DYNAMIC LIGHT SCATTERING: Single speckle

STATIC LIGHT SCATTERING: Many speckles
Dynamic Light Scattering

Measure temporal intensity fluctuations

![Intensity vs Time Graph]

Obtain an intensity autocorrelation function

\[ \frac{\langle I(t)I(t+\tau) \rangle}{\langle I \rangle^2} \]

Lag time (\( \tau \)) [s]

Measure temporal correlation function of scattered light:

Intermediate structure factor

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

\[ \langle E(0)E(t) \rangle = \left\langle A^2 \sum_{m,n} e^{i\mathbf{q} \cdot (\mathbf{r}_m(0)-\mathbf{r}_n(t))} \right\rangle \]  

Time average over all particles

\[ \sim e^{-q^2\langle \Delta r^2(t) \rangle} \]  

Correlations only between the same particles

Cumulant expansion: \( \Delta r^2(t) \sim Dt \)

\[ \sim e^{-q^2Dt} \]  

Physics: How to change the phase of the field by \( \pi \)
Each particle must move by \( -\lambda \)
Experimental Techniques

- Light scattering
  - Static light scattering
  - Dynamic light scattering
  - Ultra-small angle dynamic light scattering
  - Diffusing-wave spectroscopy
- Microscopy
- Rheology

Ultra Small Angle Light Scattering
Probe Structure

L. Cipelletti
Experimental setup

0.07 deg to 5.0 deg

Multispeckle Detection

0.07 deg to 5.0 deg
100 cm$^{-1} < q < 7000$ cm$^{-1}$

Average over constant $q$: 
- non-ergodic samples
- avoid excessive time averaging
Experimental Techniques

• Light scattering
  – Static light scattering
  – Dynamic light scattering
  – Ultra-small angle dynamic light scattering
  – Diffusing-wave spectroscopy
• Microscopy
• Rheology

Diffusing Wave Spectroscopy:
Very strong scattering

TRANSMISSION

MOST LIGHT IS SCATTERED BACK
MILK IS WHITE!!

D. Pine, P. Chaikin, E. Herbolzheimer
Diffusing Wave Spectroscopy

Laser → Fiber + beam splitter → Amp/Disc → PMTs

PROJECT LENGTHS ONTO INITIAL DIRECTION

\[ \cos \theta \]

\[ \sum \]

ANALOGY – PERSISTENCE LENGTH FOR SEMI-RIGID POLYMER

TRANSPORT MEAN FREE PATH

\[ \ell^* = \sum_i \ell \langle \cos \theta \rangle^i \]

\[ \ell^* = \frac{\ell}{1 - \langle \cos \theta \rangle} > \ell \]

PROJECT LENGTHS ONTO INITIAL DIRECTION

ANALOGY – PERSISTENCE LENGTH FOR SEMI-RIGID POLYMER
P(s): DIFFUSION EQUATION

\[ P(s) = \text{DIFFUSION EQUATION} \]

\[ t = 0 \quad \rightarrow \quad I(t) \sim \text{# PATHS OF LENGTH } s = ct \quad \rightarrow \quad P(s) \]

SINGLE PATH

\[ t=0 \quad \rightarrow \quad n \quad \text{SCATTERING EVENTS} \quad s = n\ell \rightarrow \text{PATH LENGTH} \]

[MARET & WOLFE]
\[ g_1^n (\tau) = \left\langle e^{i\sum q^j \Delta x^j (\tau)} \right\rangle \]

PHASE CHANGE DUE TO TOTAL PATH LENGTH

\[ = \left\langle e^{iq^j \Delta x^j (\tau)} \right\rangle^n_q \]

STATISTICAL APPROACH

\[ n \text{ LARGE} \rightarrow \text{REPLACE BY AVERAGE} \]

\[ \text{DON'T CONSERVE} \ q \ AT \ EACH \ SCATTERING \]

\[ = e^{-\langle q^2 \rangle \frac{\Delta x^j (\tau)}{\Delta}} \]

\[ \rightarrow \text{APPROX. AT SHORT} \ \tau \]

\[ \langle q^2 \rangle = 2k_0^2 \frac{\tau}{\ell} \]

\[ s = n/\ell \]

\[ g_1^n (\tau) = e^{-2\left(\frac{\tau}{\tau_0}\right)\langle q^2 \rangle/\ell^2} \]

\[ \tau_0 = \frac{1}{k_0^2 D} \]

CORRELATION FUNCTION:

\[ G_1(\tau) = \int_0^\infty P(s) e^{-2(\tau/\tau_0)(s/\ell^2)} ds \]

