Colloidal Gels and Glasses

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NASA , NSF, Infineum

- Relaxation in colloidal glasses
- Stress bearing chains for solid-like behavior of glass
- Attractive colloidal glasses
- Scaling of the Viscoelasticity of Colloidal Glasses
- Possible models for attractive glass transition

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

Glass Transition

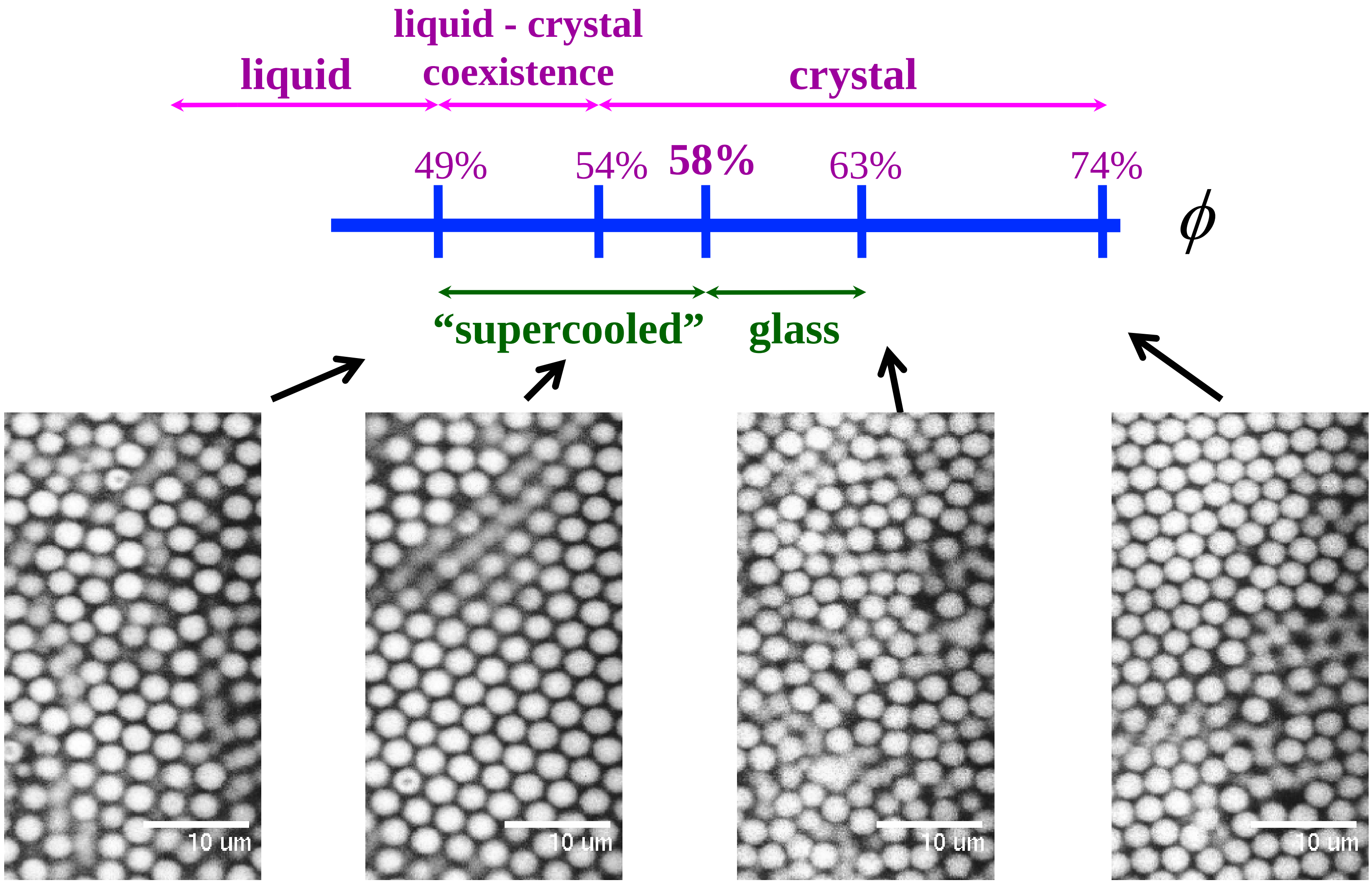
- Widely studied but poorly understood
- No structural difference between liquid and glass
- Difference defined by time scales

  → divergent structural relaxation time

New state of matter, or very slow liquid?
What happens microscopically?

Characterized by structural relaxation

Repulsive Colloidal Glasses



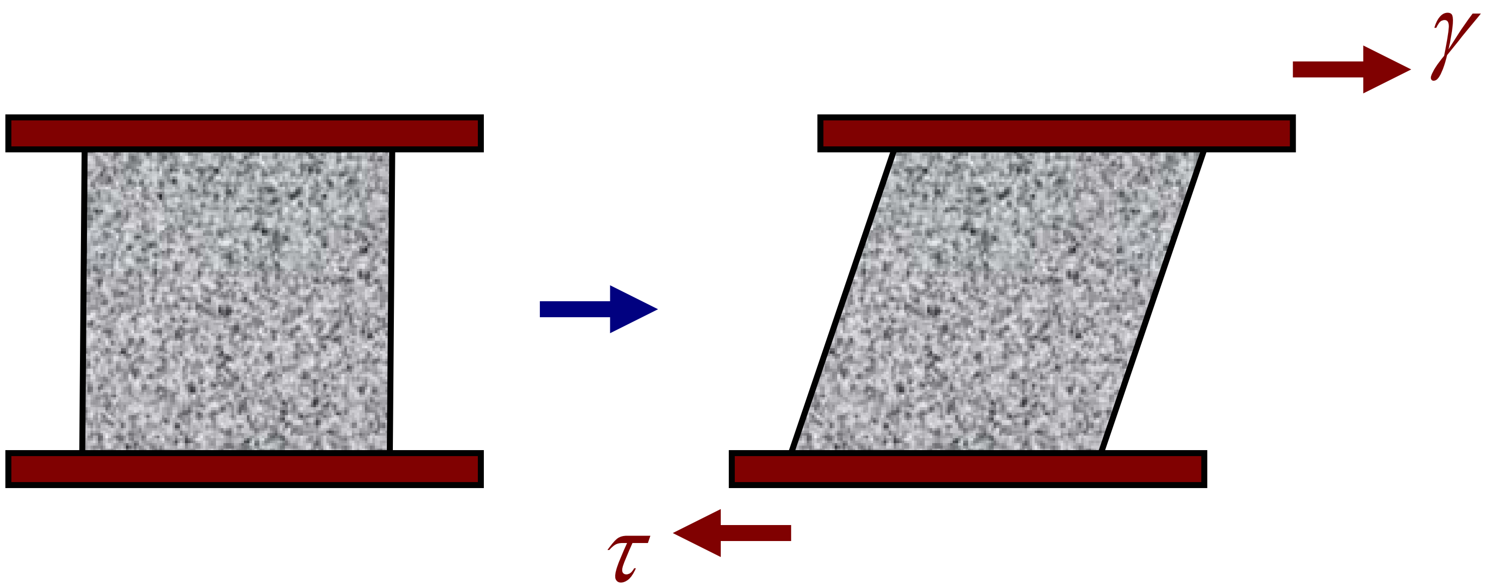
$\phi_{\text{liquid}} \approx 0.48$

$\phi_{\text{xtal}} \approx 0.54$

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

Maximum packing $\phi_{\text{HCP}} = 0.74$

Viscoelasticity of Glasses



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

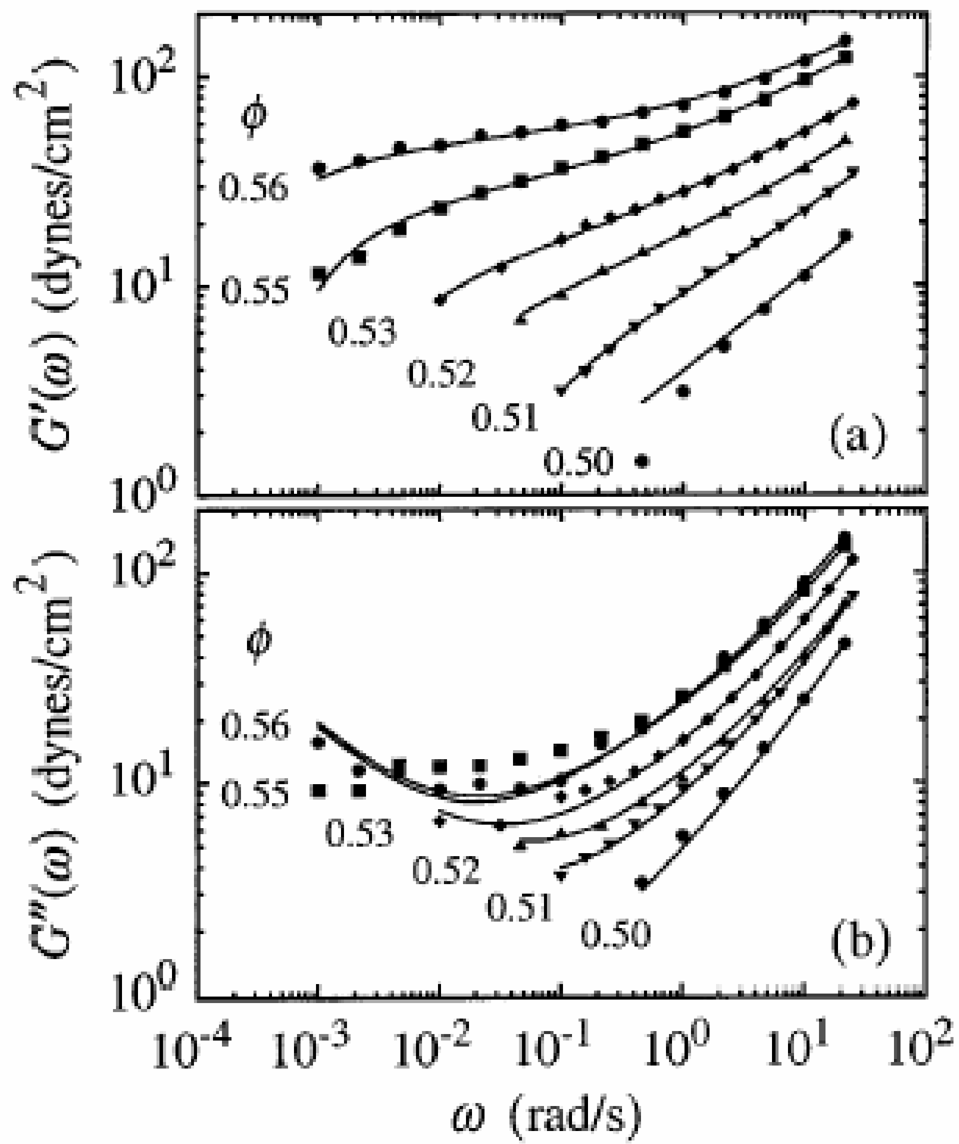
Solid: $\tau = G\gamma$

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

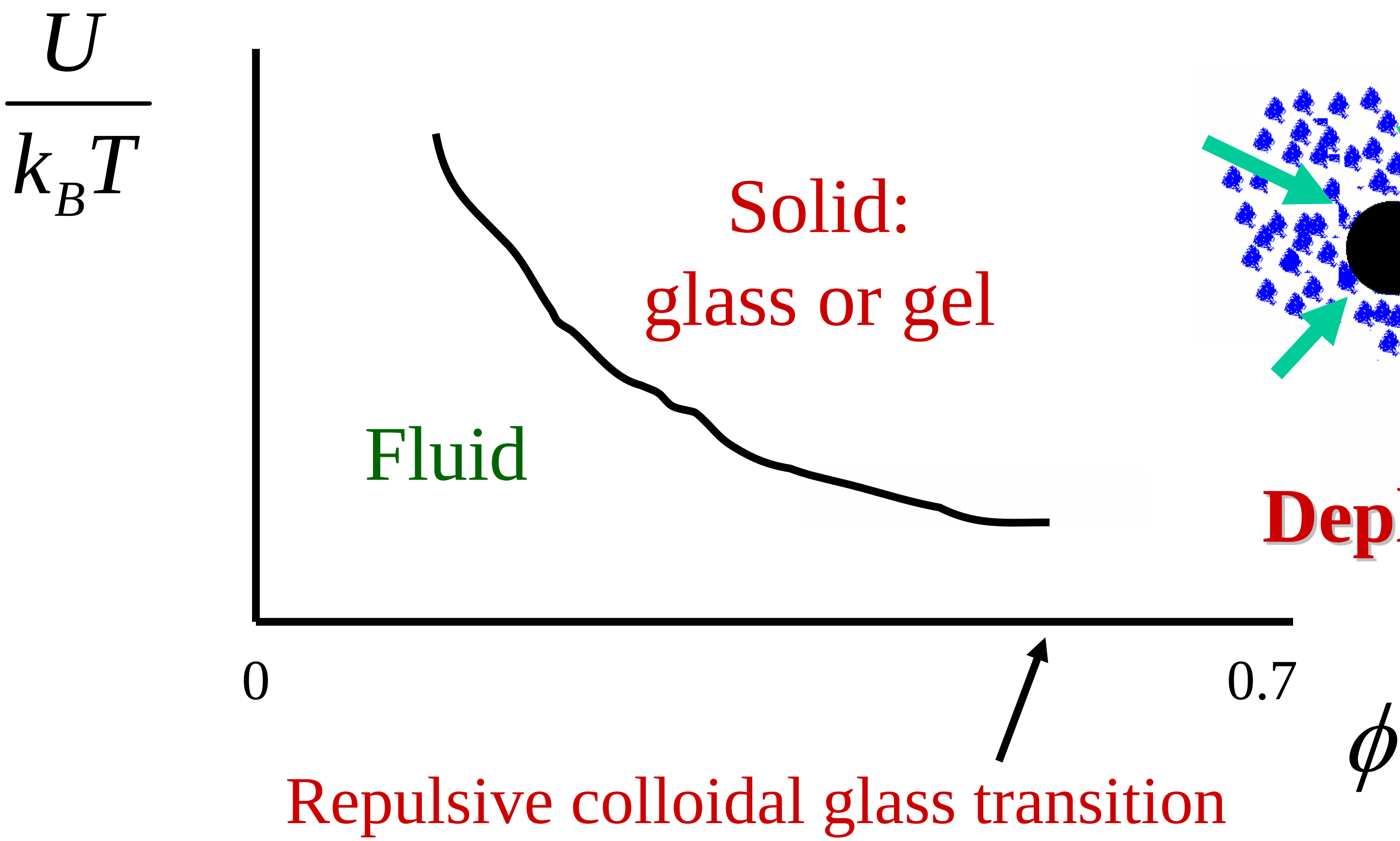
$$\longrightarrow \tau = \left[G'(\omega) + iG''(\omega) \right] \gamma$$

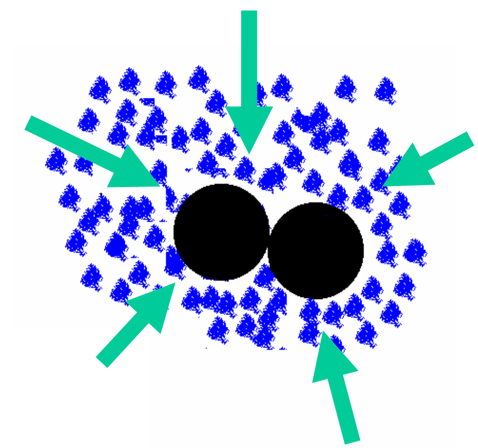
Elastic   Viscous

Rheology of Hard Spheres



Colloidal Glasses: Attractive and Repulsive



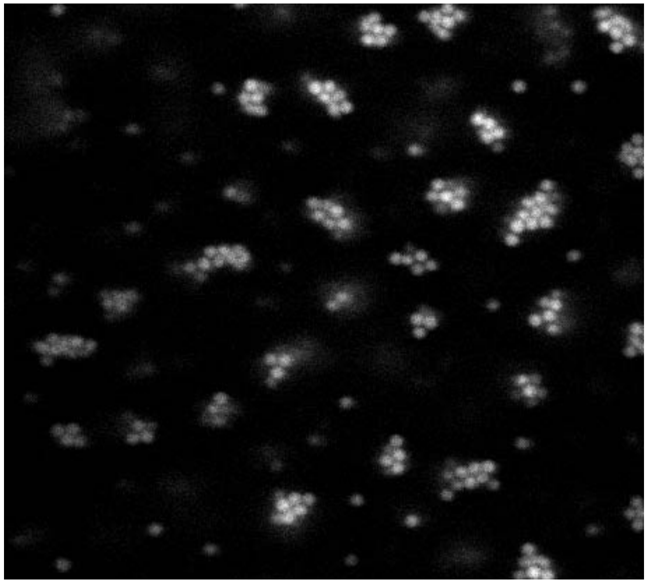


Depletion

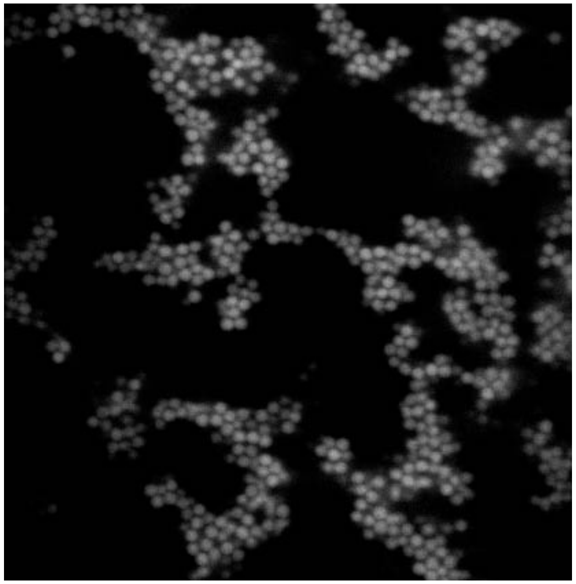
Gelation: Glass Transition of Clusters

“Jamming” of Clusters to form gel

$\phi = 0.06$, $U = 6.0\ k_BT$



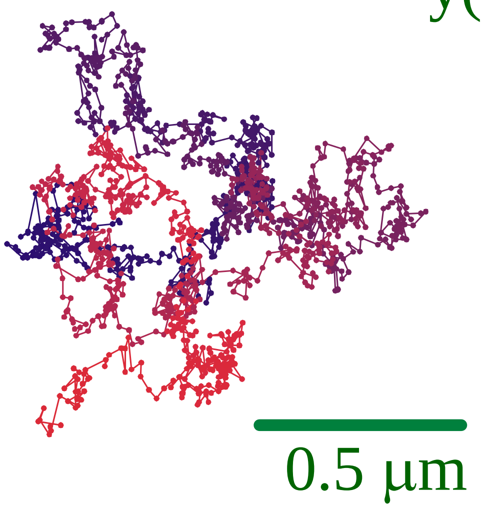
Fluid-Clusters

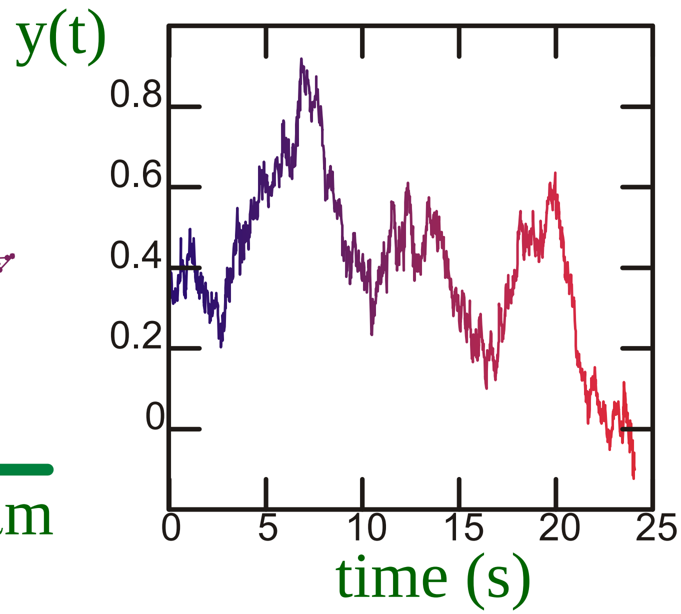


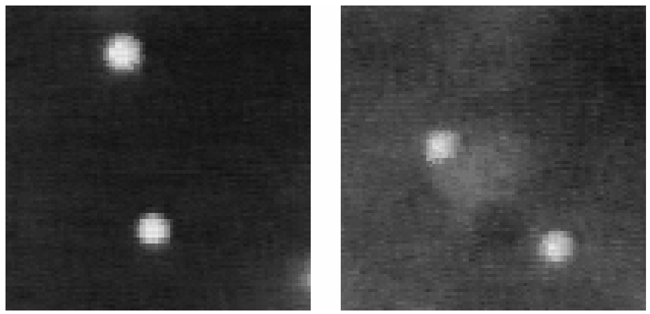
Gel

Brownian Motion

(2 μm particles, **dilute** sample)







