INVESTIGATING THE NANOSCALE STRUCTURAL PROPERTIES OF COLLOID-POLYMER SYSTEMS USING MICRORHEOLOGY TECHNIQUES

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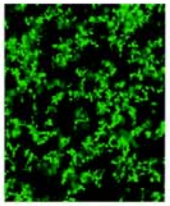
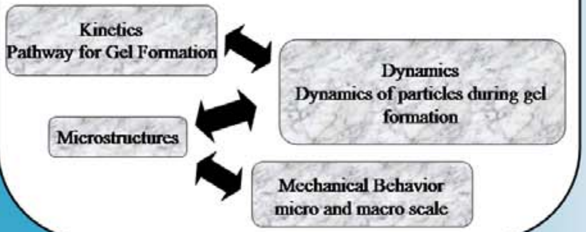
Complex Fluids: Colloidal Gels and Suspensions

Colloidal Gels

- Show a wide range of structural and mechanical properties
- Exhibit both fluid-like and solid-like behavior with the transition between the two taking a variety of different forms
- Their mechanical behavior depends
  - On the size and shape of the particles
  - The interparticle forces, the solid loading
  - The spatial arrangement of the particles (or the microstructure of a particle network)





Kinetics
Pathway for Gel Formation

Dynamics
Dynamics of particles during gel formation

Microstructures

Mechanical Behavior
micro and macro scale

Microrheology: A Technique to Study Fast and Slow Relaxation Times and Time-Dependent Dynamics

Tracer particle microrheology enables one to determine the structure and rheology of polymer network by measuring the thermally-driven motion of embedded probe particles

Relates MSD, <Δr2(t)> , of colloidal particles to the linear viscoelastic properties of material

Because of its large frequency range (0.1-106 Hz), minimal perturbation, and sensitivity of local response, microrheology is becoming increasingly important for probing individual cells and cytoskeletal biopolymers

Probes very localized mechanical properties using tracer particles embedded in a complex fluid

Tracer particles embedded in a Gel network

•Purely viscous fluids:

$\langle \Delta r^2 \rangle = 2nDt$

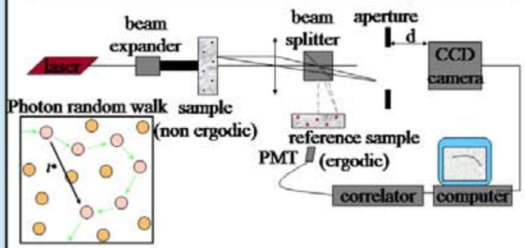
$D = k_B T / 6\pi \eta a$ (Stokes-Einstein Equation)

•Elastic Materials:

$\kappa = 3\, k_B T / \langle \Delta r_m^2 \rangle$

Multispeckle Diffusive Wave Spectroscopy

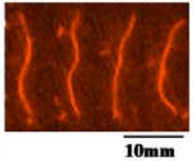
A combination of 2-cell technique and Multispeckle DWS



- 2-cell technique to overcome the problem of non-ergodicity
- Multispeckle for studying slow relaxation processes
- Extended range of relaxation times: from a few nanoseconds to minutes or hours
- Length scales below 1 nm up to a few microns
- Elastic properties range from 1 Pa to several kPa

F-actin : A Semi-Flexible Polymer

Fluctuations of a single actin filament



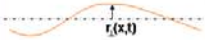
Large persistence length

$$L_p \equiv \frac{\kappa}{k_b T} \approx 15\text{-}20\,\mu\text{m}$$

Anisotropic Dynamics

Transverse dynamics $\langle \Delta r_\perp^2(t) \rangle \sim t^{3/4} \kappa^{-1/4}$

Longitudinal dynamics $\langle \Delta r_\parallel^2(t) \rangle \sim t^{7/8} \kappa^{-5/8}$

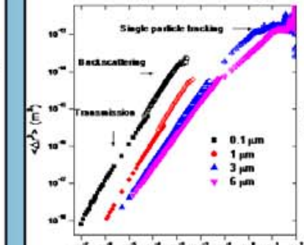


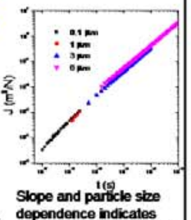
Transverse dynamics dominate at high frequencies

$(\langle \Delta r^2(t) \rangle \sim t^{3/4})$

Effect of Probe on F-actin Dynamics

BSA-coated particles in 0.63mg/ml F-actin



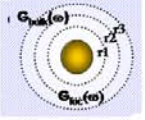


Slope and particle size dependence indicates free diffusion of particles

$J(t) = (\pi a \langle \Delta r^2(t) \rangle) / (k_B T)$

BSA-coated beads are insensitive to polymer network at short times

Viscoelastic Shell Model

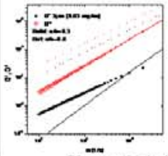


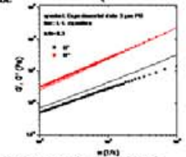
$$G_{bulk}(\omega)/G_{measured}(\omega) = \frac{4\beta^6\kappa'^2 - 9\beta^5\kappa\kappa' + 10\beta^3\kappa\kappa' - 9\beta\kappa'^2 - 15\beta\kappa' + 2\kappa\kappa'}{2(\kappa' - 2\beta^5\kappa')}$$