SUM OVER DISTRIBUTION OF LIGHT PATHS.

\[ P(s) \] DISTRIBUTION OF PATHS

\[ \text{OF LENGTH} \ s \]

\[ \rightarrow \text{DEPENDS ON GEOMETRY} \]

\[ \rightarrow \text{DIFFUSION OF EQUATION FOR LIGHT} \]

MARET & WOLF

SINGLE SCATTERING DECAY

NUMBER OF (RANDOMIZING) SCATTERING EVENTS
TRANSMISSION THROUGH A SLAB

FUNCTIONAL FORMS ARE KNOWN

-- USE MORE EXACT BOUNDARY CONDITIONS

-- J. de Phys. 51, 2101 (1990)

POINT SOURCE:

\[
g_1(t) = \int_{\frac{t}{2L}}^{\infty} \left[ A(s) \sinh s + e^{-s(1-\frac{4\epsilon^*}{L})} \right] ds
\]

with \[
A(s) = \frac{\left( \frac{3}{4} \frac{\epsilon^*}{s} - 1 \right) \frac{\epsilon^*}{s} e^{\frac{\epsilon^*}{s}} + \left( \sinh s + \frac{3}{4} \frac{\epsilon^*}{s} \cosh s \right) e^{-\left( \frac{4\epsilon^*}{L} \right)}}{\left( \sinh s + \frac{3}{4} \frac{\epsilon^*}{s} \cosh s \right)^2 - \left( \frac{\epsilon^*}{s} \right)^2}
\]
EXTENDED SOURCE

\[ g_1(t) \approx \frac{\left( \frac{L}{\ell} + \frac{3}{2} \right) \sqrt{\frac{6t}{\tau_0}}}{\left( 1 + \frac{8t}{3\tau_0} \right) \sinh \left[ \frac{L}{\ell} \sqrt{\frac{6t}{\tau_0}} + \frac{4}{3} \sqrt{\frac{6t}{\tau_0}} \cosh \left[ \frac{L}{\ell} \sqrt{\frac{6t}{\tau_0}} \right] \right]} \]

CHARACTERISTIC TIME SCALE: \( \tau_0 \left( \frac{\ell}{L} \right)^2 \)

TRANSMISSION

\[ d = 0.6 \mu m \]
\[ \phi = 2\% \]
PHYSICS

-- TOTAL PATH LENGTH CHANGES BY \( \lambda \)

-- CONTRIBUTIONS FROM MANY SCATTERING EVENTS

SMALL \( \tau \) \( \rightarrow \) LONG PATH \( \rightarrow \) MANY SCATTERERS

\( \rightarrow \) SMALL MOTION \( \rightarrow \) FAST DECAY

LARGE \( \tau \) \( \rightarrow \) SHORT PATH \( \rightarrow \) FEW SCATTERERS

\( \rightarrow \) LARGER MOTION \( \rightarrow \) SLOWER DECAY

DWS PROBES MOTION ON SHORT LENGTH SCALES

PHASE OF PATH CHANGES WHEN PATH LENGTH CHANGES BY
\(~1\) WAVELENGTH

\( \lambda \approx 5000 \ \text{Å} \)

BUT: LIGHT IS SCATTERED FROM MANY PARTICLES

\[
\left( \text{Estimate:} \quad \left( \frac{L}{\epsilon} \right)^2 \approx \left( \frac{10^3}{10} \right)^2 \approx 10^4 \right)
\]

\( \therefore \) MOTION OF EACH INDIVIDUAL PARTICLE CAN BE MUCH LESS

\( \searrow \) CAN MEASURE PARTICLE MOTION ON SCALE OF
\(~5 \ \text{Å} \)
Experimental Techniques

• Light scattering
  – Static light scattering
  – Dynamic light scattering
  – Ultra-small angle dynamic light scattering
  – Diffusing-wave spectroscopy

• Microscopy

• Rheology

The “PINK Monster”
Keep that door closed!!!!
Confocal microscopy for 3D pictures

Scan many slices, reconstruct 3D image

Brownian Motion
(2 μm particles, dilute sample)

 Leads to normal diffusion:

\[ \langle \Delta x^2 \rangle = 2Dt \]

\[ D = \frac{k_B T}{6\pi \eta a} \]

Particle size \( a \)

viscosity \( \eta \)
Brownian Motion in Real Time

Experimental Techniques

- Light scattering
  - Static light scattering
  - Dynamic light scattering
  - Ultra-small angle dynamic light scattering
  - Diffusing-wave spectroscopy
- Microscopy
- Rheology
Mechanical Properties of Soft Materials:
Viscoelasticity