Leads to
normal diffusion: $\langle \Delta x^2 \rangle = 2Dt$

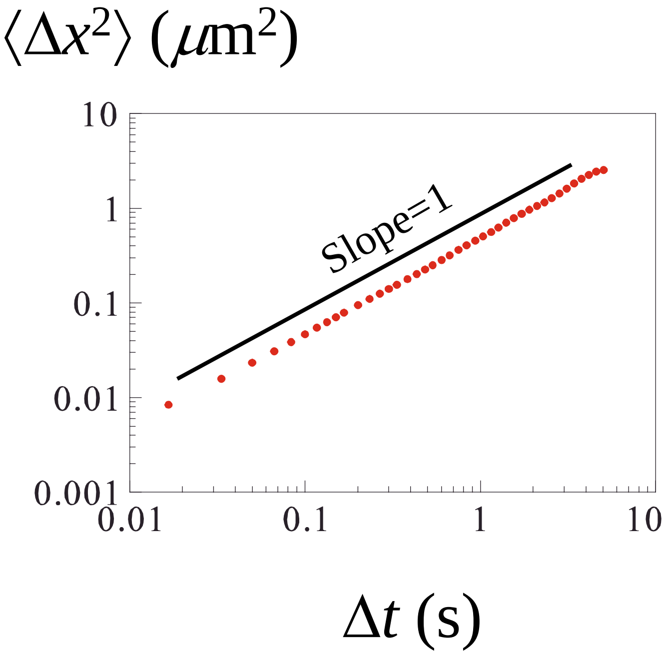
$$D = \frac{k_B T}{6\pi\eta a}$$

Particle
size a

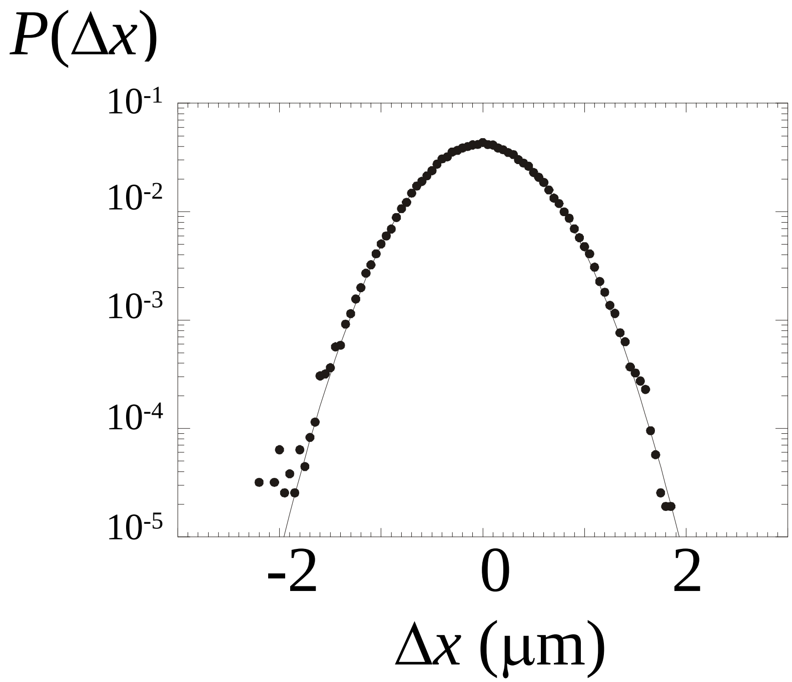
viscosity η

Diffusion: **dilute** samples

Mean square displacement:



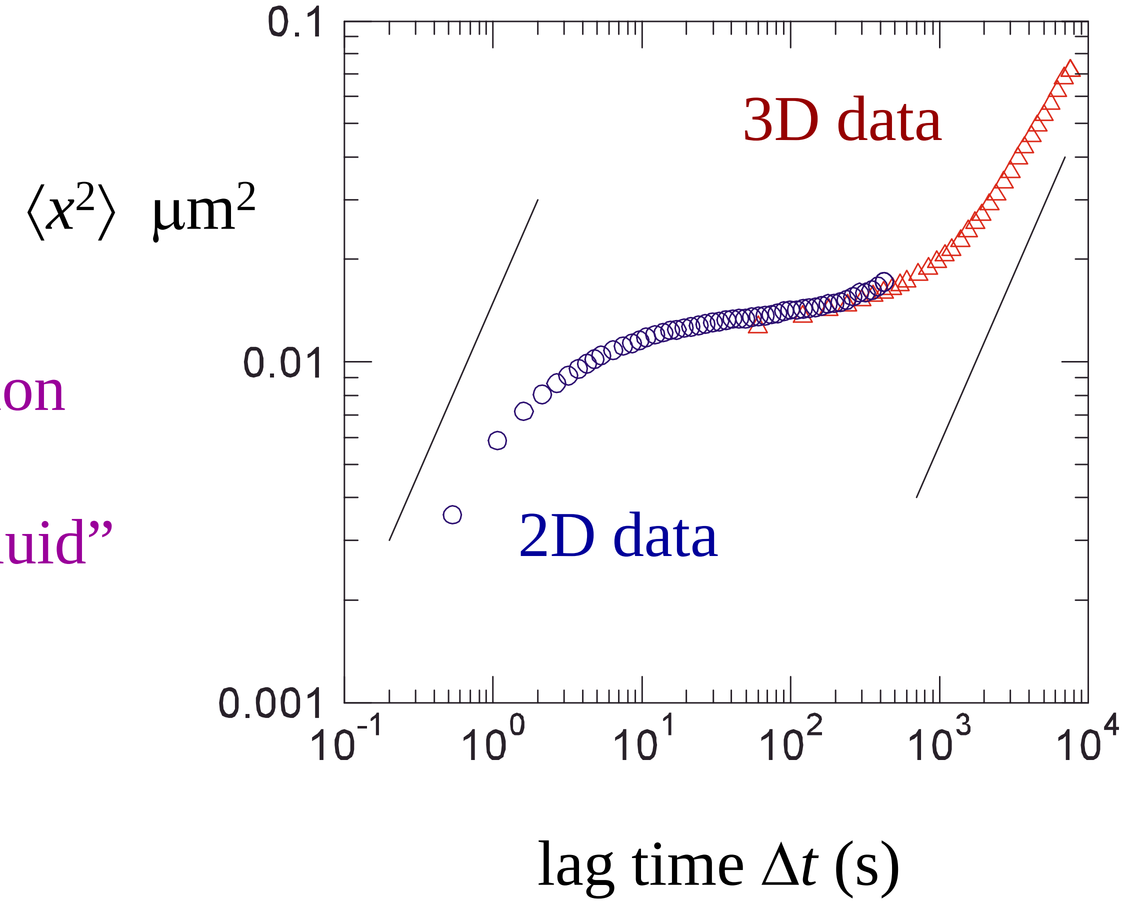
Displacement distribution function:



Δt=0.5s

Gaussian

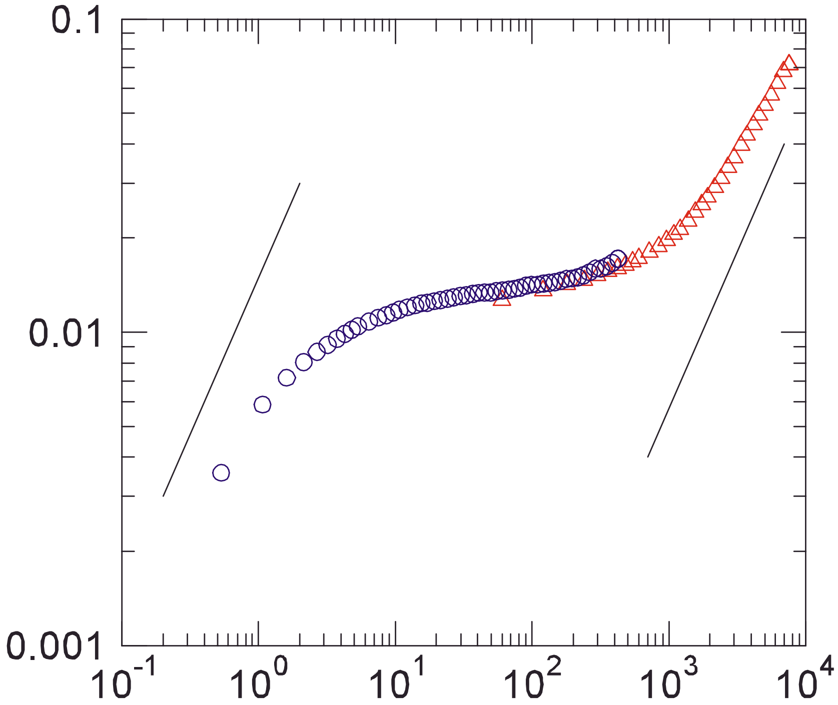
Mean square displacement

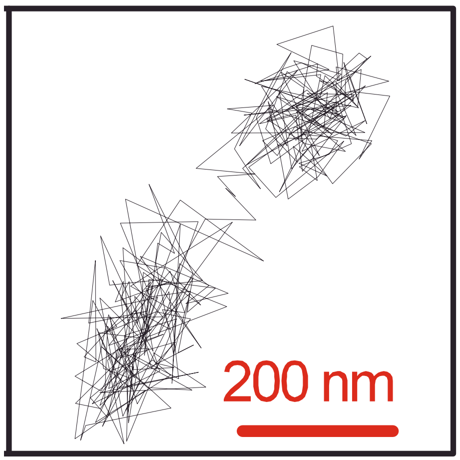


Volume fraction
ϕ=0.53
"supercooled fluid"

Mean-squared displacement

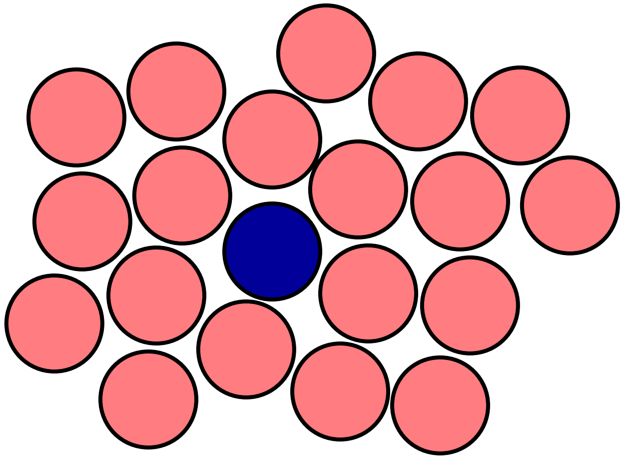
ϕ=0.53 -- “supercooled fluid”





ϕ=0.56, 100 min
(supercooled fluid)

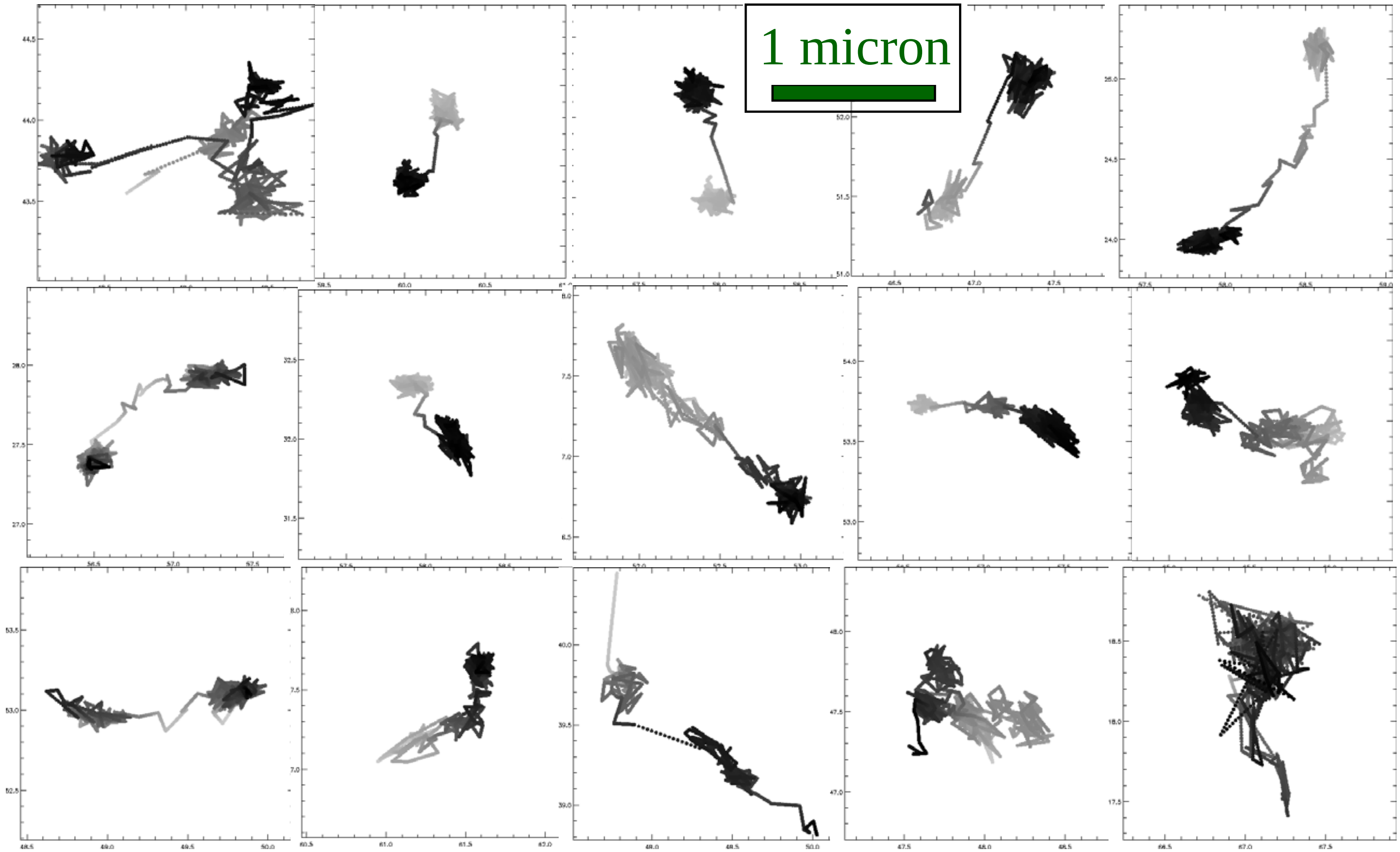
Cage trapping:



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

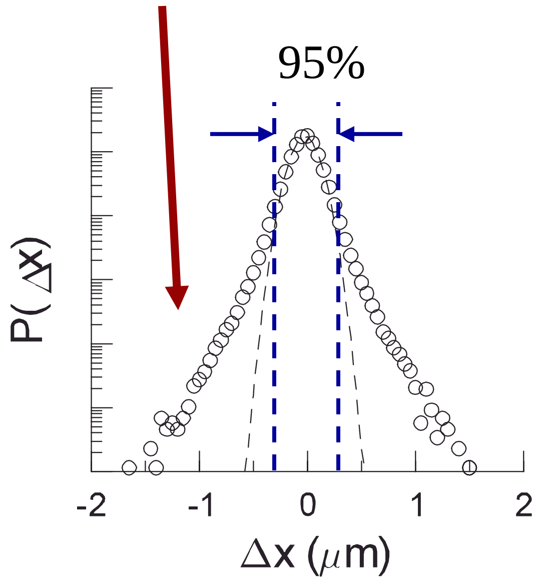
Trajectories of "fast" particles, ϕ=0.56

shading indicates depth



Time Scale and Length Scale

top 5% = tails
of Δx distribution



ϕ=0.53, supercooled fluid

Time scale:

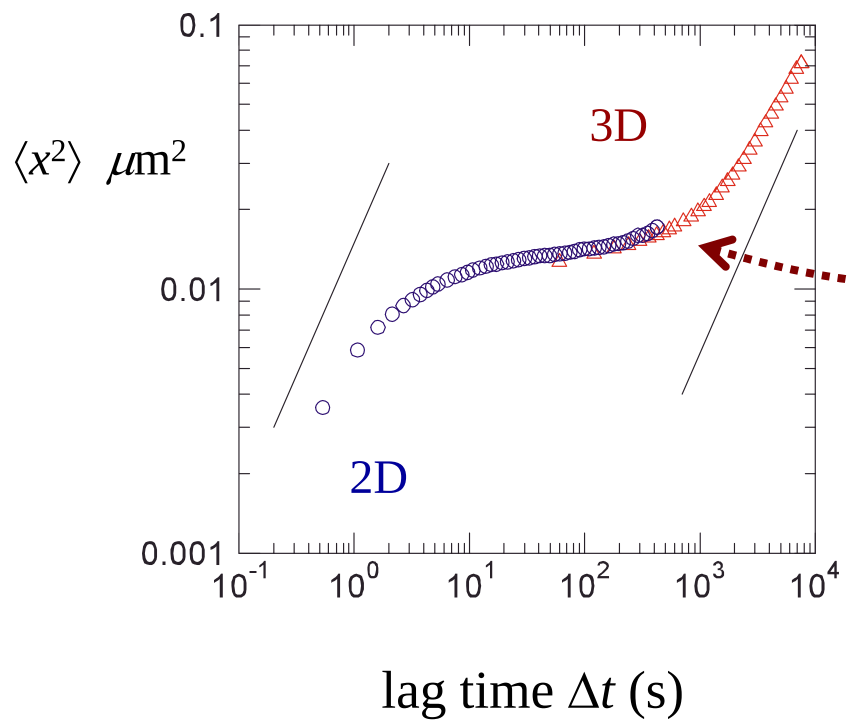
Δt^* when nongaussian parameter α_2 largest

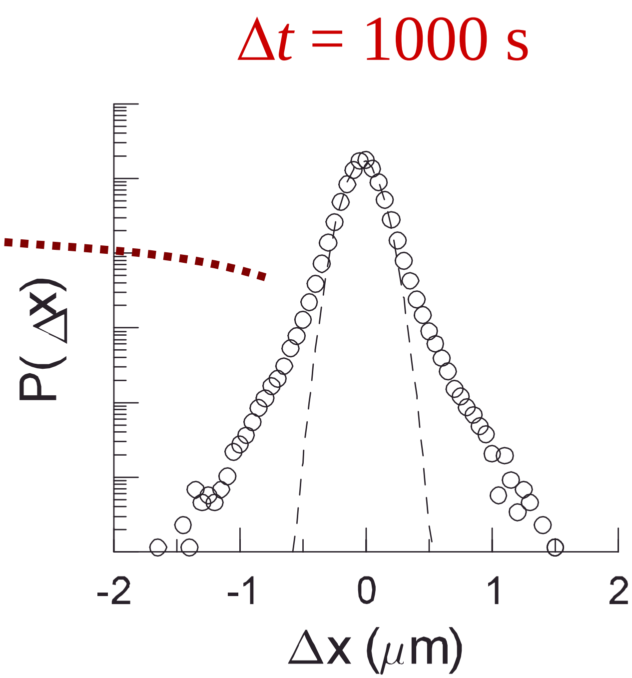
Length scale:

Δr^* on average, 5% of particles have $\Delta r(\Delta t^*) > \Delta r^*$

$\boxed{\approx \text{cage rearrangements}}$

Displacement distribution function



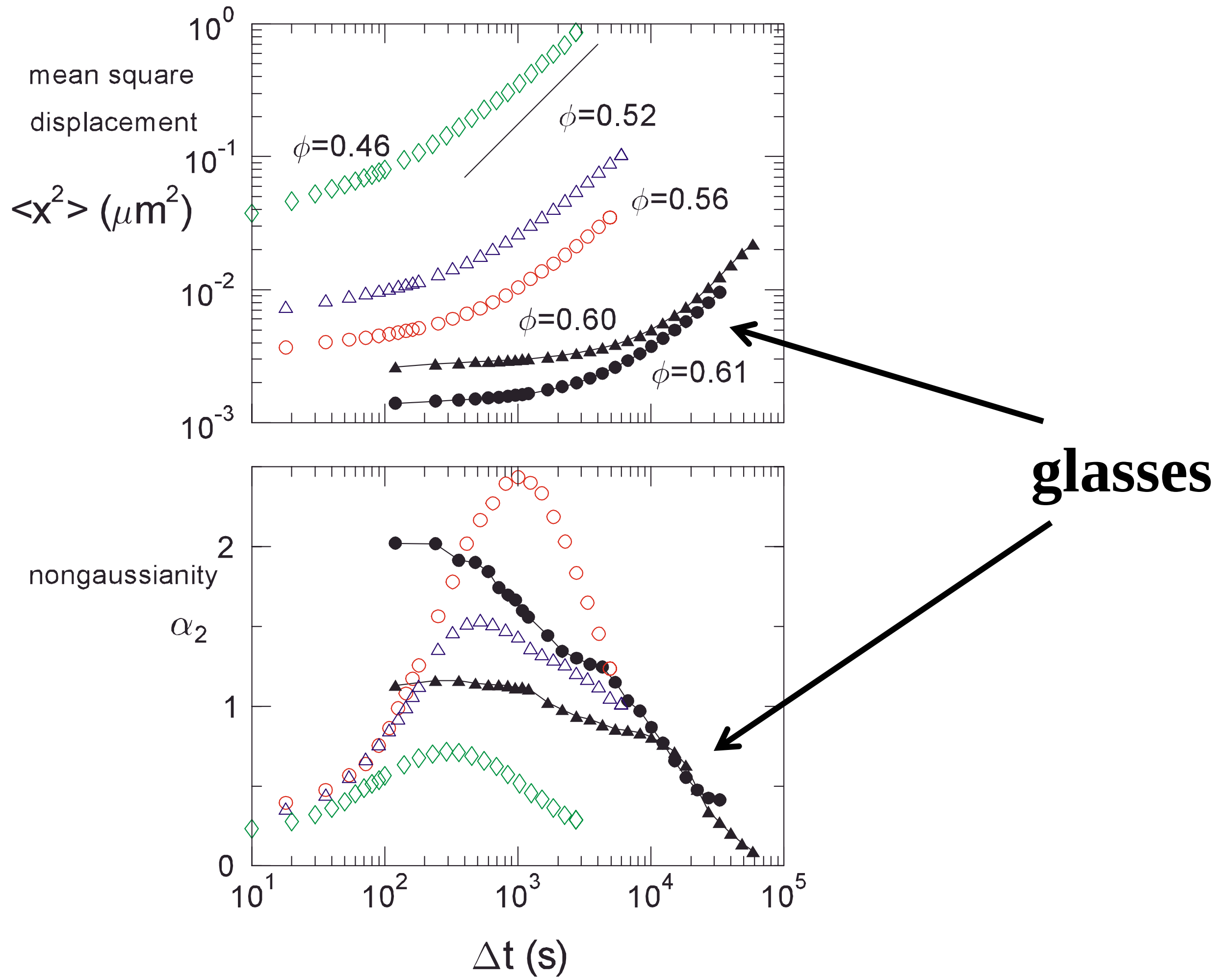


ϕ = 0.53: "supercooled fluid"

Nongaussian Parameter

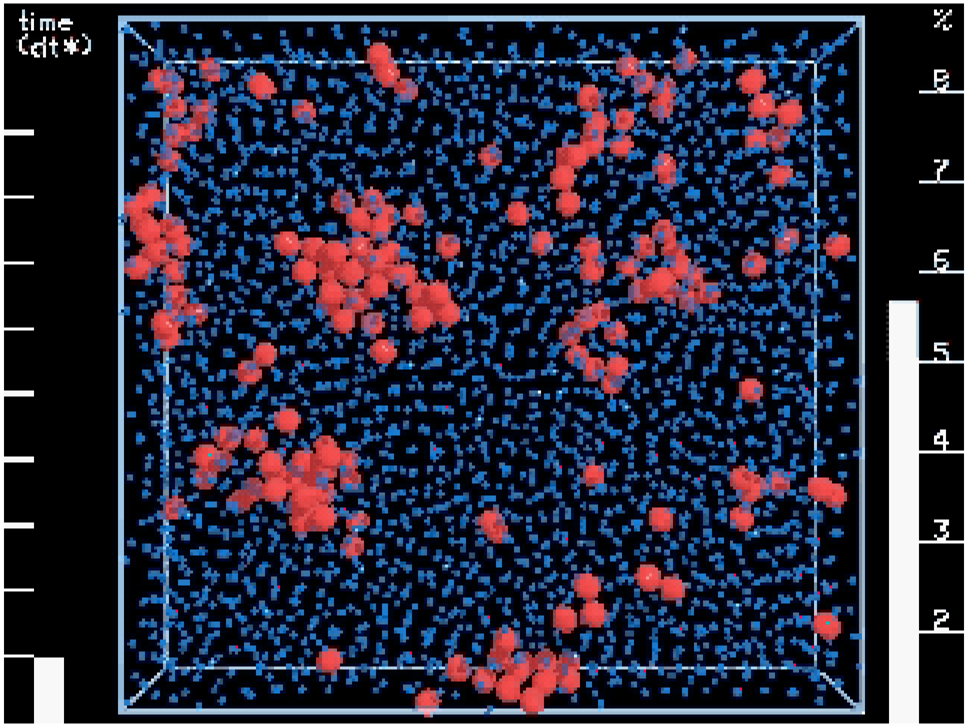
$$\boxed{\alpha_2 = \frac{\langle x^4 \rangle}{3\langle x^2 \rangle^2} - 1}$$

How to pick Δ*t** for glasses?



