



Glassy Dynamics of Confined Colloidal Suspensions in Polar and Non-polar Media

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Confined Systems Surround Us!

Confined systems are ubiquitous in nature and modern technology

- Jamming of erythrocytes in blood vessels
- Self-assembly of micro/nano-particles in micro/nano-fluidic devices
- Manufacturing of plasma/LCD displays
- Biolubrication

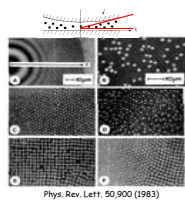
Questions arise:

- How is packing configuration altered?
- What are the dynamics and rheological properties of colloids under confinement?



The Problems at Hand

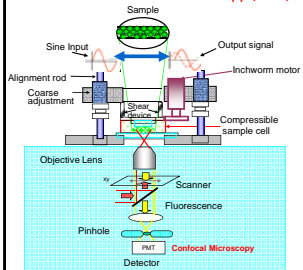
- Confinement effect on structure and dynamics extensively studied with molecular fluids
 - Glass transition in molecularly thin liquid films
 - Drastic increase in viscosity of molecular fluids
 - Often force based measurements yet without direct visualization of microstructural dynamics
- Confinement effects in colloidal systems relatively unexplored
 - Order vs. Disorder at less thickness, i.e. ~ several particle layers thick?
 - In situ rheological and dynamic characterization



Goal: Establish the correlation between structure and dynamics of colloidal thin films of varied thickness

Experimental Setup

Interfacial Force Microscopy (IFM)

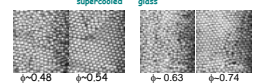
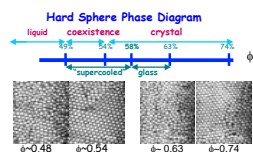


- Film thickness: nm to mm
- Compressible sample cell
- Shear force measurement
- Direct structural & dynamic visualization
- Single particle resolution!

Systems Explored

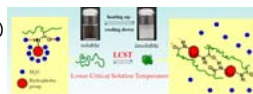
Model "hard-sphere" sterically stabilized poly(methyl methacrylate), $d = 1.2 \mu\text{m}$

- Bulk volume fraction: $\phi = 0.43-0.61$
- Suspended in density and refractive index matched solvents



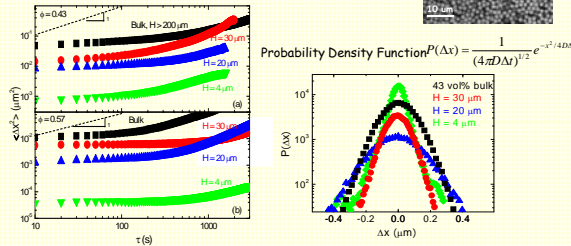
Charge stabilized "sticky spheres" poly-(N-isopropylacrylamide) (PNIPAM)

- Lower Critical Solubility Temperature (LCST) close to body temperature
- Synthesized via Emulsion Polymerization
- Suspended in aqueous media (~6% polydispersity)



The Slow Down of PMMA Mobility by Confinement

Mean Square Displacement (MSD) $\langle \Delta x^2 \rangle = \langle (x(t) - x(\tau))^2 \rangle$



- Consistent reduction in mobility with decreasing film thickness
- Onset of an apparent "super-cooled" regime occurs for $\phi = 0.43$ at $H = 20 \text{ nm}$ where cage trapping is apparent for $t < 100 \text{ s}$, followed by long-time diffusive behavior
- Longer Plateau in MSD with decreasing film thickness

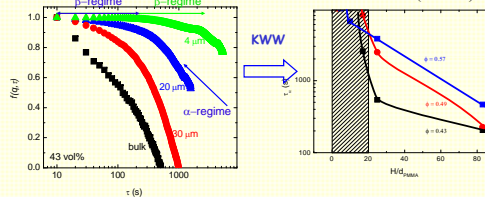
Structural Relaxation Impeded

Intermediate Scattering Function

$$\langle F_s(\vec{q}, \tau) \rangle = \frac{1}{N} \sum_{j=1}^N \langle \exp(i\vec{q} \cdot [\vec{r}_j(\tau) - \vec{r}_j(0)]) \rangle$$