Solid: $\tau = G\gamma$
Fluid: $\tau = \eta\gamma$

$\gamma = \gamma_0 e^{i\omega t}$

$\tau = [G'(\omega) + iG''(\omega)]\gamma$

Elastic Viscous

Rheology of soft materials

Scaling plot

Dispersant Series
- 4.0% CB $\Phi = 0.149$
- 3.0% CB $\Phi = 0.111$
- 2.5% CB $\Phi = 0.097$
- 2.0% CB $\Phi = 0.078$
- 1.8% CB $\Phi = 0.073$
- 1.6% CB $\Phi = 0.064$
- 1.4% CB $\Phi = 0.056$

$G'(\omega)$
$G''(\omega)$

Scaling plot

$G'(\omega) \cdot b$, $G''(\omega) \cdot b$
State diagram for colloidal particles

- **Weak attractions**
  - low $\phi$
  - Network formation

- **Strong attractions**
  - high $\phi$
  - Local caging

Nonequilibrium solid states

Equilibrium

Hard spheres

$\phi_g$ $\phi$

Fractal gels

$\phi \approx 10^{-3}$

Weakly attractive "gels" at intermediate volume fractions

Glasses

$\phi \approx 0.6$

Storage and Loss Modulii of Hard Spheres

**Storage**

$G'(\omega)$

**Loss**

$G''(\omega)$
Origin of Elasticity

Distort equilibrium positions

State diagram for colloidal particles

Fractal gels

Strong attractions
low $\phi$
Network formation

Weakly attractive “gels” at intermediate volume fractions

Glasses

Weak attractions
high $\phi$
Local caging
Viscoelasticity of Hard Spheres

DWS correlation function of Hard Spheres
Mean Squared Displacement for Hard Spheres

\[
\langle \Delta x^2(t) \rangle (\text{cm}^2)
\]

\[10^{-10} \quad 10^{-11} \quad 10^{-12} \quad 10^{-13} \quad 10^{-14} \quad 10^{-15} \quad 10^{-16}
\]

\[10^{-8} \quad 10^{-6} \quad 10^{-4} \quad 10^{-2} \quad 10^0 \quad 10^2 \quad 10^4 \quad 10^6 \quad 10^8 \]

t (sec)

\(\tilde{G}(s)\) (dyne/cm²)

Frequency-Dependent Modulus for Hard Spheres

\[
\tilde{G}(s) \quad (\text{dyne/cm}^2)
\]

\[10^3 \quad 10^4 \quad 10^5 \quad 10^6 \quad 10^7
\]

\[10^{-2} \quad 10^0 \quad 10^2 \quad 10^4 \quad 10^6 \quad 10^8 \]

\(s \quad (\text{sec}^{-1})\)
Frequency-Dependent Viscoelasticity for Hard Spheres

Correlation function of Hard Spheres
Viscoelasticity of Hard Spheres

Low frequency relaxation

Glassy plateau

High frequency response

Fluid contribution

Cage trapping:

• Short times: particles stuck in “cages”
• Long times: cages rearrange

Mean-squared displacement

\( \phi = 0.53 \) -- “supercooled fluid”

\( \phi = 0.56, 100 \text{ min} \)

(supercooled fluid)

E. Weeks, J. Crocker
Trajectories of “fast” particles, $\phi = 0.56$

shading indicates depth

Displacement distribution function

$\phi = 0.53$: “supercooled fluid”

Nongaussian Parameter

$$\alpha_2 = \frac{\langle x^4 \rangle}{3 \langle x^2 \rangle^2} - 1$$
How to pick $\Delta t^*$ for glasses?

Structural Relaxations in a Supercooled Fluid

Relaxing particles are highly correlated spatially
Structural Relaxations in a Glass

Relaxing particles are NOT correlated spatially

Fluctuations of fast particles

Supercooled fluid $\phi = 0.56$  
Glass $\phi = 0.61$
Cluster size grows as glass transition is approached

\[ \langle N_c \rangle \]

What is a Glass?