Structural Relaxations in a Supercooled Fluid

time

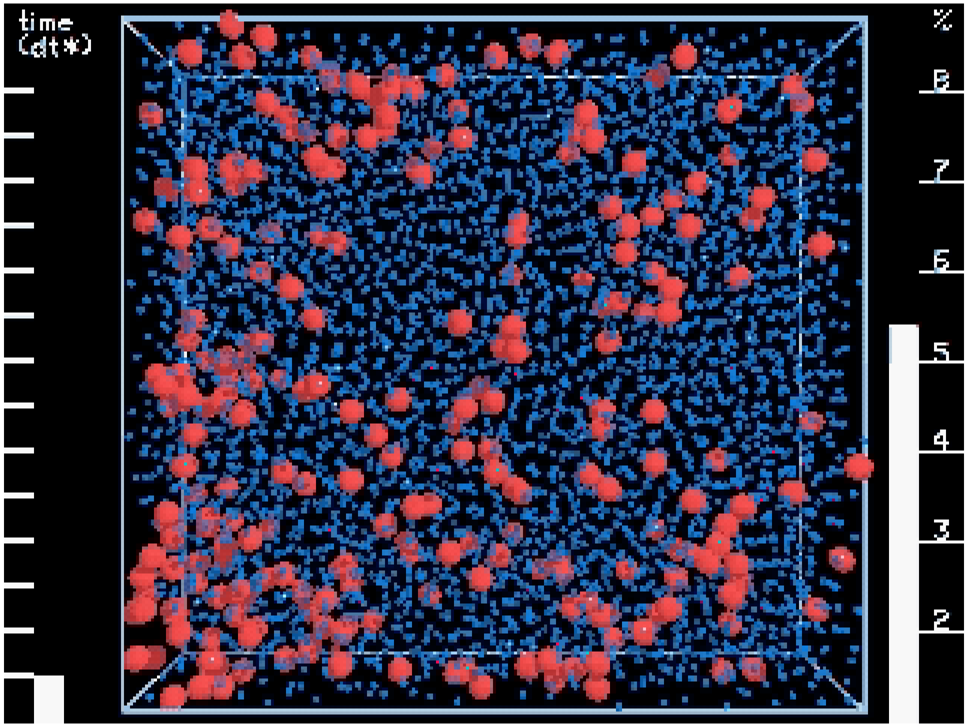


Number of relaxing particles

Relaxing particles are highly correlated spatially

Structural Relaxations in a Glass

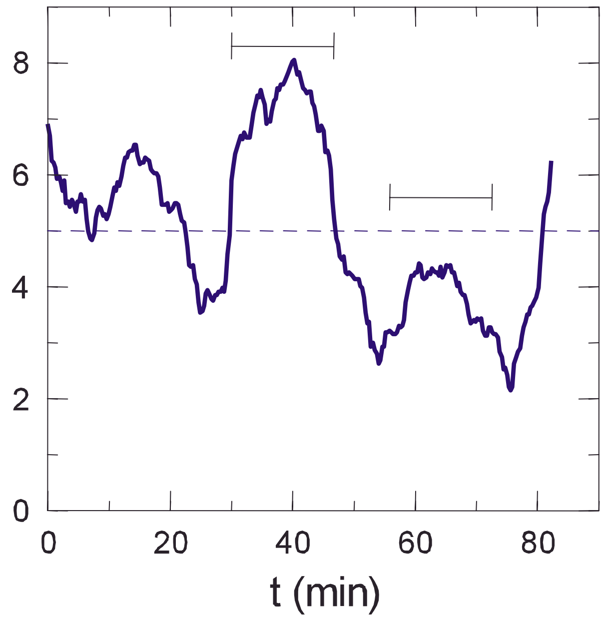
time



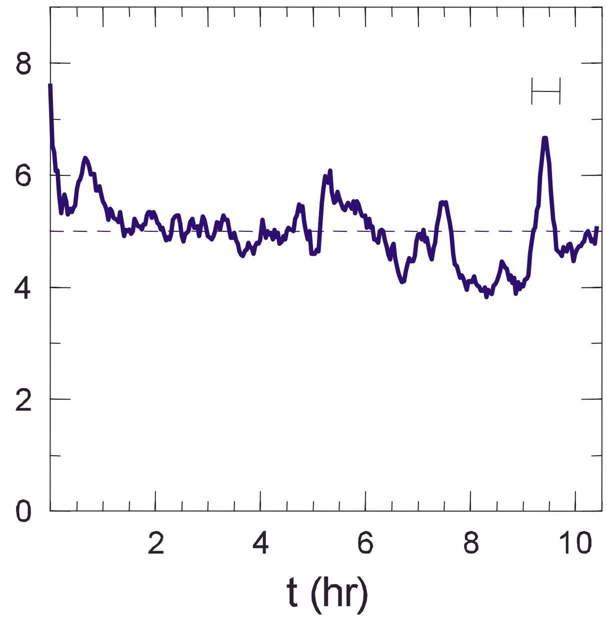
Number of relaxing particles

Relaxing particles are NOT correlated spatially

Fluctuations of fast particles

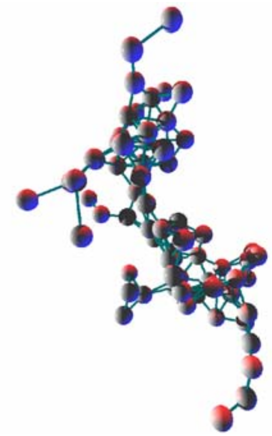


Supercooled fluid $\phi = 0.56$

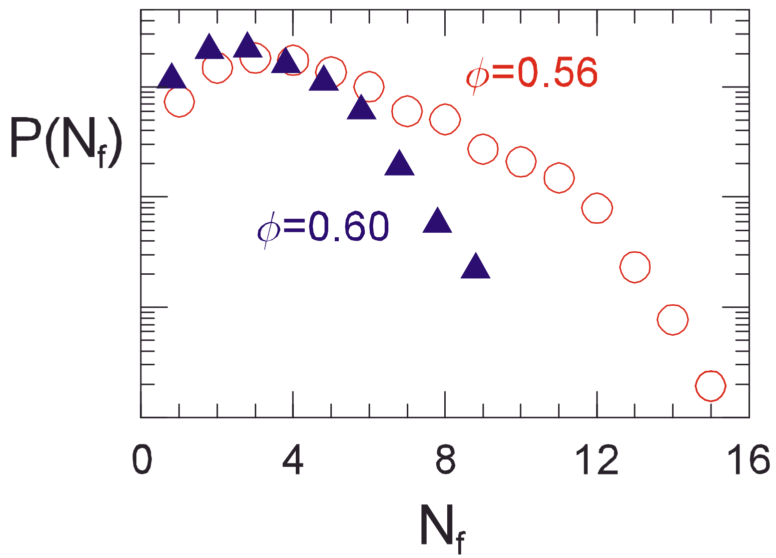


Glass $\phi = 0.61$

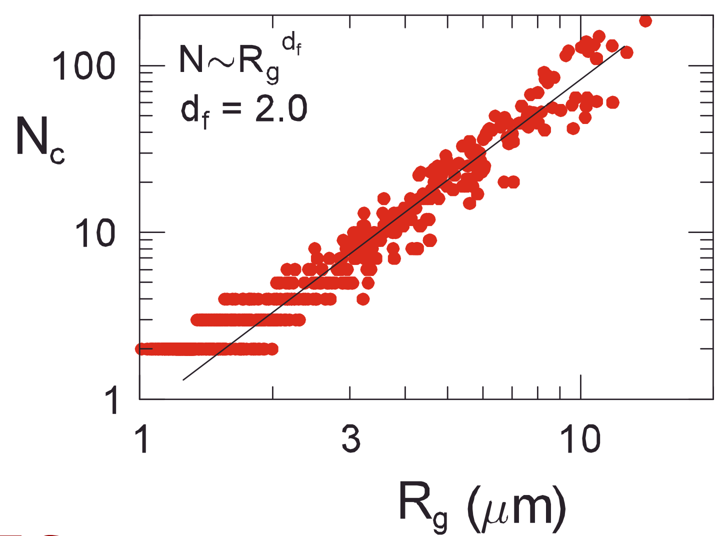
Cluster Properties



Number N_f of fast neighbors to a fast particle:



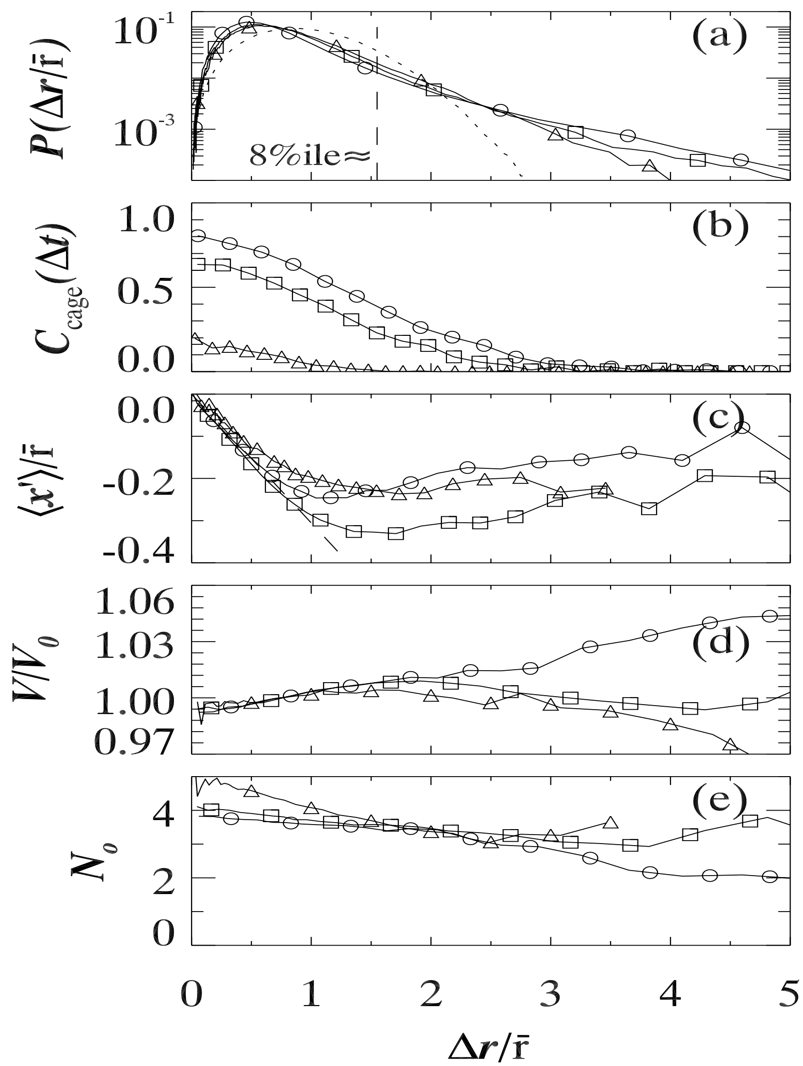
Fractal dimension:



$\phi = 0.56$

supercooled fluid

Dependence on Step Size



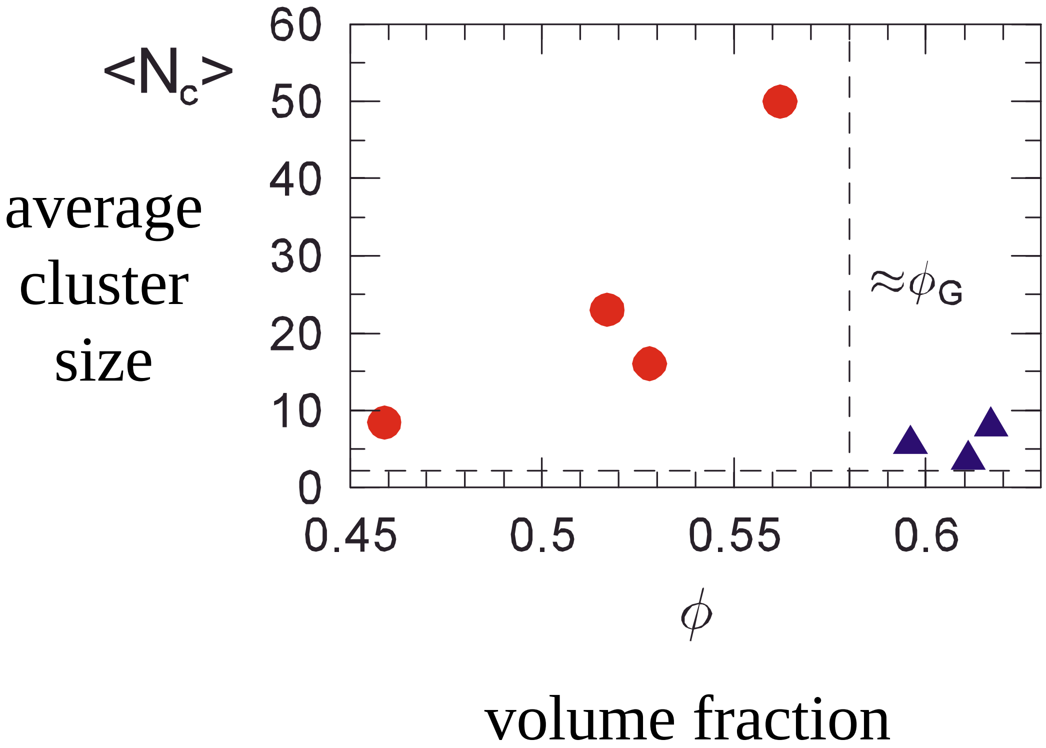
Bigger step → less likely

Bigger step → cage breaking

Bigger step → more *V*

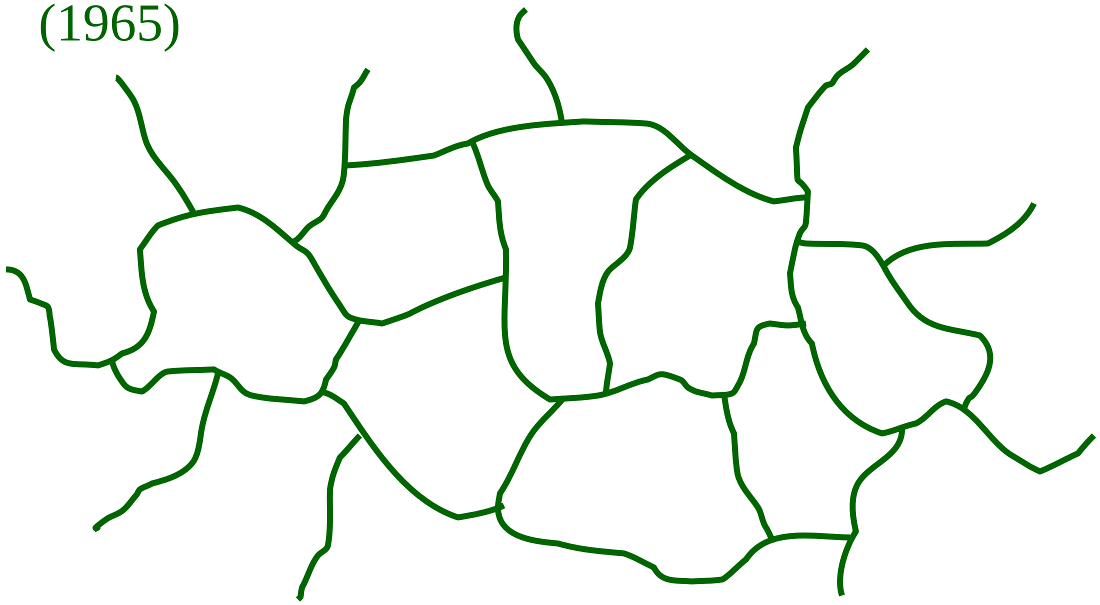
Bigger step → less crystalline

Cluster size grows as glass transition is approached



Dynamical Heterogeneity:
possible *dynamic* length scale

Adam & Gibbs: "**cooperatively rearranging regions**"
(1965)

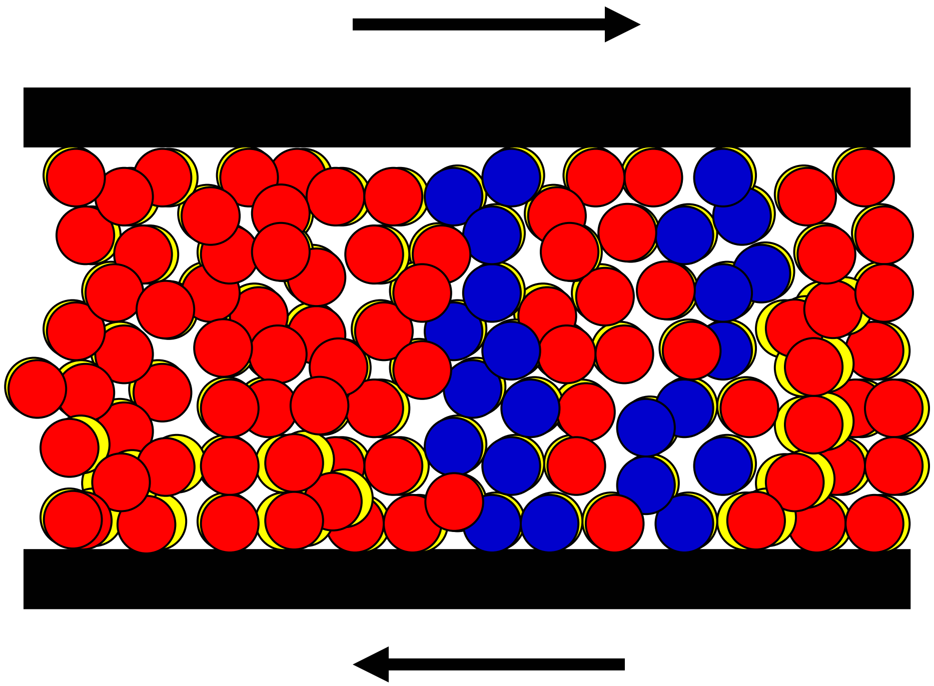


Simulations: •**Glotzer, Kob, Donati, et al (1997, Lennard-Jones)**

Photobleaching: •Cicerone & Ediger (1995, o-terphenyl)

NMR experiments: •Schmidt-Rohr & Spiess (1991, polymers)

What is a Glass?