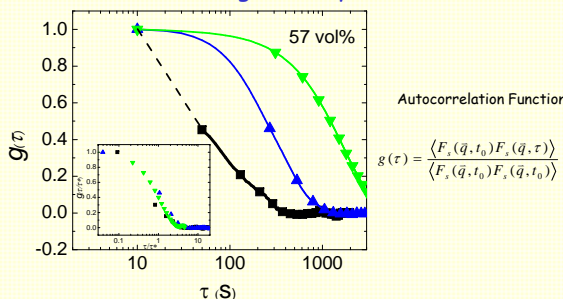
Kolrausch-Williams-Watts (KWW) formula

$$f(q, \tau) = A \exp\left(-\left(\frac{\tau}{\tau_\alpha}\right)^\beta\right)$$



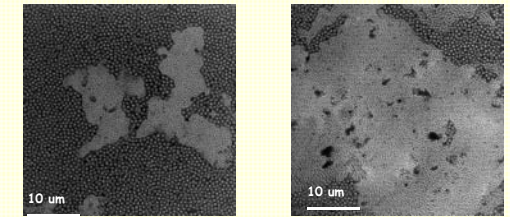
- Rapid decay for the bulk and at $H = 30 \text{ nm}$ (fluid)
- Two α step decay at $H = 20 \text{ nm}$ ("supercooled" liquid)
- Non-ergodicity sets in at $H = 20 \mu\text{m}$
- α -relaxation time diverges at $H/d \gg 20$ layers for all volume fractions

Deducing Memory Effects



- Simple Langevin decay for $\phi = 0.43$ bulk sample as well as $H/d = 25$.
- The negative dip in the autocorrelation function ($\phi = 0.43$, $H/d = 20$) is indicative of backscattering, or "recoil" where the cages behave as elastic solids.
- As film thickness decreases to $H < 10d_{PMMA}$, the correlation function decay is significantly retarded yet backscattering is not observed.

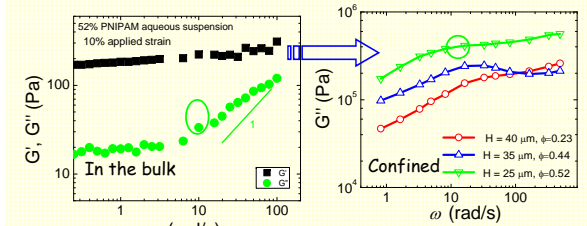
PNIPAM Gelation under Confinement



In the bulk

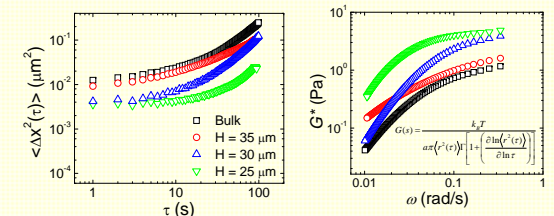
$H = 25 \mu\text{m}$

Enhanced Viscoelasticity of Hydrogel Films (Ensemble-Averaged)



- Viscosity increases by orders of magnitude upon confinement induced gelation.
- terminal relaxation time shifts to longer timescales as decreasing film thickness.

Film Thickness dependences of Microrheology (A Single Particle Level, Local Environment)



Summary

"Hard Sphere" PMMA system

- A glass transition can be induced
- "sooner" by confinement
- Scaling behavior evident
- $\sqrt{\text{MSD}}$; $\sqrt{\text{ISF}}$; $\sqrt{\tau_\alpha}$
- Confinement reveals new length scale Critical dimension for glassy behavior: $H/d \sim 15-20$

Attractive PNIPAM system

- Divergence in gel structure size
- Viscoelastic enhancement as film thickness is reduced
- Reveals new length scale for onset of the gel transition

Acknowledgments