- Glass must have a low frequency shear modulus
- Must have force chains to transmit stress

J. Conrad, P Dhillon, D. Reichman
Topological Change: $Δnn (Δt)$

Identify nearest neighbors, calculate $Δnn(Δt)$

$Δnn = 1$

$Δnn = 2$


Static Particles ($Δnn = 0$) – $φ = 0.52$
Static Particles ($\Delta n = 0$) – $\phi = 0.60$

Static Particles Move Much Less

\[<\Delta x^2(t)> \text{ [\mu m]}^2\]

\[
\begin{array}{c}
\text{Time [sec]} \\
\hline
10 & 100 & 1000 & 1E4 \\
1E-3 & 0.01 & 0.1 \\
\end{array}
\]

\[
\phi:
\begin{array}{c}
0.52 \\
0.55 \\
0.60 \\
\end{array}
\]
Rheology of slow particles

Intermezzo – nucleation of HS crystals

2.3 μm diameter PMMA spheres

Must identify incipient crystal nuclei

U. Gasser, E. Weeks, J. Crocker
Colloidal Crystallization

Crystal Nucleus Structure

$R \sim R_c \quad \phi = 0.47$
Finding Surface Tension

\[ \Delta G = \gamma (4 \pi r^2) - \Delta \mu \left( \frac{4}{3} \pi r^3 \right) \]

- Surface energy
- Chemical potential

\[ P(r) \approx \exp \left( \frac{-\Delta G}{k_B T} \right) \approx \exp \left( -\gamma r^2 \right) \]

(for small \( r \))

Measurement of Surface Tension

Surface tension is very low
Fractal Dimension of the Nuclei

State diagram for colloidal particles

- Fractal gels
- Strong attractions
- Low $\phi$
- Network formation

- Weakly attractive “gels” at intermediate volume fractions

- Nonequilibrium solid states

- Glasses
- Weak attractions
- High $\phi$
- Local caging

Hard spheres

Equilibrium

$U / k_B T$
COLLIOID AGGREGATION

DILUTE, STABLE SUSPENSION

\[ D = \frac{kT}{6\pi \eta R} \]

DESTABILIZE

Aggregation Time

Time (min)

[Pyridine]
$d_f \sim 1.70$

M. Oliveria
FRACTAL:

• SELF-SIMILAR
  NO CHARACTERISTIC LENGTH SCALE

\[ M \sim R^{d_f} \]

\[ d_f: \text{ FRACTAL DIMENSION} \]

\[ \log M = \frac{3}{d_f} \quad d_f < d \]

DENSITY: DECREASES WITH SIZE

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

\[ \log \rho = \frac{1}{d_f} \log L \quad \leftrightarrow \text{FRACTAL} \]
STRUCTURE OF AGGREGATES
- SCALE INVARIANT - FRACTAL

\[ M \sim R^{d_f} \]
\[ d_f < d \]

\[ g(r) \sim \frac{1}{r^{d-d_f}} \]

\[ S(q) \sim \frac{1}{q^{d_f}} \]
\[ S(q) \sim N_q M_q^2 \sim \frac{M}{M_q} M_q^2 \sim R^{d_f} \sim q^{-d_f} \]
DIFFUSION-LIMITED COLLOID AGGREGATION

\[ d_j^1 + d_j^2 + d_i = 1.75 + 1.75 + 2 > 3. \]

\[ d_j^1 + d_j^2 + d_e = 1.75 + 0 + 2 > 3. \]

NO INTERPENETRATION
BUT CLUSTERS STICK WITH OTHER CLUSTERS
\[ \therefore d_j \sim 1.8 \text{ in 3-d.} \]
### DIFFUSION-LIMITED GELATION

<table>
<thead>
<tr>
<th>MASS $M_0$</th>
<th>NUMBER $N_0$</th>
<th>VOLUME FRACTION $\phi_0$</th>
</tr>
</thead>
</table>

\[
M_c = \left( \frac{R}{a} \right)^{d_f} \\
N_c = \frac{N_0}{M_c} = N_0 \left( \frac{R}{a} \right)^{-d_f} \\
\phi_c = \frac{V}{V_c} N_c = \frac{R^3}{V} N_0 \left( \frac{R}{a} \right)^{-d_f} = \phi_0 \left( \frac{R}{a} \right)^{3-d_f}
\]

\[
\phi_s = \phi_c = 1 \\
R_c = a \phi_0^{1/3-d_f}.
\]

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**Static scattering from gelling colloid**

![Graph showing static scattering from gelling colloid](image)

Carpineti and Giglio, PRL (1992)
Scaling of static scattering from gelling colloid

DYNAMICS OF A FRACTAL COLLOIDAL GEL

- CONSIDER BLOB OF SIZE \( \frac{v}{q} = R_i \)
- MOTION DUE TO FLUCTUATIONS OF ALL OTHER CONNECTED BLOBS
  - INDEPENDENT MODES
  - OVERDAMPED