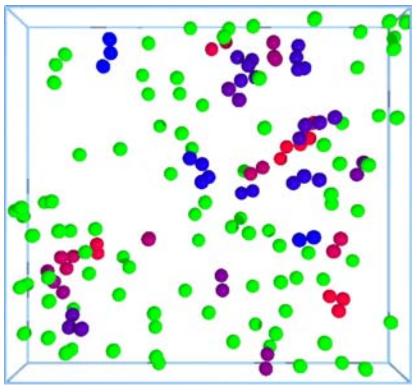


•Glass must have a low frequency shear modulus

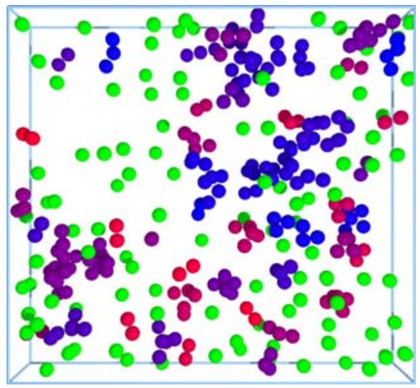
•Must have force chains to transmit stress

$\Delta r(\Delta t)$ gives no obvious definition of slow

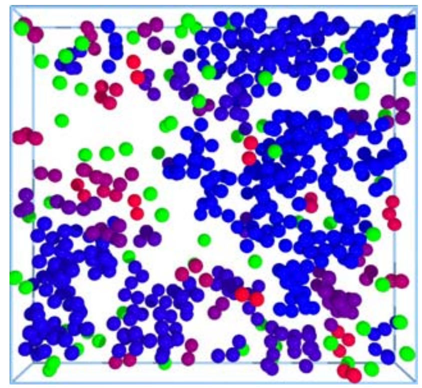
$\phi = 0.56$



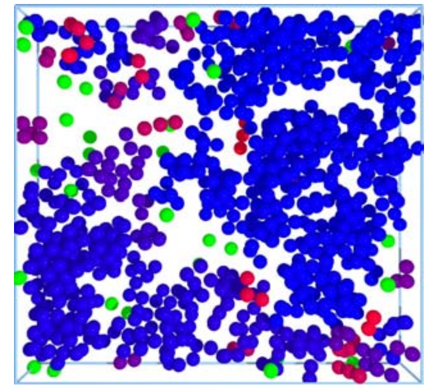
5%



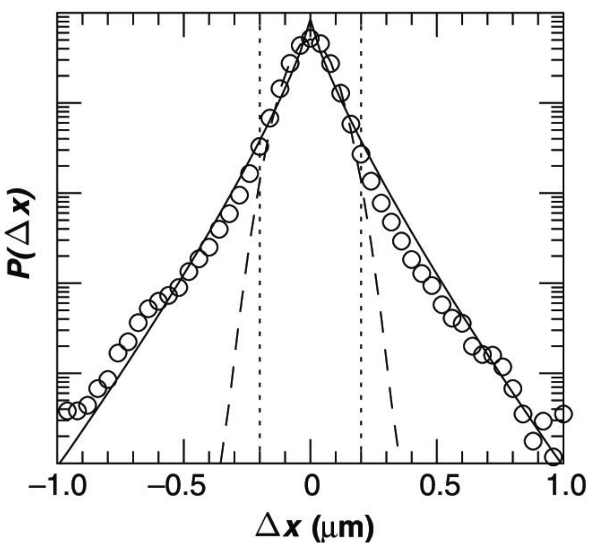
10%

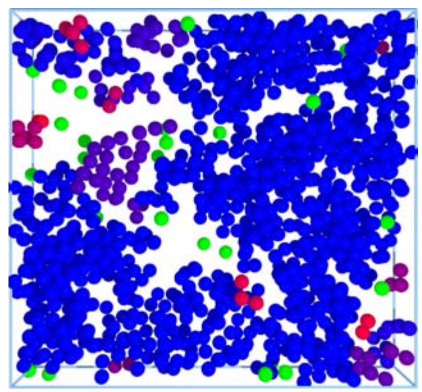


20%



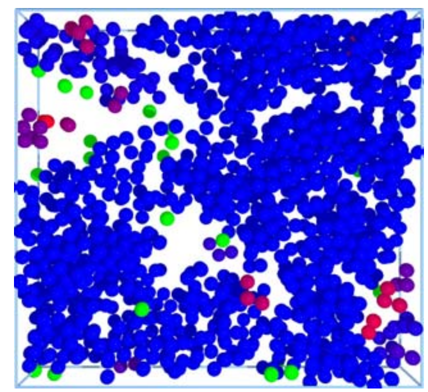
30%





35%

(first percolating cluster)

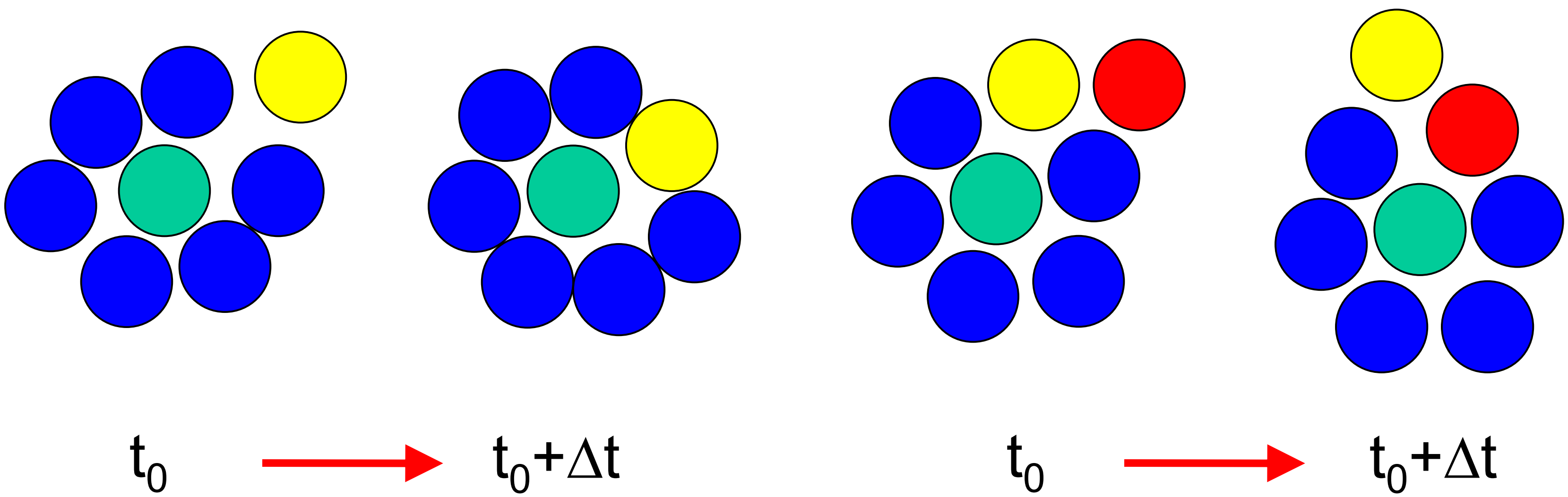


40%

E.R. Weeks et. al, Science **287**, 627 (2000)

Topological Change: $\Delta nn\ (\Delta t)$

Identify nearest neighbors, calculate $\Delta nn(\Delta t)$

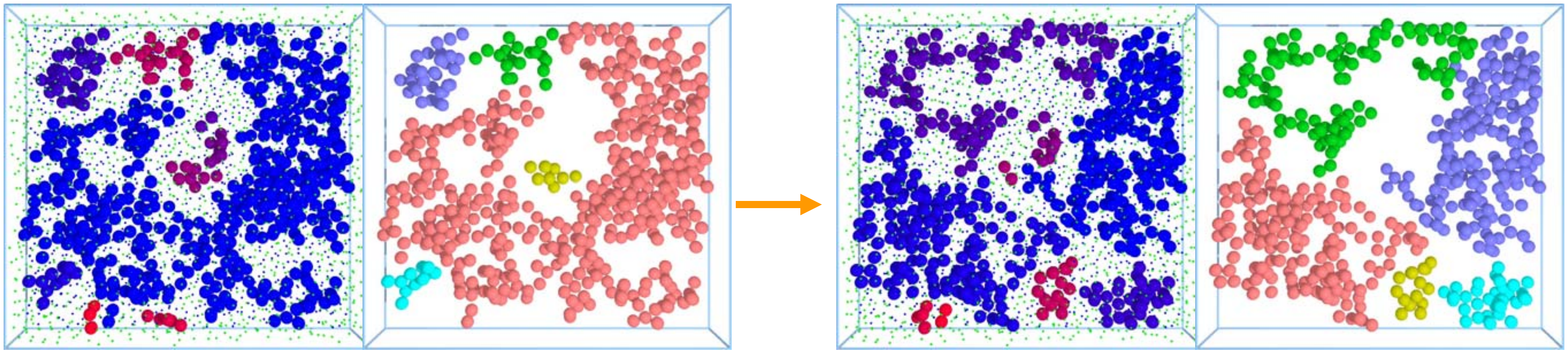


$\Delta nn = 1$ $\Delta nn = 2$

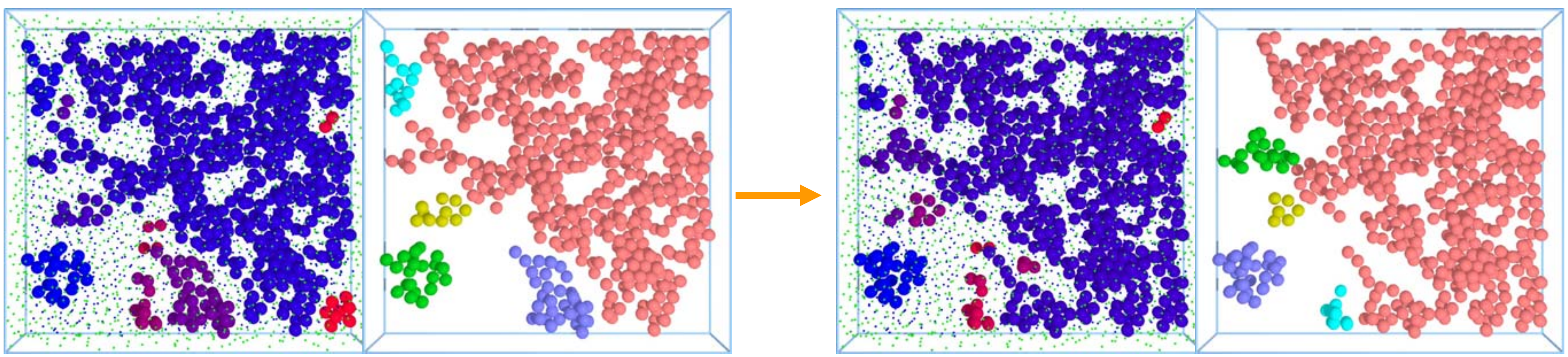
B. Doliwa and A. Heuer, J. Non-Cryst. Solids **307**, 32 (2002).

Percolation clusters break up in supercooled fluids

$\Delta nn = 0$

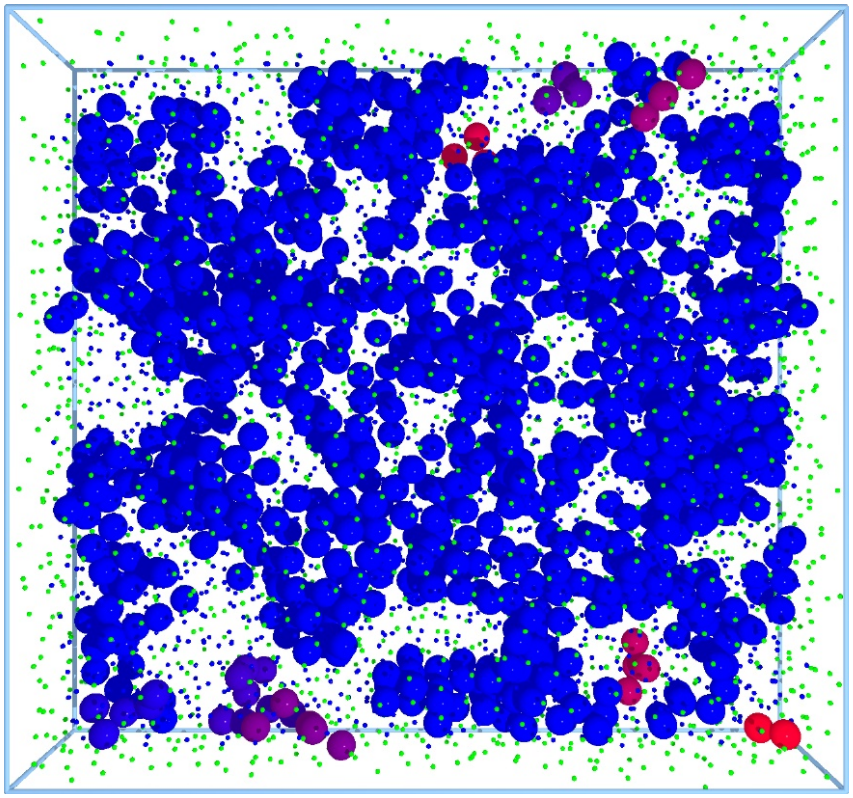


ϕ=0.52: $\Delta t_{\text{breakup}} \sim \Delta t^*$



ϕ=0.56: $\Delta t_{\text{breakup}} \sim 4\Delta t^*$

Glasses Have Connected Cluster for Entire Time

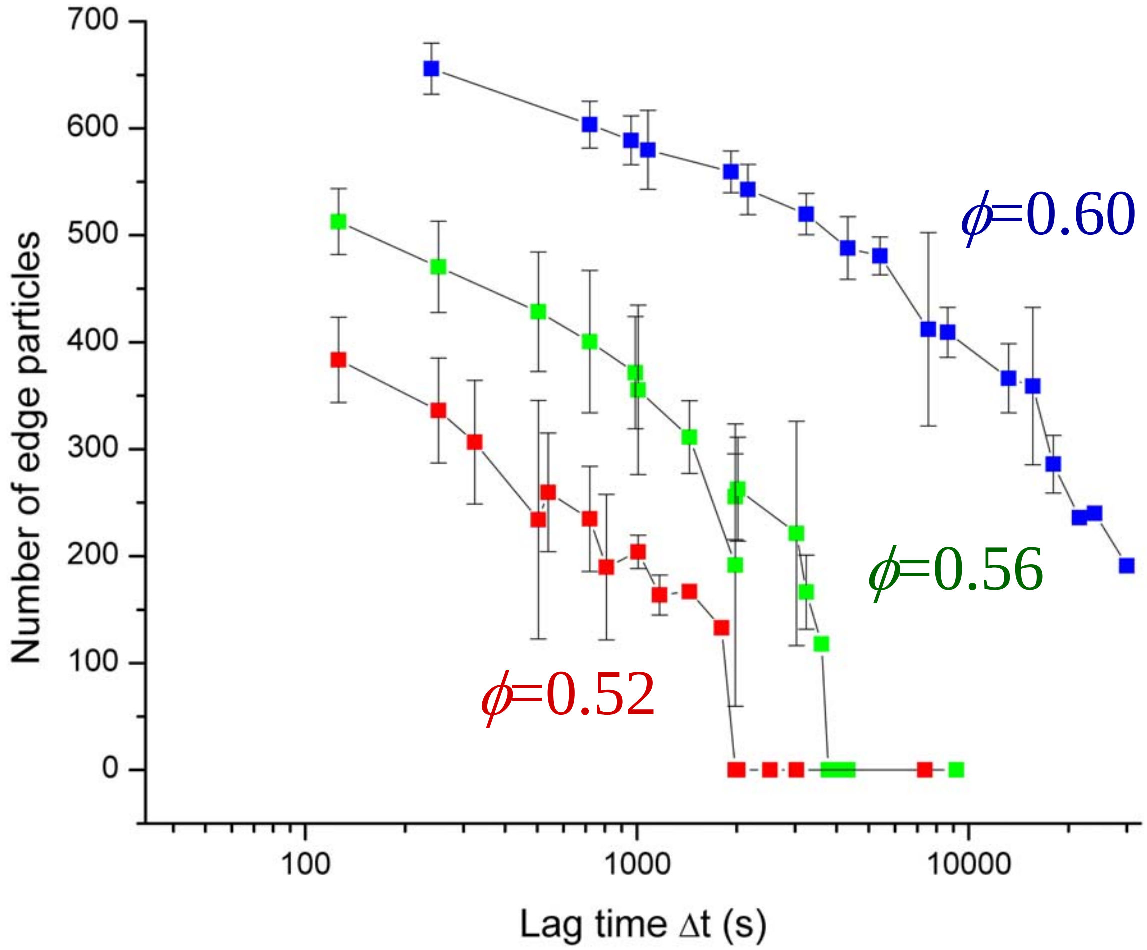


ϕ=0.60

Total run length is roughly 35,000 s

- Look for connectivity among $\Delta nn(\Delta t)=0$ particles
- Even at Δt~35,000 s all $\Delta nn=0$ particles form a connected network

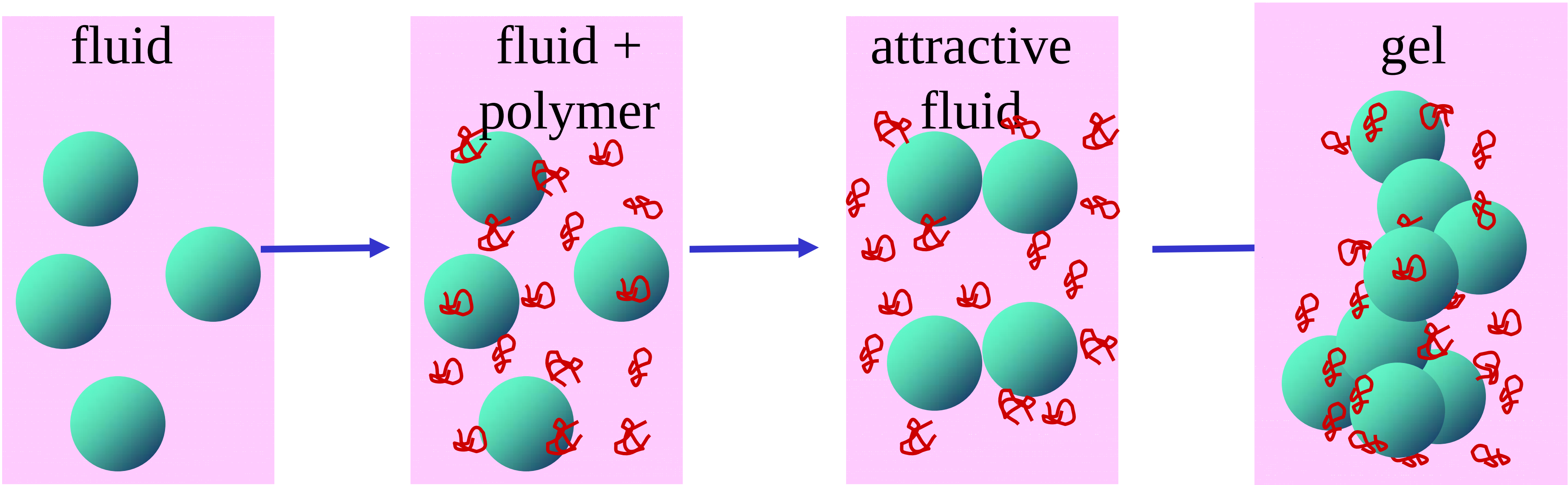
Number of Edge Particles in Connected Cluster
Δnn=0



Weak Attractive Interaction

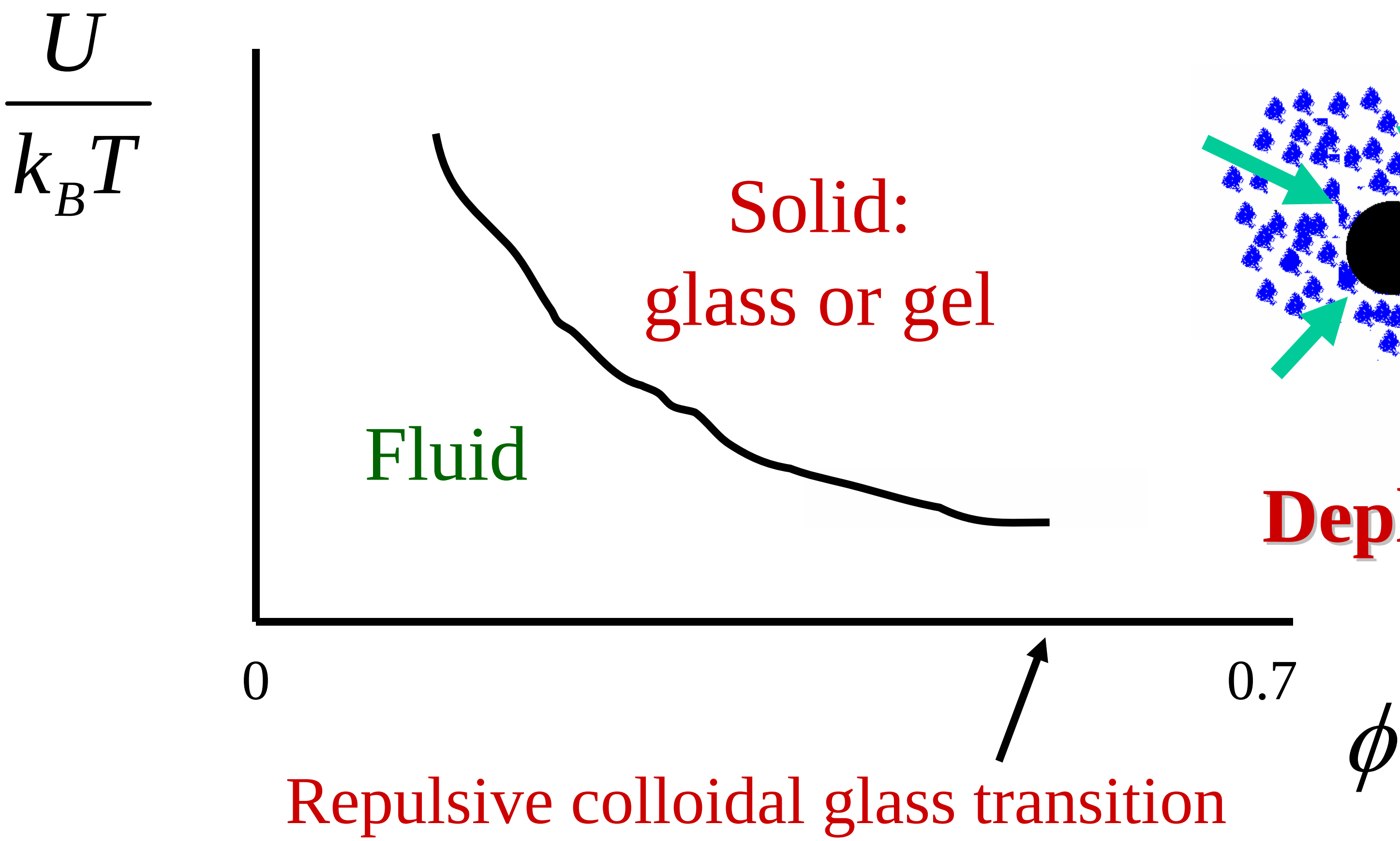
Colloid-polymer mixtures

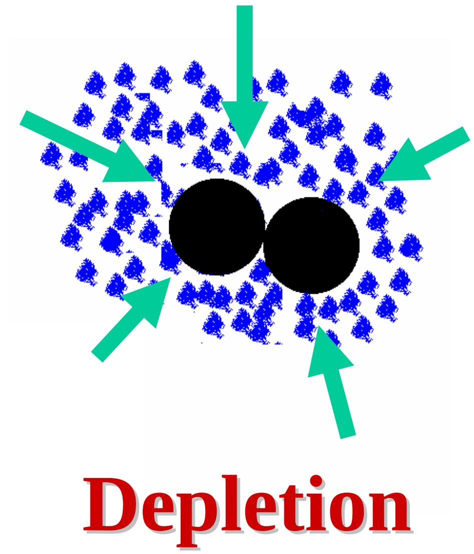
Depletion attraction



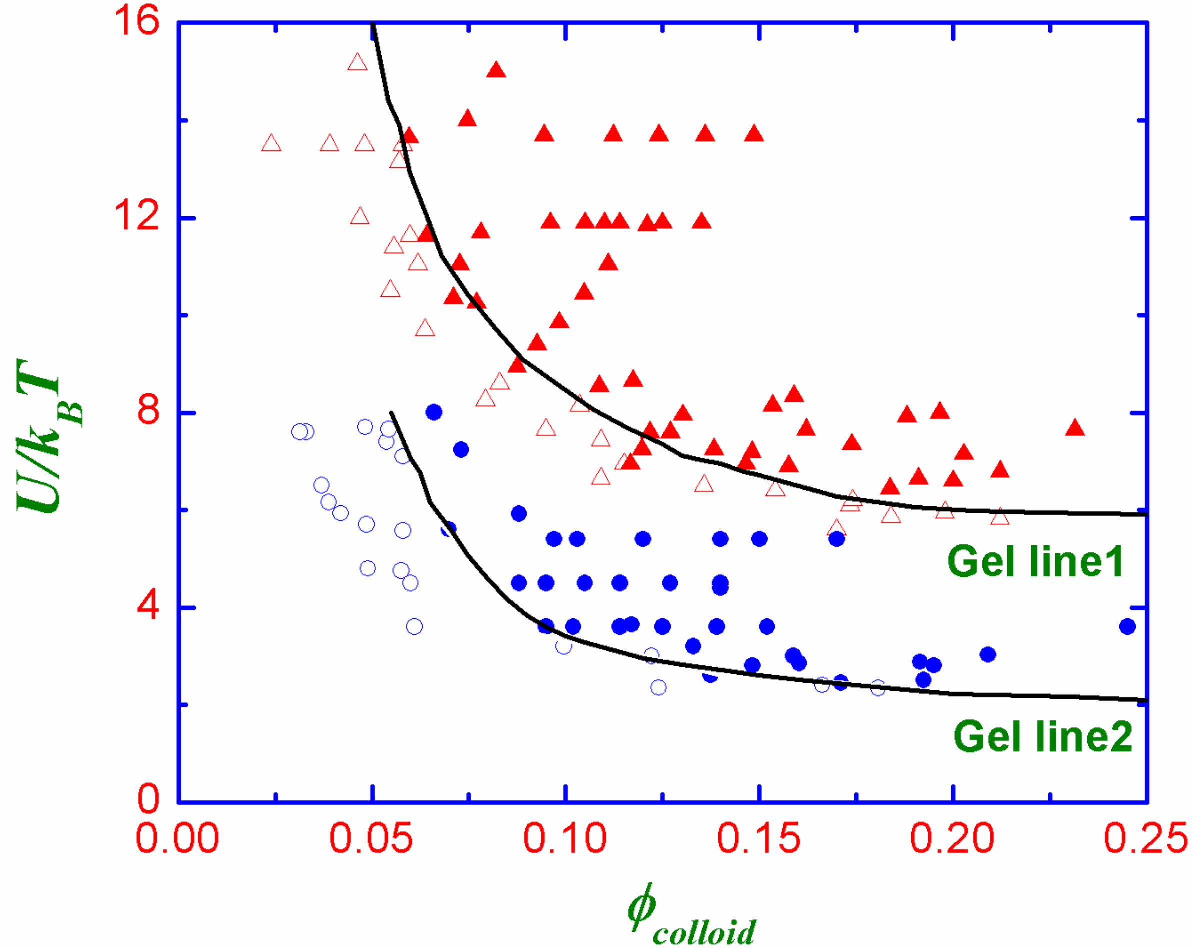
Polystyrene polymer, R_g=37 nm + PMMA spheres, r_c=350 nm