$\beta = a/b \qquad \kappa = G^*_{bulk} / G^*_{loc}$

$\kappa' = \kappa - 1$

$G^*_{loc} = i\omega t$ (viscous) $\qquad G^*_{loc} = G' + iG''$ (viscoelastic)





Shows that viscoelastic property involved depletion layer, and the layer thickness is two times larger than particle radius

Conclusions

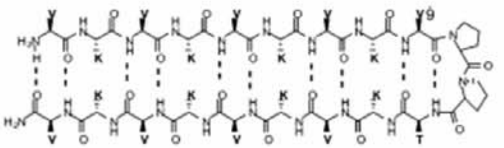
- BSA coated particle is less sensitive to network corresponding with depletion of polymer surrounding the probes
- We proposed that the depletion is due to size exclusion
- The adhesion of particles to F-actin shows good agreement with the trend of bulk modulus
- This adhesion results in a breakdown of the generalized Stokes-Einstein relationship dependence on particle size

Acknowledgements

This work is supported by the Army Research Laboratory through the Composite Materials Research program.

MAX1(β-hairpin Peptide)

A small peptide, forms responsive hydrogels
Propensity to self-assemble by intramolecular folding



MAX1: VKVKVKVKV^{D}PPTKVKVKVKV-NH$_2$

K (Lysine) – $(CH_2)NH_3^+$
(hydrophilic part)

V (Valine) – $CH(CH_3)_2$
(hydrophobic part)

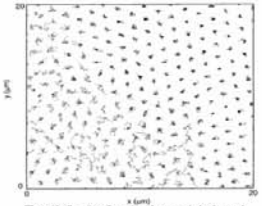
Multiple Particle Tracking Method for Investigating the Kinetics and Microstructure of the Gelation Process

Use Fluorescence Microscope to grab images and study the gelation process

- Measure confinement of particles with video microscopy
- Particle center found using centroid method (accurate to ~15nm)

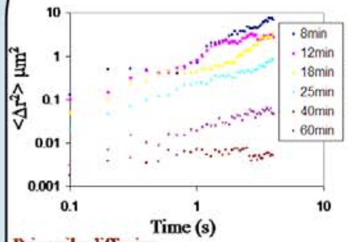
IDL software for tracking multiple particles

A typical fluorescent image

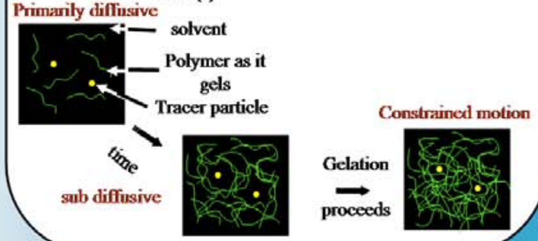


Particle trajectories obtained from IDL

MAX1-0.15%

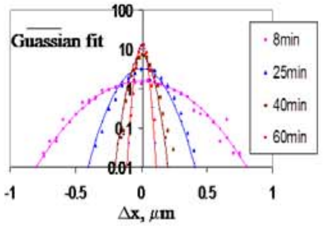


- $<\Delta r^2(t)>$ decreases with time
- Attains plateau at long time intervals
- Indicating that the particles get constrained within the network



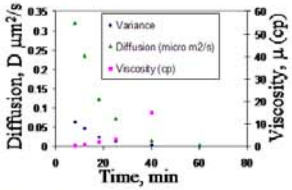
Probability Distribution Function: MAX1

Probability distribution function
$P(\Delta x,t) = (4\pi Dt)^{-1/2} \exp(-<\Delta x^2>/4Dt)$



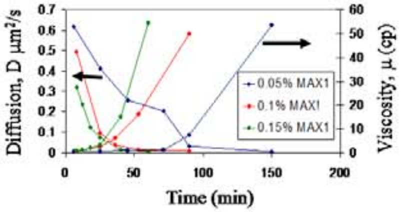
Variance is a measure of diffusion coefficient (D)

Transient Local Properties of MAX1 as Gelation Progresses



- $<\Delta r^2(t)>$ decreases as gelation process proceeds
- Complex viscosity increases monotonically with time
- D decreases monotonically with time

Effect of Concentration on MAX1 Gelation Dynamics



Time for gelation decreases with decrease in peptide concentration

Future Work

- Investigate the microstructure of the gel network using different probe particles
  - Effect of probe particle size
  - Effect of surface properties of the probe
- Investigate the inhomogeneity of the gel by fluorescently staining the self-assembled peptide
  - using confocal microscopy
- Extend the work to composite and bio materials

Acknowledgements:
Funding provided by
CCM (Center for Composite Materials)
&
University of Delaware Research Foundation