LARGER BLOBS: LARGER DISPLACEMENT SLOWER TIMESCALES

Carpineti and Giglio, PRL (1992)
DYNAMICS “INSIDE” CLUSTER
KANTOR, WEBMAN; BALL

\[ \Delta \approx S^2 \left( \frac{x}{a} \right)^{\beta} \frac{1}{k_B T f} \]

SIZE-DEPENDENT SPRING CONSTANT

\[ k(x) = k_0 \left( \frac{x}{a} \right)^{-\beta} \quad \beta = 2 + \frac{d_B}{a} = 3.1 \]

\[ k(x) = k_c \left( \frac{x}{R_c} \right)^{-\beta} \]

AVERAGE CLUSTER SPRING CONSTANT

DYNAMICS OF SINGLE MODE, S

CONSTRAINED BROWNIAN MOTION

\[ \langle \Delta \xi^2(t) \rangle = \frac{kT}{k(s)n(s)} \left[ 1 - e^{-\phi(t)} \right] \]

1. SPRING CONSTANT:

\[ k(x) = k_0 \left( \frac{x}{a} \right)^{-\beta} \]

SINGLE PARTICLE SPRING CONSTANT

2. TIME CONSTANT:

\[ \tau(x) = \frac{k_B T \rho(x)}{k(s)} \]

SINGLE PARTICLE TIME CONSTANT

3. MAXIMUM AMPLITUDE:

\[ \delta_x^2 \approx \frac{kT}{k(s)n(s)} \]

SINGLE PARTICLE MAXIMUM AMPLITUDE

1. SPRING CONSTANT:

KANTOR-WEBMAN

\[ \beta = 2 + \frac{d_B}{a} \]

BOND” DIMENSION

2. TIME CONSTANT:

VISCOUS DAMPING

\[ \rho(x) \propto n(x) \]

n(x): DENSITY OF LOCAL MODES

\[ n(x) = N_c \left( \frac{x}{a} \right)^{\nu} \]

SINGLE PARTICLE SPRING CONSTANT
DYNAMIC LIGHT SCATTERING FROM COLLOIDAL GEL

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

\[ \phi_0 = 5.0 \times 10^{-3} \]
\[ 1.5 \times 10^{-3} \]
\[ 1.7 \times 10^{-4} \]

SCALING STRETCHED EXPONENTIAL

\[ P = 0.66 \]
VOLUME FRACTION DEPENDENCE
LIGHT SCATTERING PROBE OF MODULUS

\[
G = \frac{k}{R_c}
\]

BUT \(\tau \sim \frac{R}{k_c}\)

\(G \sim \phi^{3.9}\)

\(R_c\) ONLY LENGTH IN PROBLEM

---

Polystyrene gel (19nm diameter particles)
\(\phi = 0.0089; 6\text{mM MgCl}_2\)

\[
G(\omega), G'(\omega) [\text{dyn cm}^{-1}]
\]

\(\omega\) [rad/s]

\(G(\omega)\)
\(G'(\omega)\)

strain = 0.8%
Weak attractions

Strong attractions
low $\phi$
Network formation

Weakly attractive “gels” at intermediate volume fractions

Glasses

$\phi \approx 0.6$

Fractal gels

$\phi \approx 10^{-3}$

Nonequilibrium solid states

Equilibrium

Hard spheres $\phi_g$ $\phi$

State diagram for colloidal particles

Attractive colloidal particles

Spinodal

Binodal

Critical Point

Gel Line

Fluid

Glass Transition

$\frac{U}{k_B T}$

Attraction $U/k_B T$

Colloid Volume Fraction $\phi$ →
Attractive colloidal particles

![Graph showing Attraction U/k_B vs Colloid Volume Fraction φ]

- Gel Line
- Fluid
- Glass Transition

Attractive colloidal particles

![Graph showing Attraction U/k_B vs Colloid Volume Fraction φ]

- Gel Line
- Fluid
- Glass Transition
Spinodal Decomposition of Colloid Polymer

Col-Pol Critical Point: Sample Evolution

Large scale phase separation - Totally unprecedented  
Structure is 10,000 times larger
Stable clusters: Binodal decomposition
Shorter-range interaction

Stable clusters: Binodal decomposition
Long-range interaction
Structure depends on range

Long-range attraction

Short-range attraction

Unified Picture
Gel structure – long-range attraction

State diagram for colloidal particles

Fractal gels

Strong attractions
low \( \phi \)
Network formation

Weakly attractive "gels" at intermediate volume fractions

Nonequilibrium solid states

Equilibrium

Hard spheres

\( \phi_g \)

\( \phi \)

Glasses

Weak attractions
high \( \phi \)
Local caging