Attractive Colloidal Glasses





Phase diagram: Depends on Range



Short –range

M_w = 96,000 g mol^{-1}

▲ - Gel

Δ - Fluid cluster

Long-range

M_w = 2,000,000 g mol^{-1}

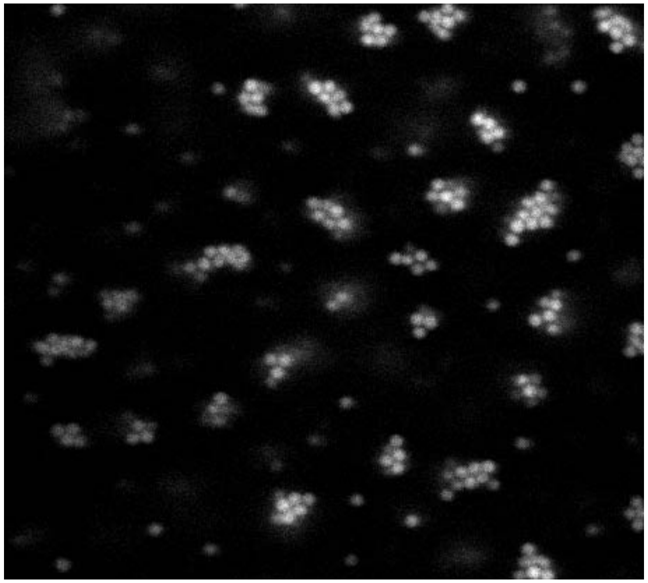
● - Gel

○ - Fluid cluster

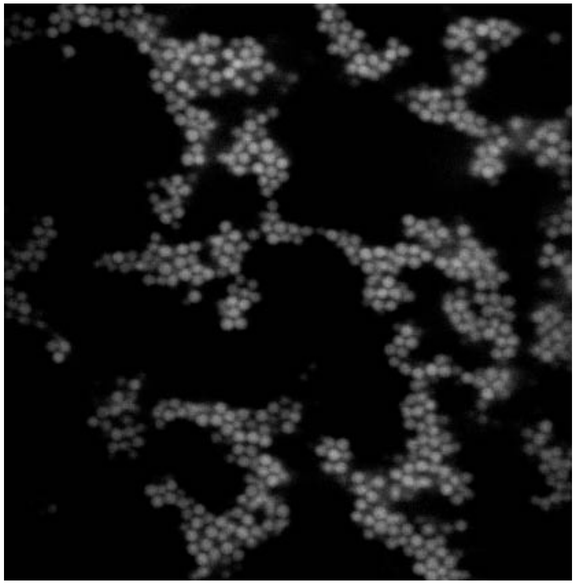
Gelation: Glass Transition of Clusters

“Jamming” of Clusters to form gel

$\phi = 0.06$, $U = 6.0\ k_BT$

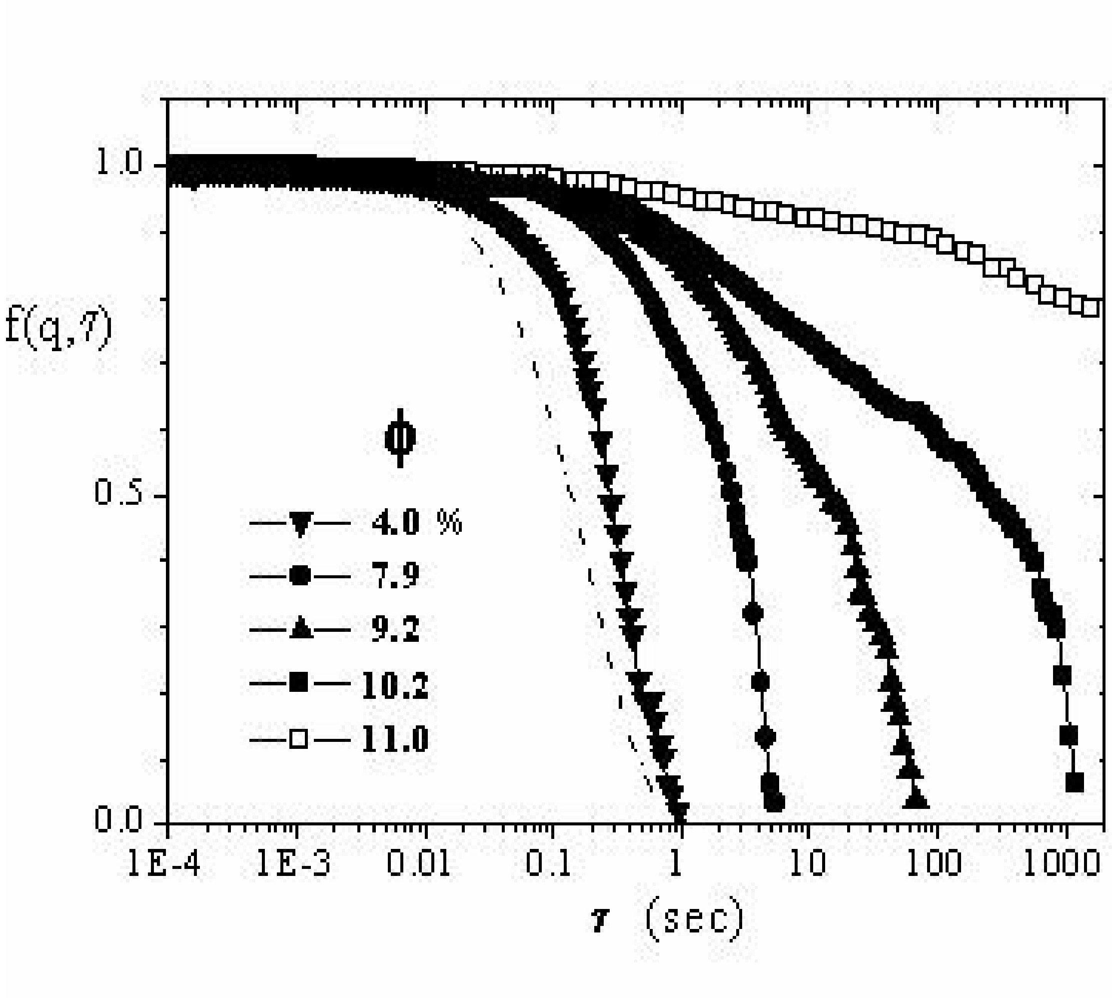


Fluid-Clusters

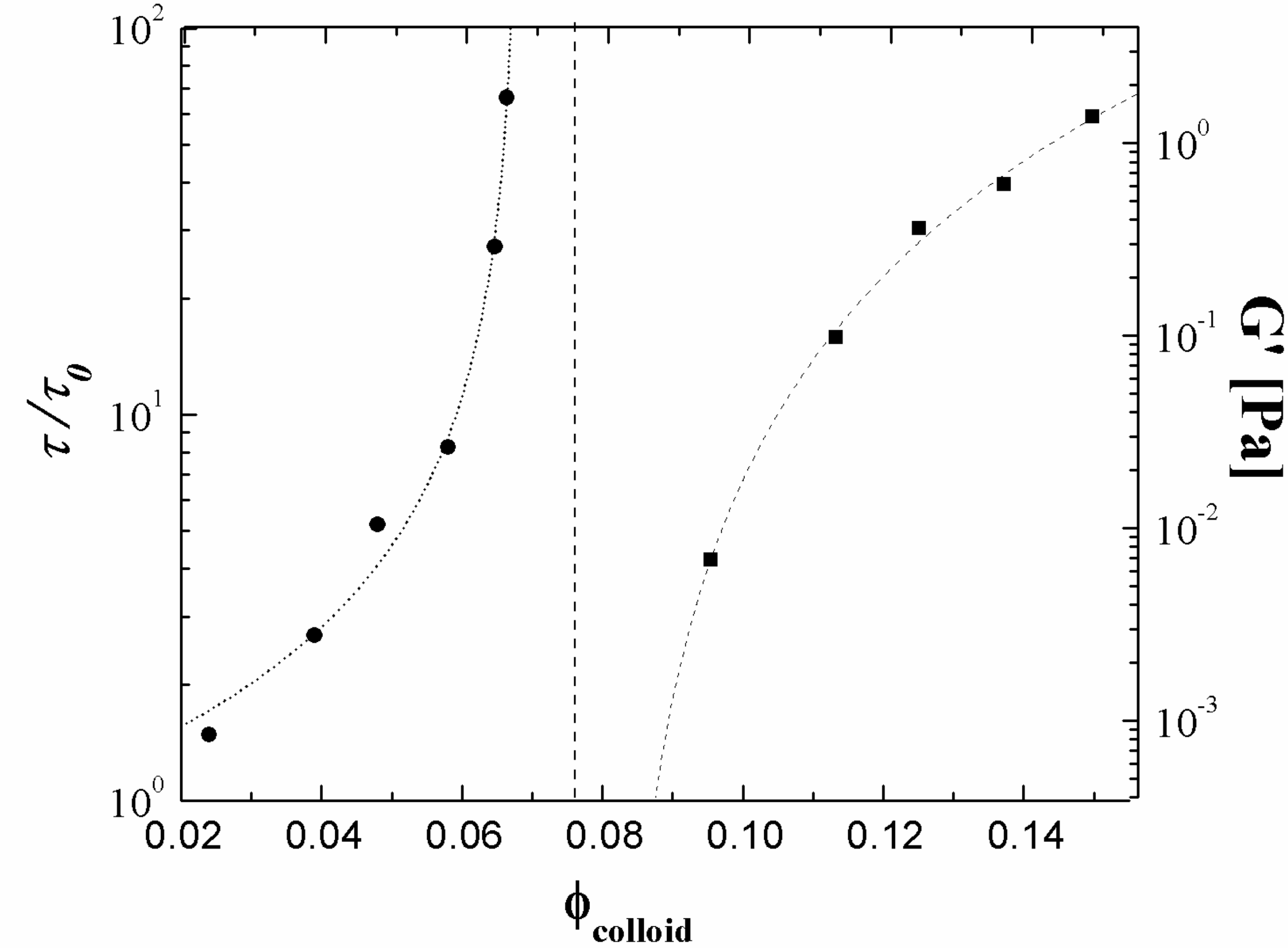


Gel

Dynamic Light Scattering from Attractive Colloids

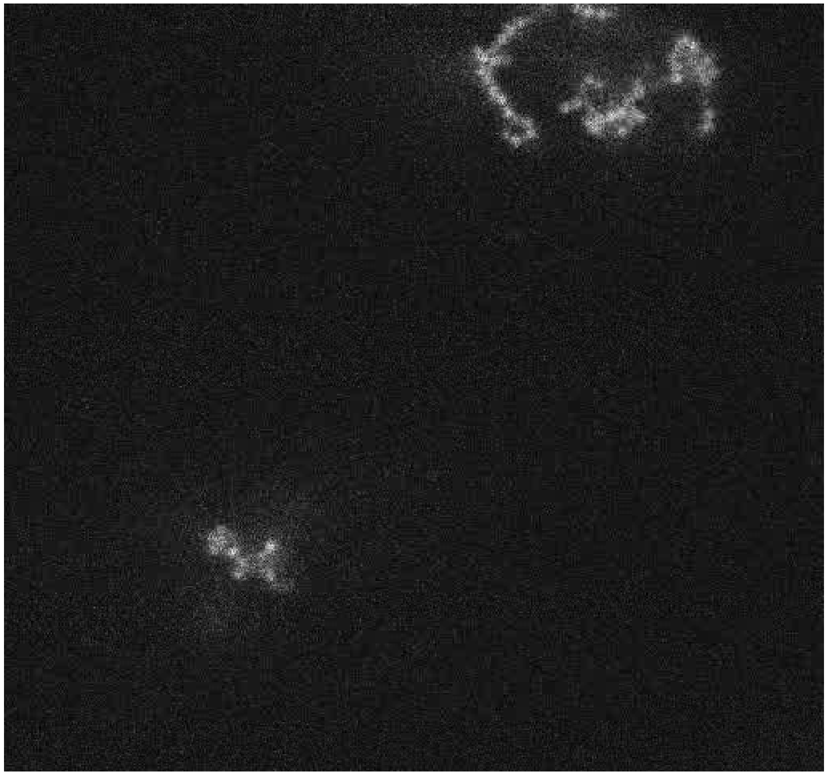


Gelation Transition for Attractive Colloids



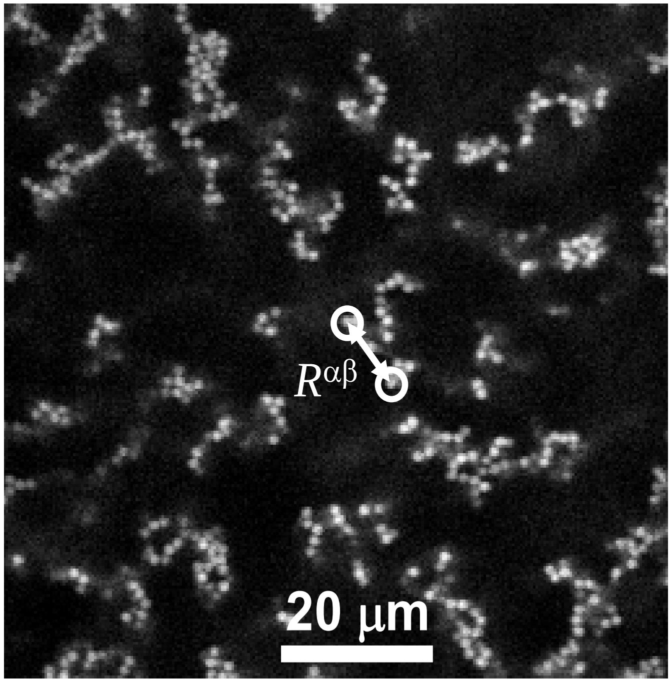
Fluid-solid transition at well-defined ϕ

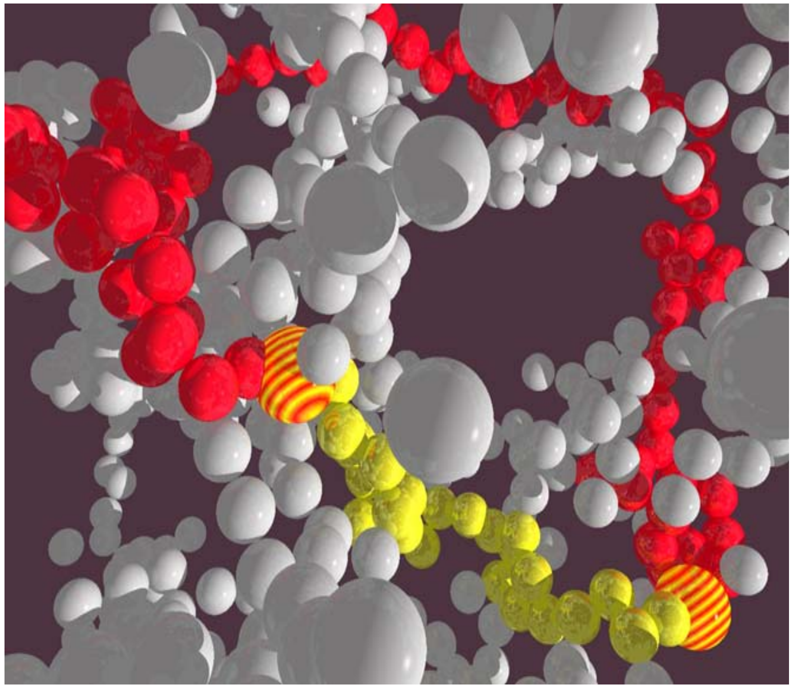
Colloidal Gel



Confocal microscope image: Slice through gel
PMMA particles, $a = 0.35\ \mu$m

Colloidal Gel: Chains Connect Particles



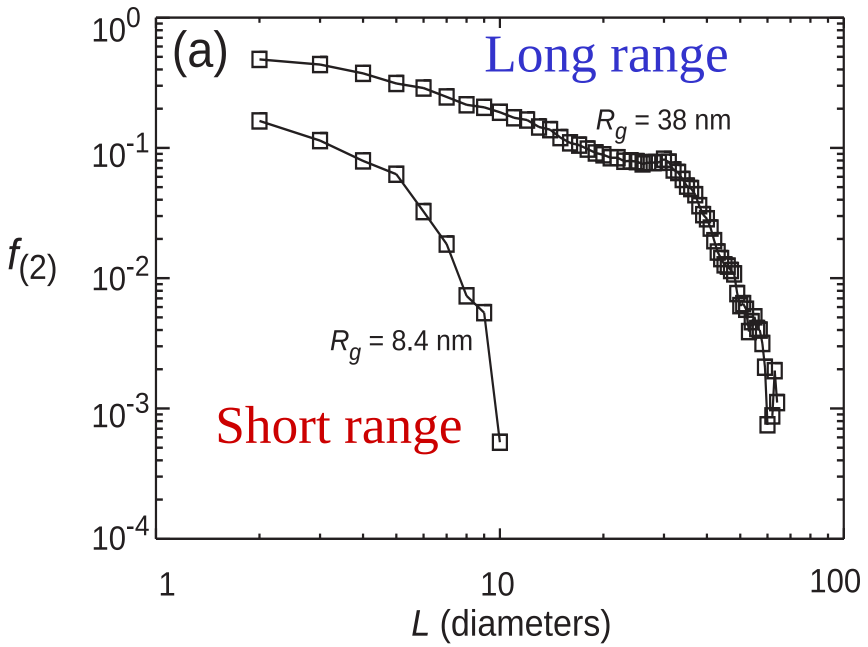


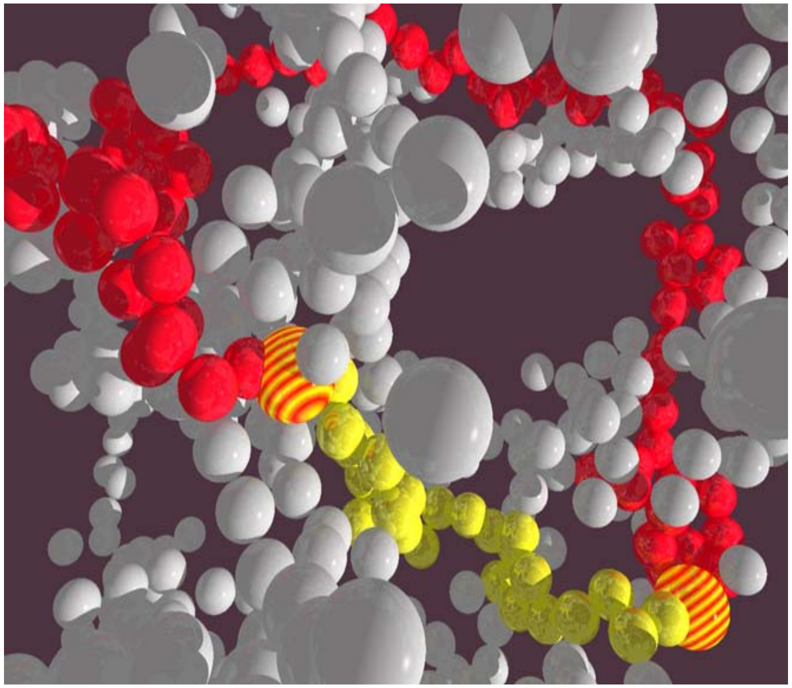
Confocal microscope: Cut through gel
PMMA particles

Rendered image showing chains

Colloidal Gel: Chains Connect Particles

Probability of 2nd Loop for Length L



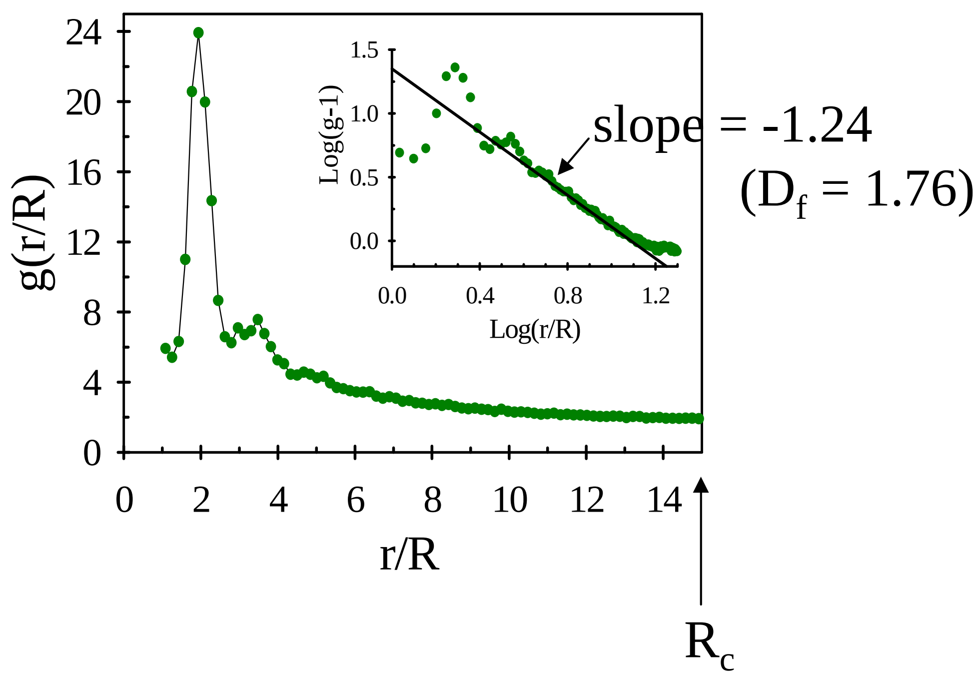


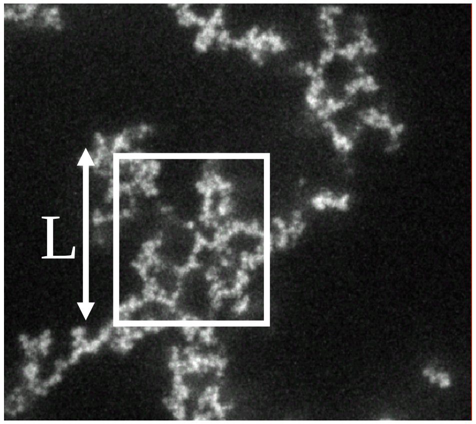
Rendered image showing chains

Short-range interaction – Fewer loops

Long-range interaction – More loops

Fractal scaling





$M \propto R^{d_f}$

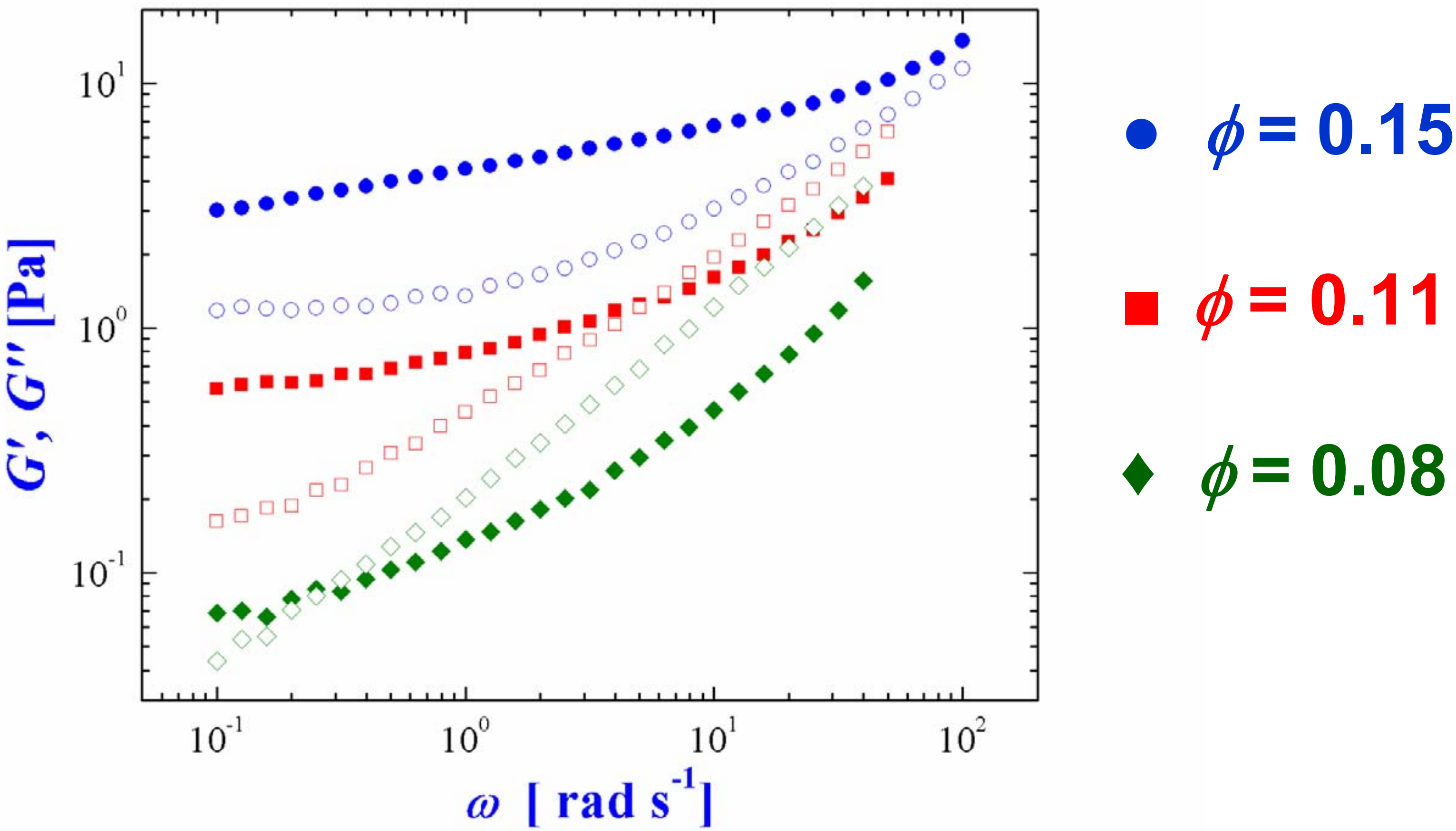
$\phi(R) \propto R^{D_f - 3}$

R_c is set by $\phi(R=R_c) \equiv \phi$

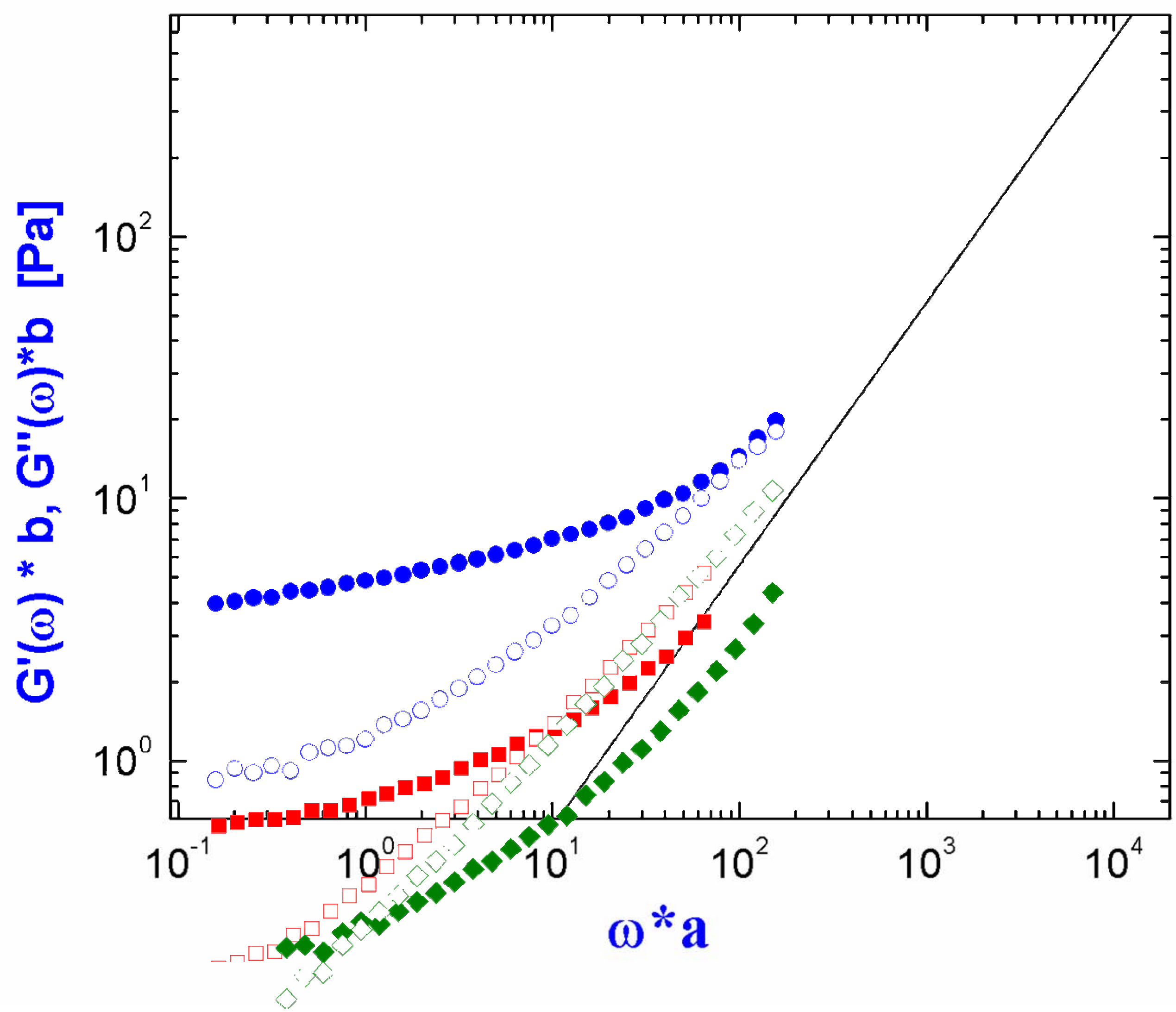
$R_c = \phi^{(1/d_f - 3)}$

Viscoelastic behavior

$(U_{dep} / k_B T = 7.1, \xi = 0.168)$

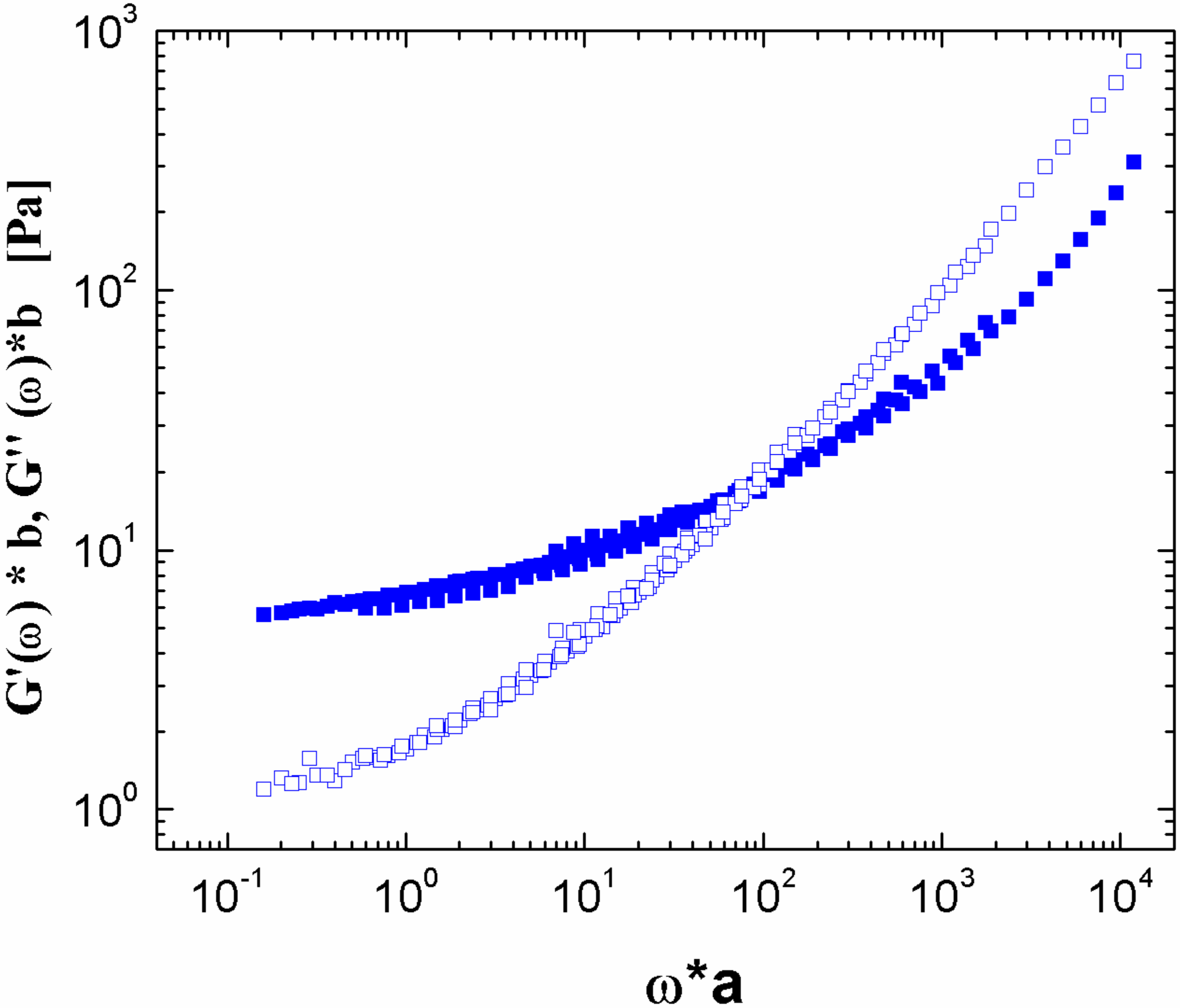


Scaling behavior

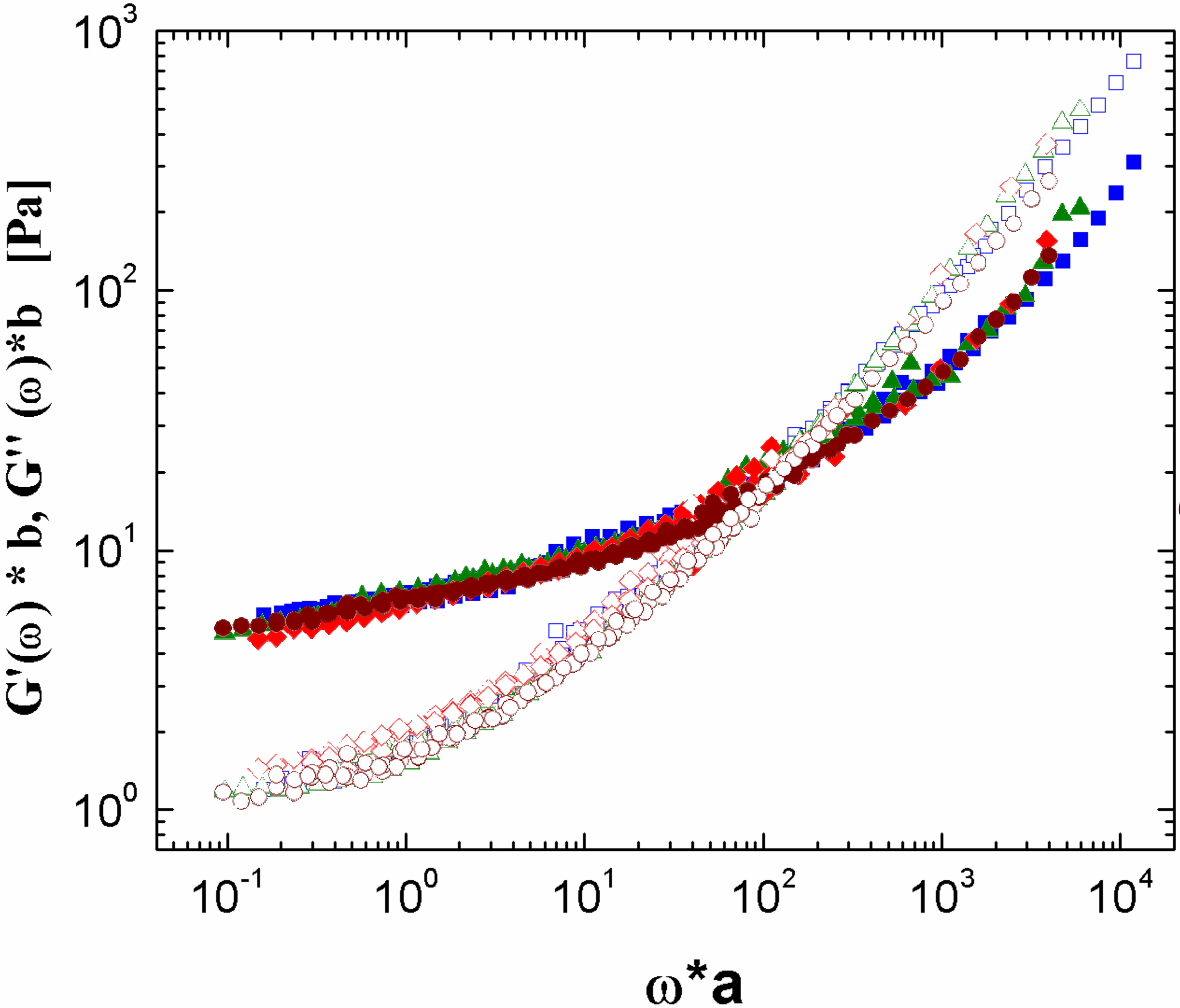


Same Universal Master Curve

U_{dep}/k_BT = 7.1, $\xi = 0.168$



Same Universal Master Curve



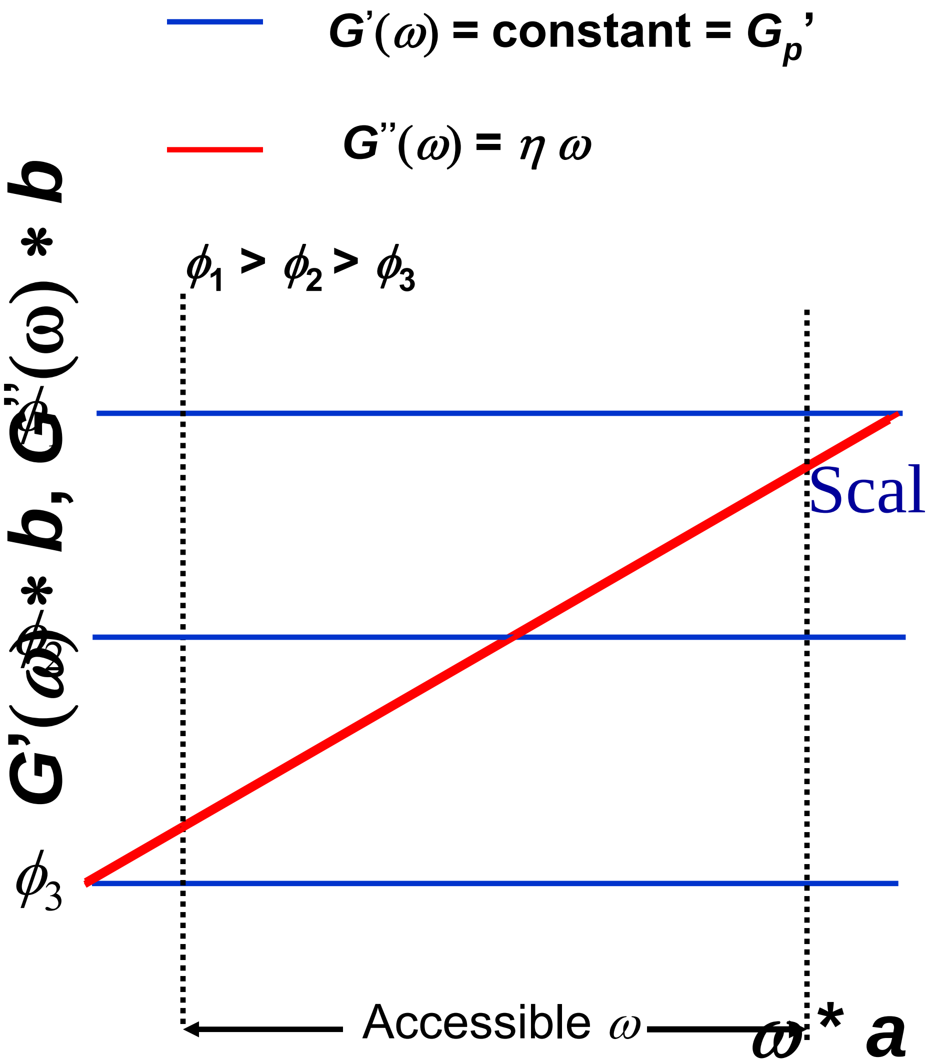
U_{dep}/k_BT = 7.1, $\xi = 0.168$

U_{dep}/k_BT = 13.7, $\xi = 0.04$

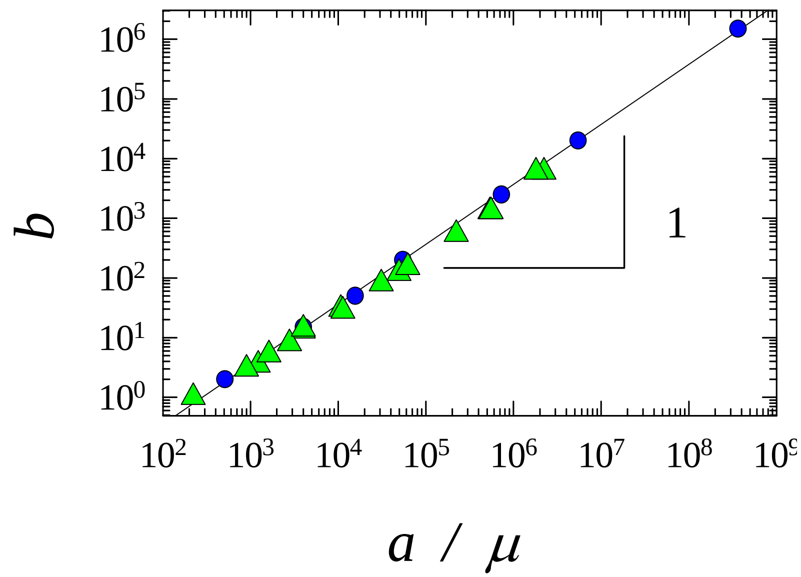
U_{dep}/k_BT = 11.9, $\xi = 0.04$

U_{dep}/k_BT = 5.4, $\xi = 0.18$

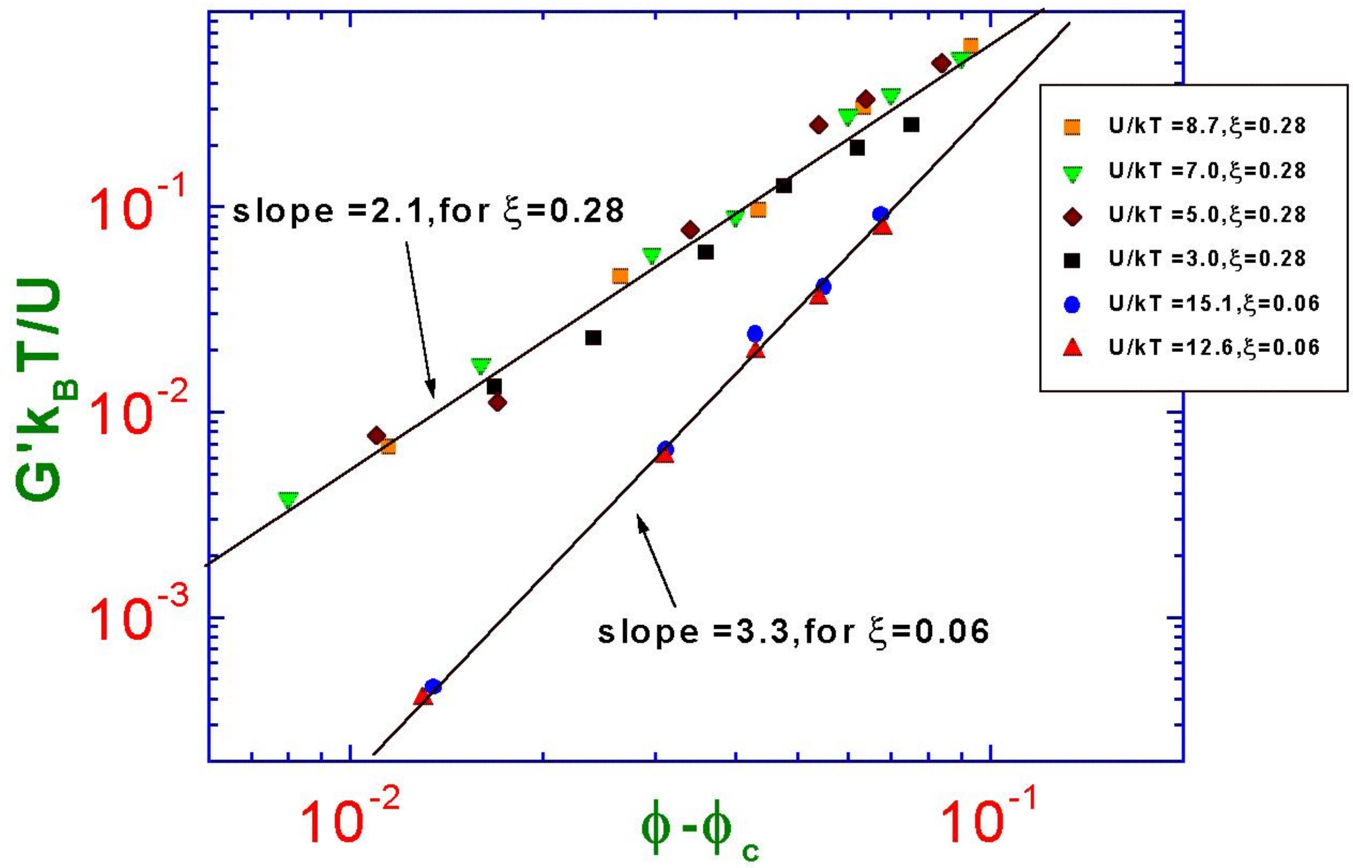
Two Component Model



Scale along the background viscosity



Scaled Critical Onset of Plateau Moduli for Colloidal Gels Depends on ***Range*** of Interaction



Exponents Depend on Interaction

Rigidity Percolation

Map $\phi \rightarrow p$

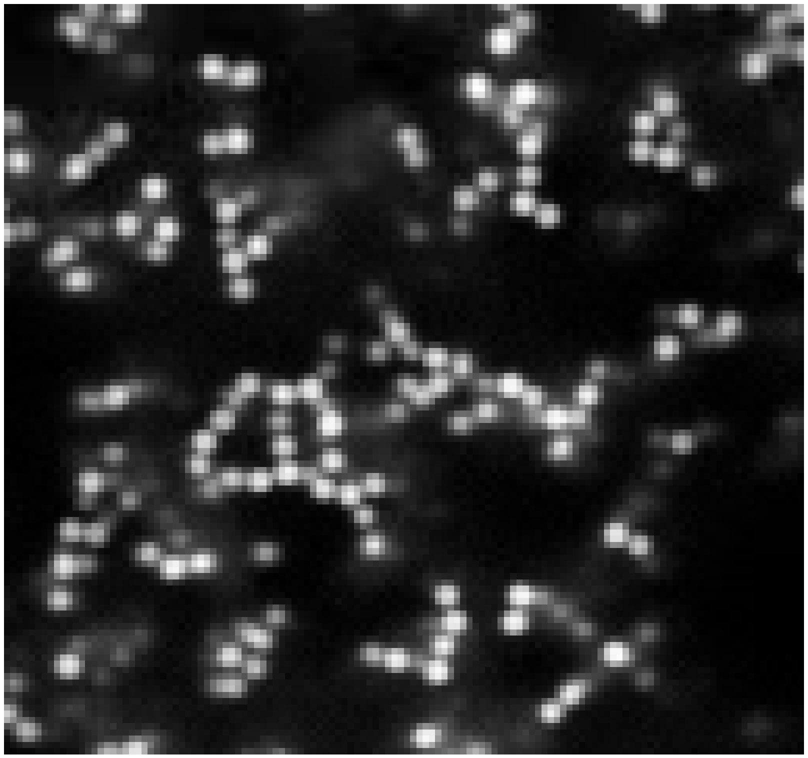
Non-central forces:

$$G \sim (\phi - \phi_0)^{3.8}$$

Central Forces:

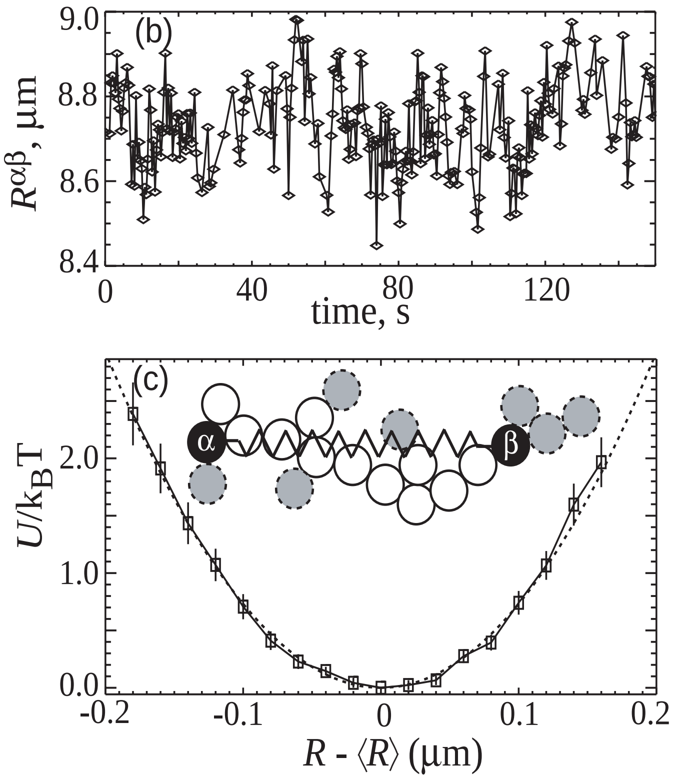
$$G \sim (\phi - \phi_0)^2$$

Spring Constant Determined from Thermal Fluctuations



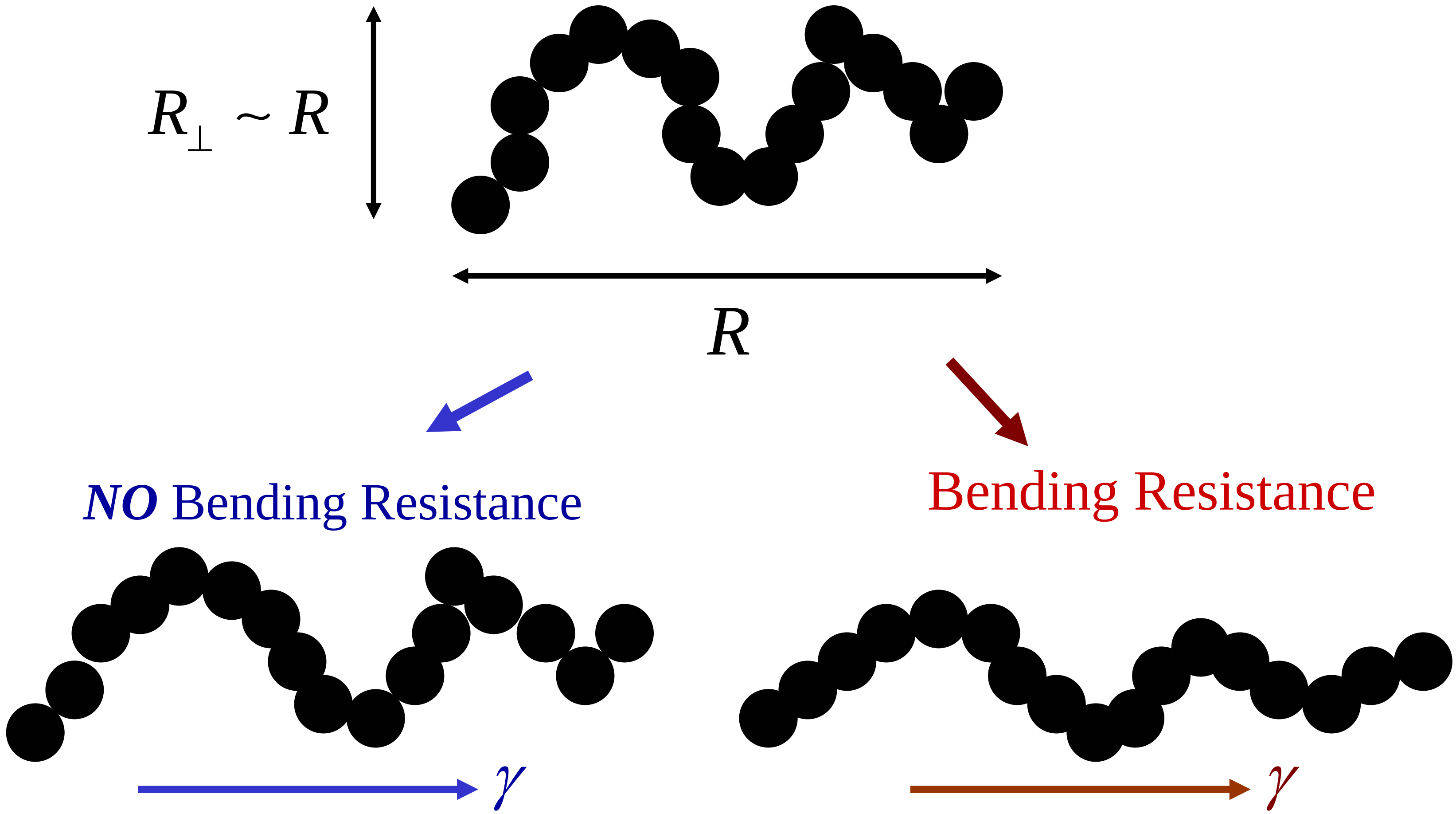
Movie of Fluctuations

$$P(\Delta R) \propto \exp\{-U(\Delta R)/k_B T\}$$



Harmonic Spring
Curvature is κ

Length dependence of Spring Constant



$\kappa \sim R^{-1}$

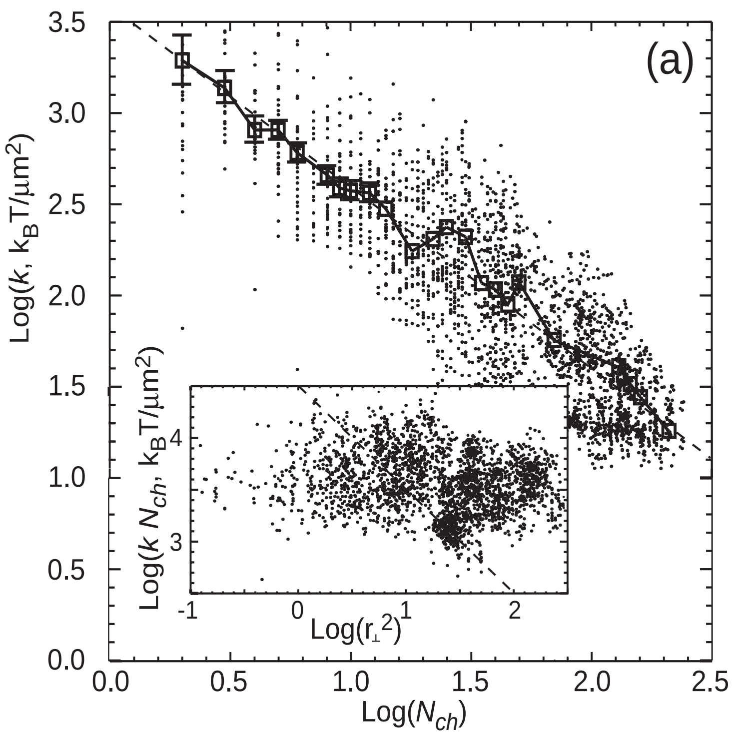
No dependence on *width* of chain

$\kappa \sim R_\perp^{-2} R^{-d_B} \sim R^{-3}$

Depends on *width* of chain

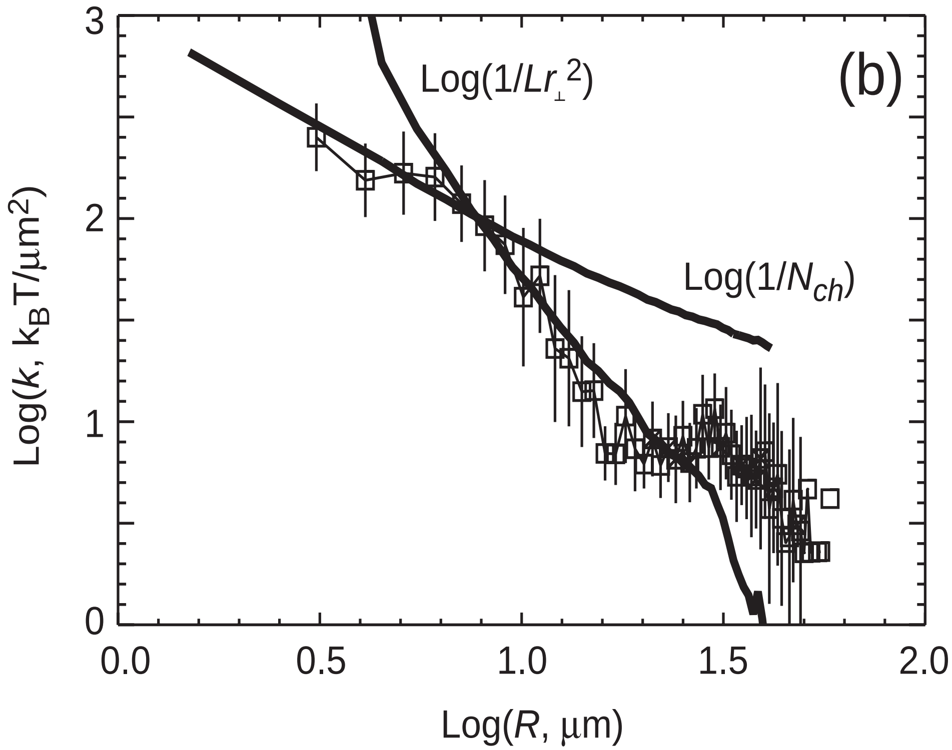
Scaling of Spring Constant with Chain Length

Long-range interaction



Centro-symmetric

Short-range interaction



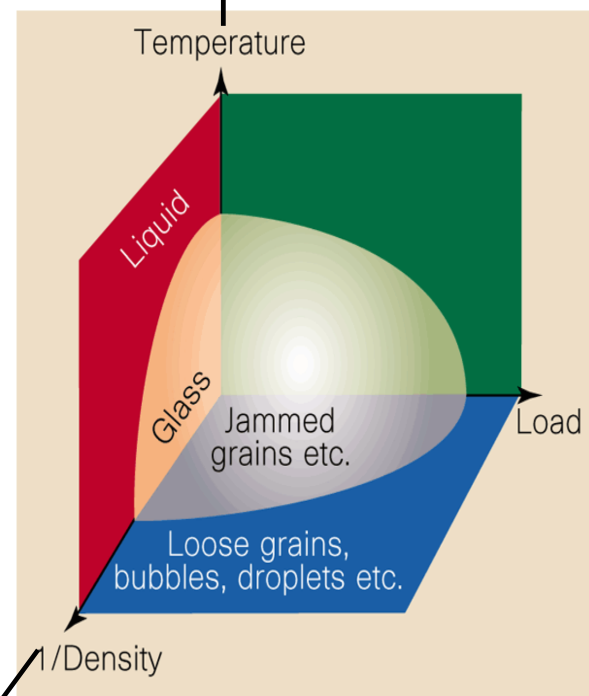
Non centro-symmetric

Supports bond bending

Jamming Transition – Arrest of Motion

Temperature
Vibration, Shaking

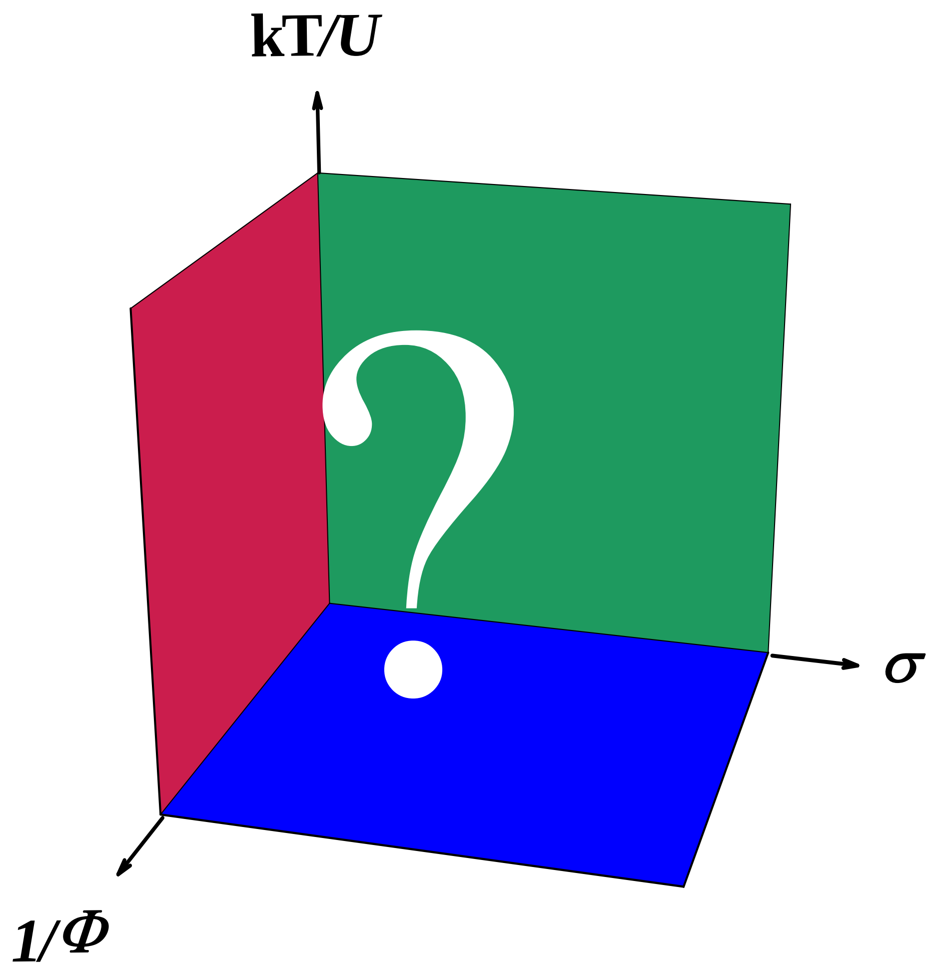
Andrea Liu, Sidney Nagel
Nature 386 (1998) 21



Load
Incompatible Stress
Stress

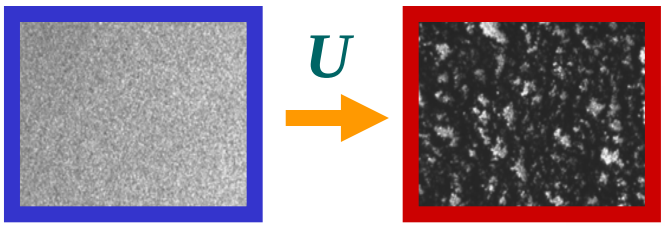
Density
Compatible Stress
Pressure
Osmotic Pressure
Attractive Potential

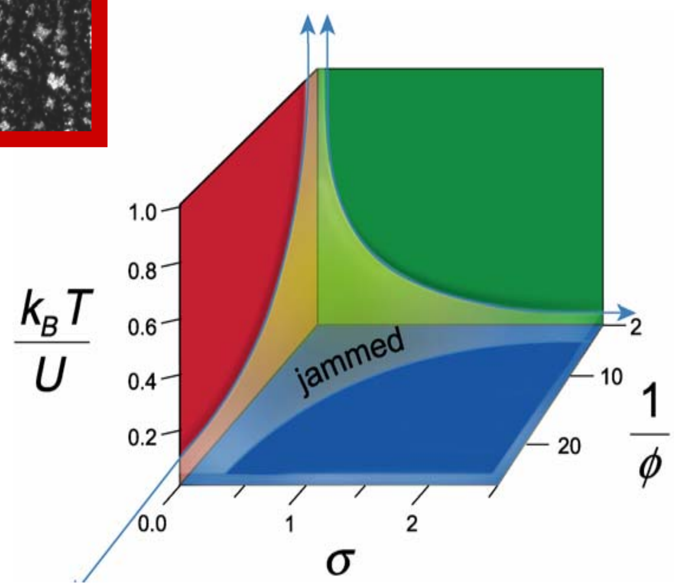
Jamming Transitions for Colloidal Systems with Attractive Interactions

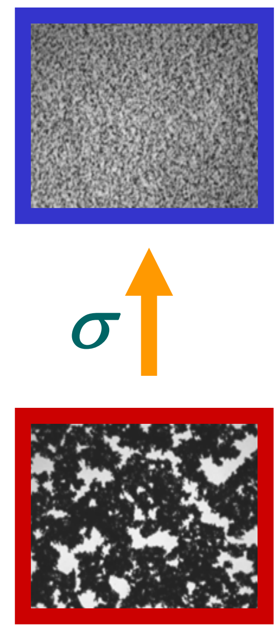


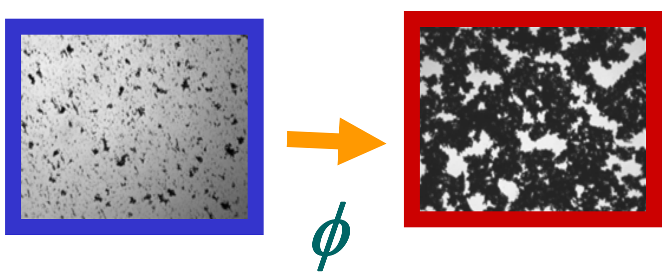
Jamming Phase Diagram for Attractive Systems

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





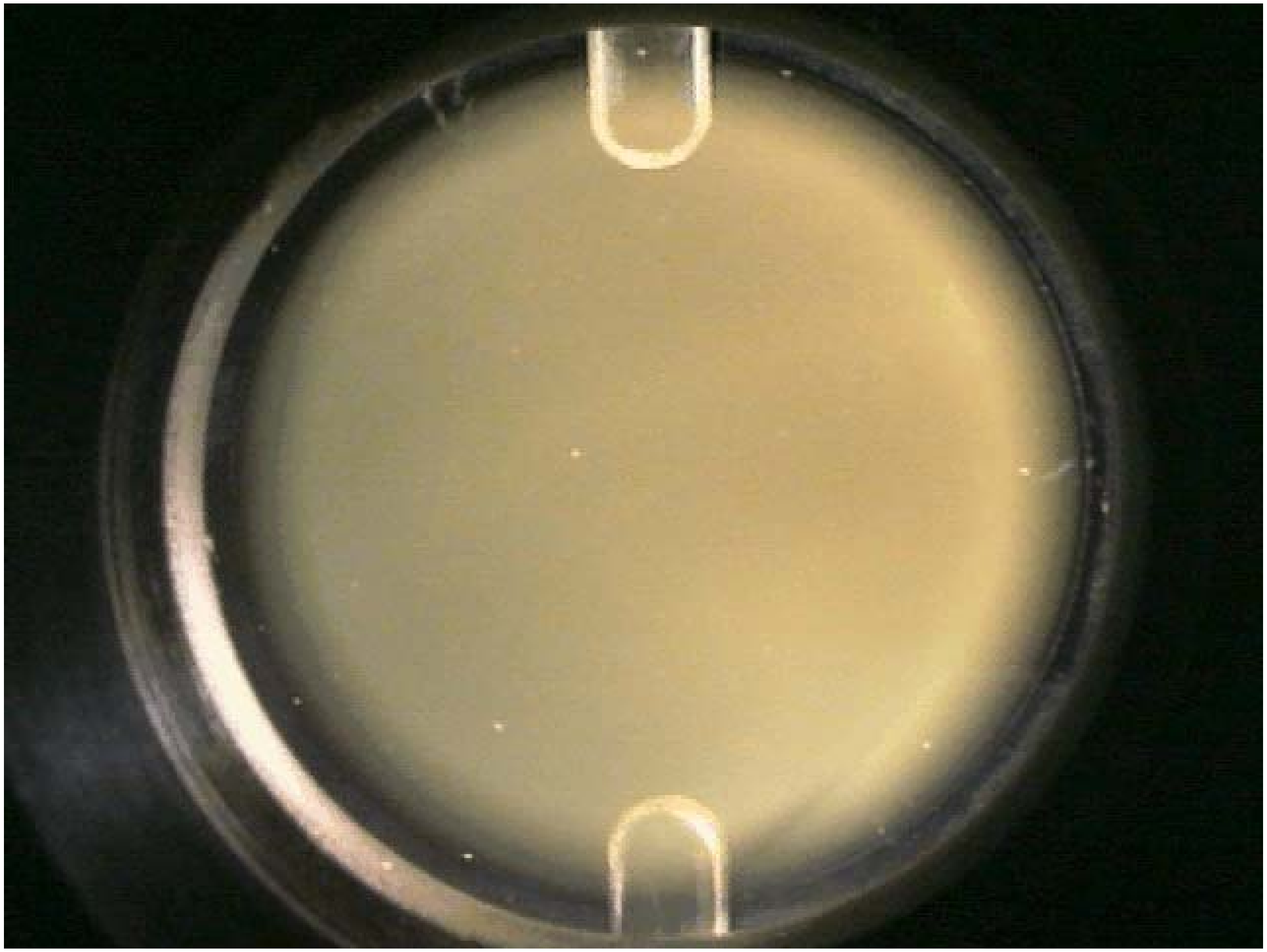




Spinodal Decomposition of Colloid Polymer

Longer-range Interaction

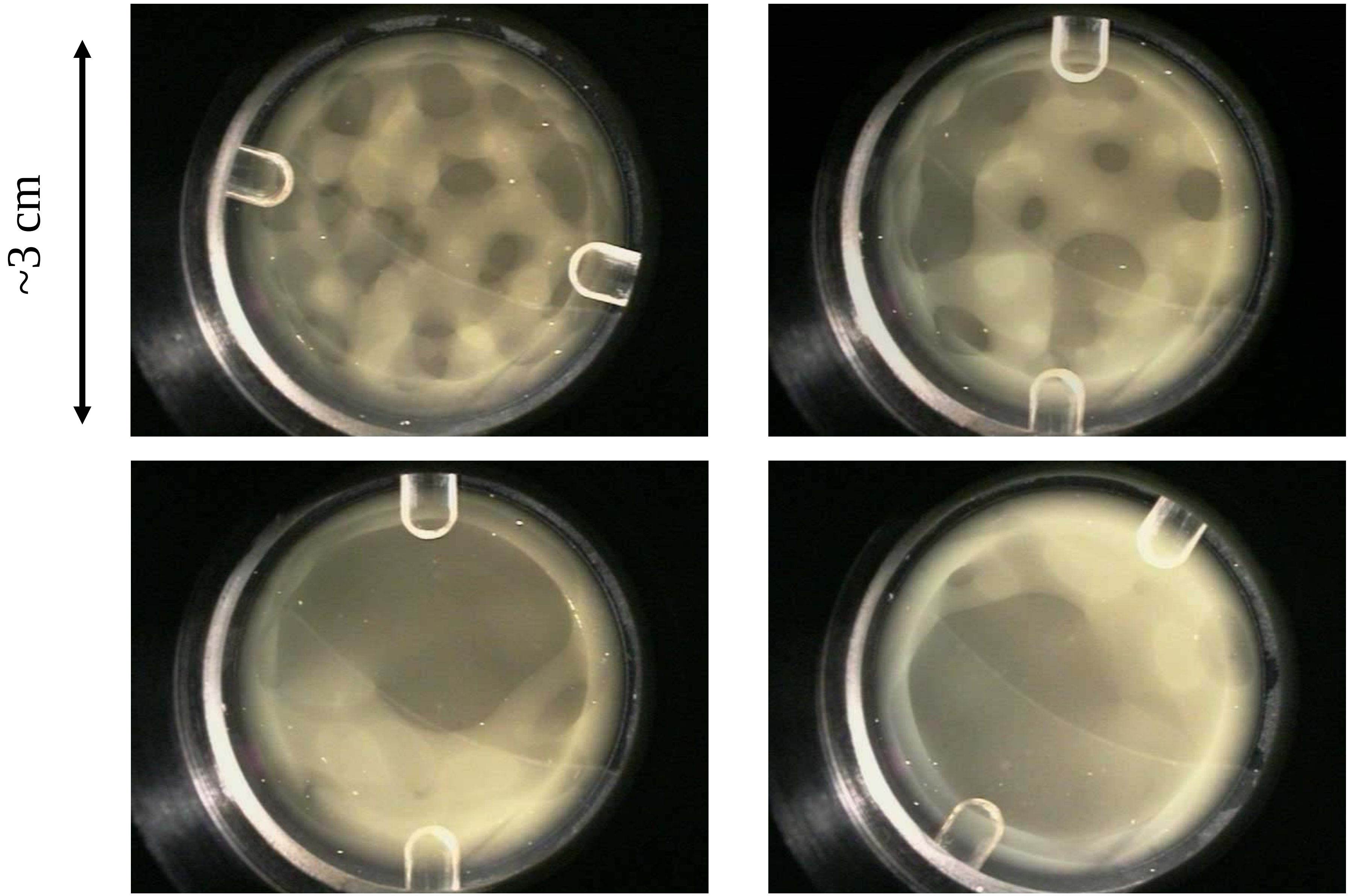
~3 cm



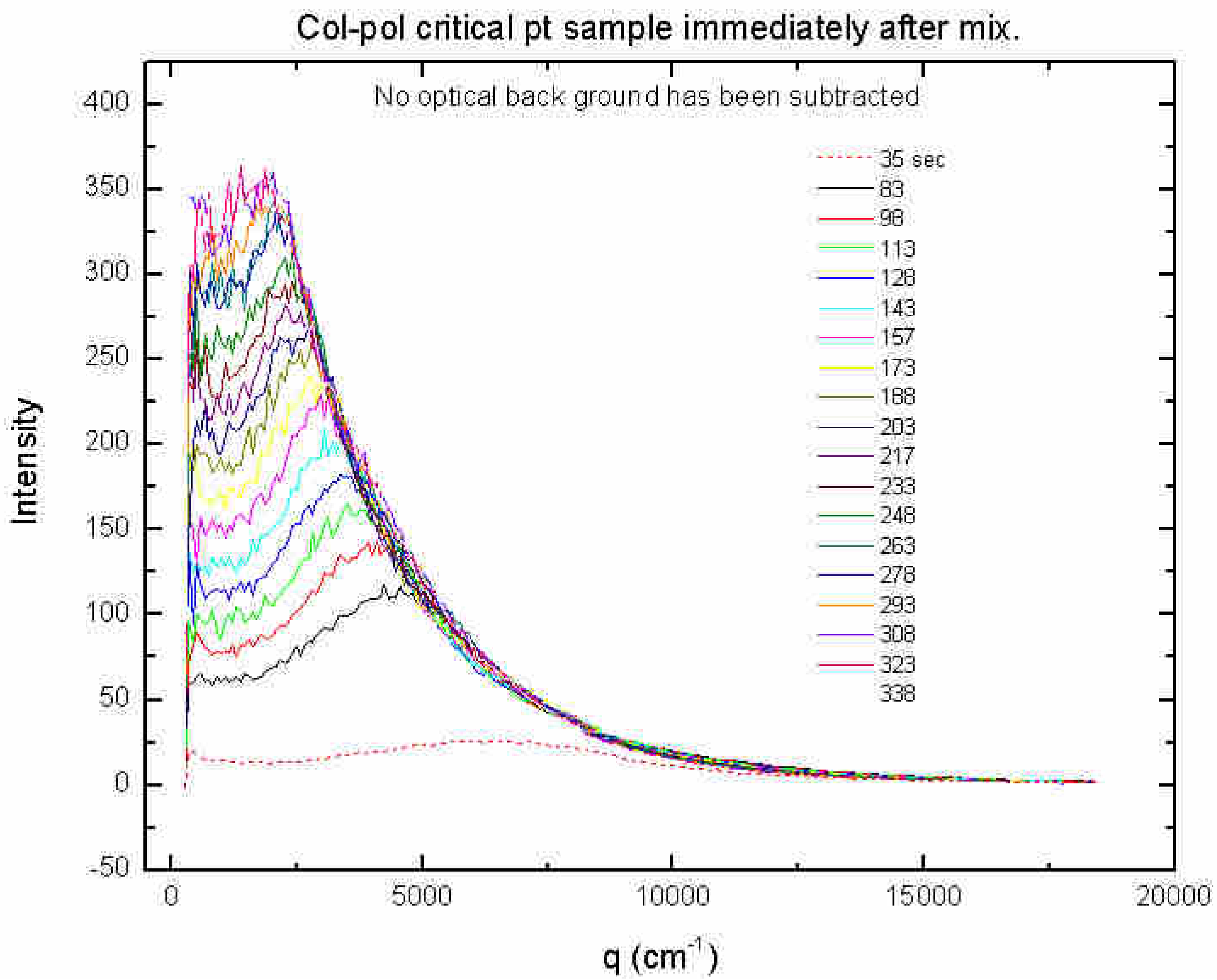
~16 hrs

A. Bailey, L. Cipelletti, U. Gasser, S. Manely, P. Segre, ISS

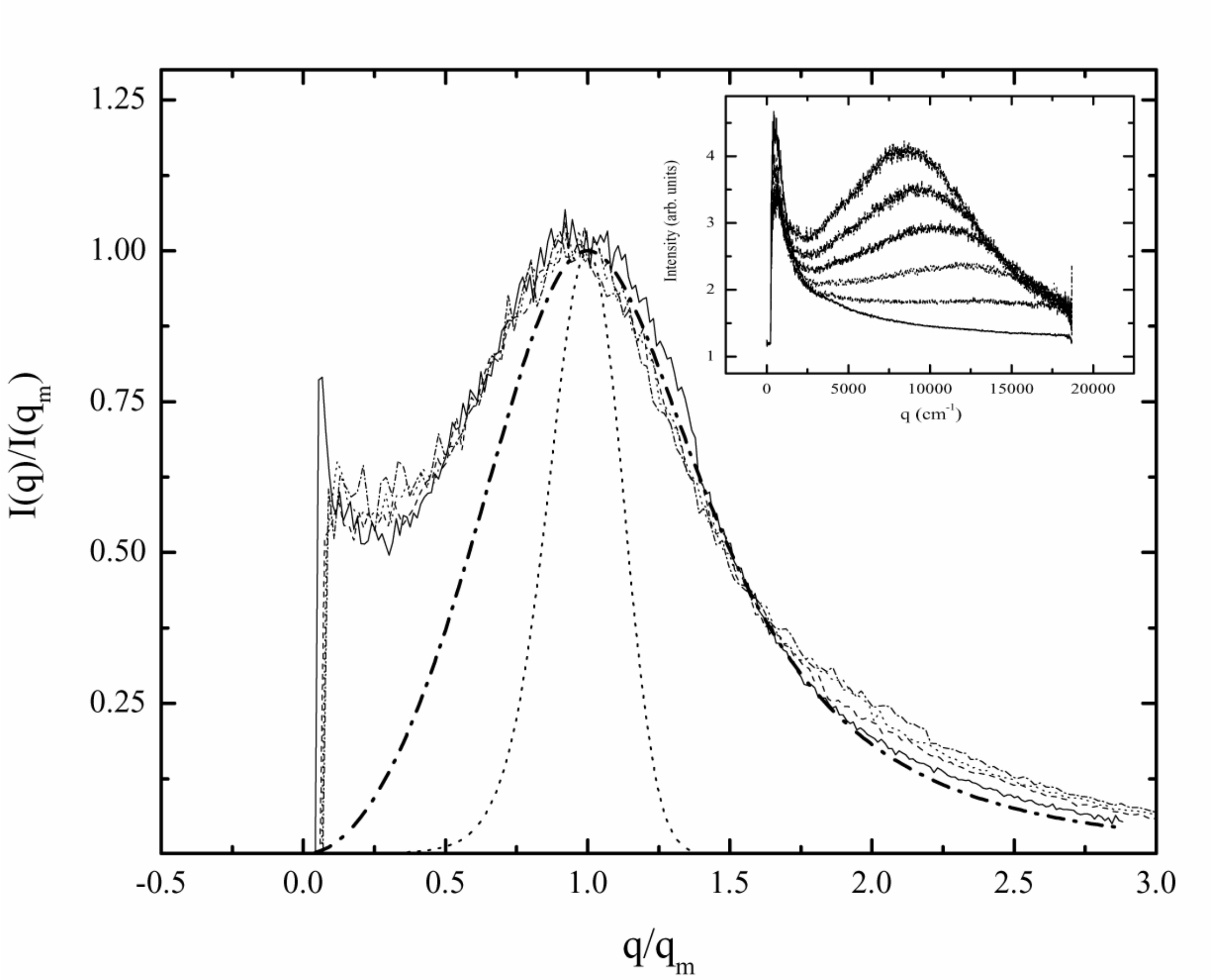
Time Evolution of Phase Separation



Short-Time Evolution of Small-Angle Light Scattering after Mix

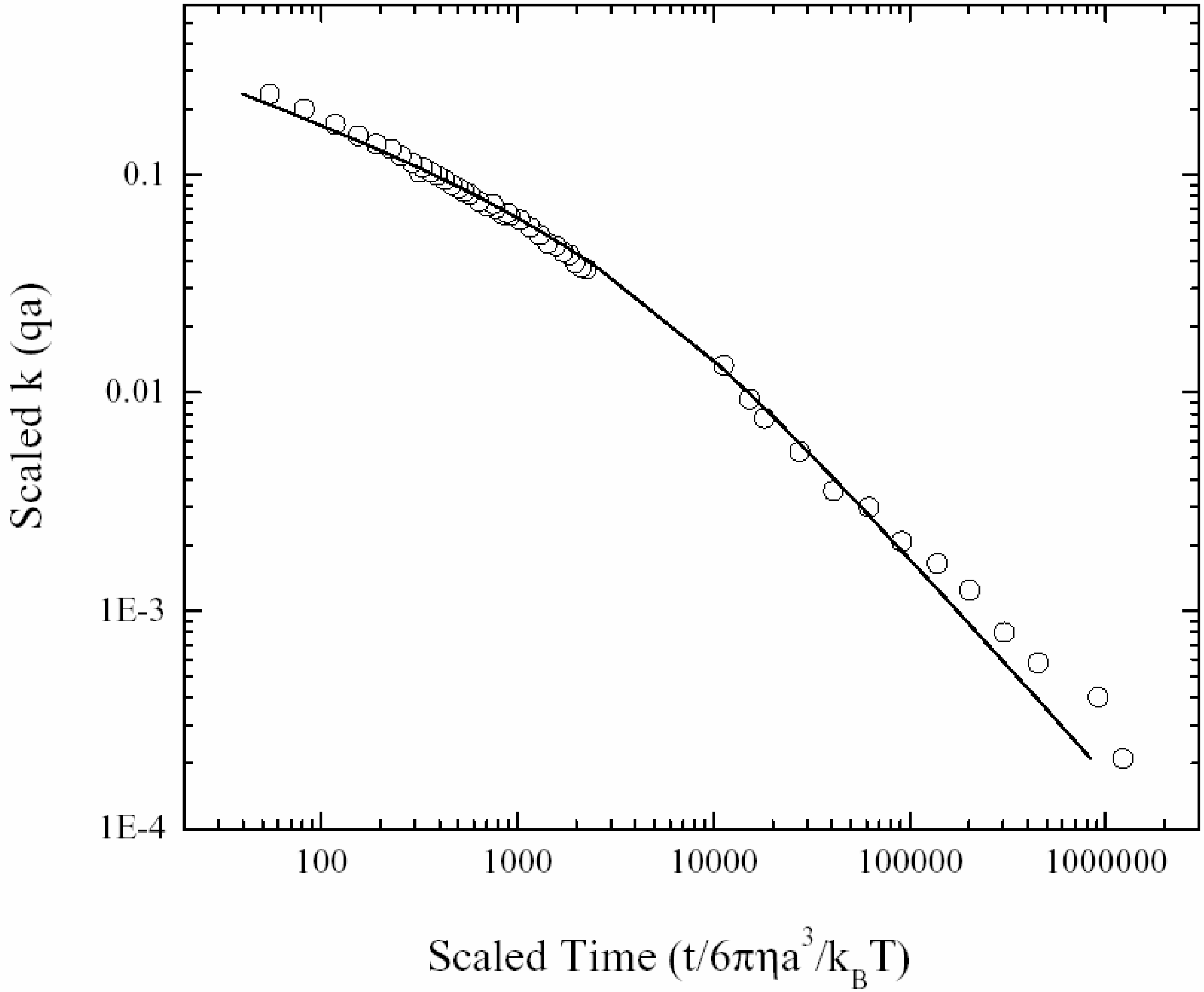


Scaling of Scattering at Small Angles



Follows Theory – Furukawa

Comparison with Theory: Furukawa



- Like Binary Fluid very close to critical point
  - ξ is much larger → colloidal particle

Conclusions

- Repulsive glasses have percolation clusters of slow particles
- Attractive colloidal systems are similar to glasses
- Viscoelastic behavior exhibits scaling
  - Defines critical gelation for transition
- Phase behavior depends on range of interaction
- Different rheology for different ϕ
- Microscopic motion of particles provides insight into rheology