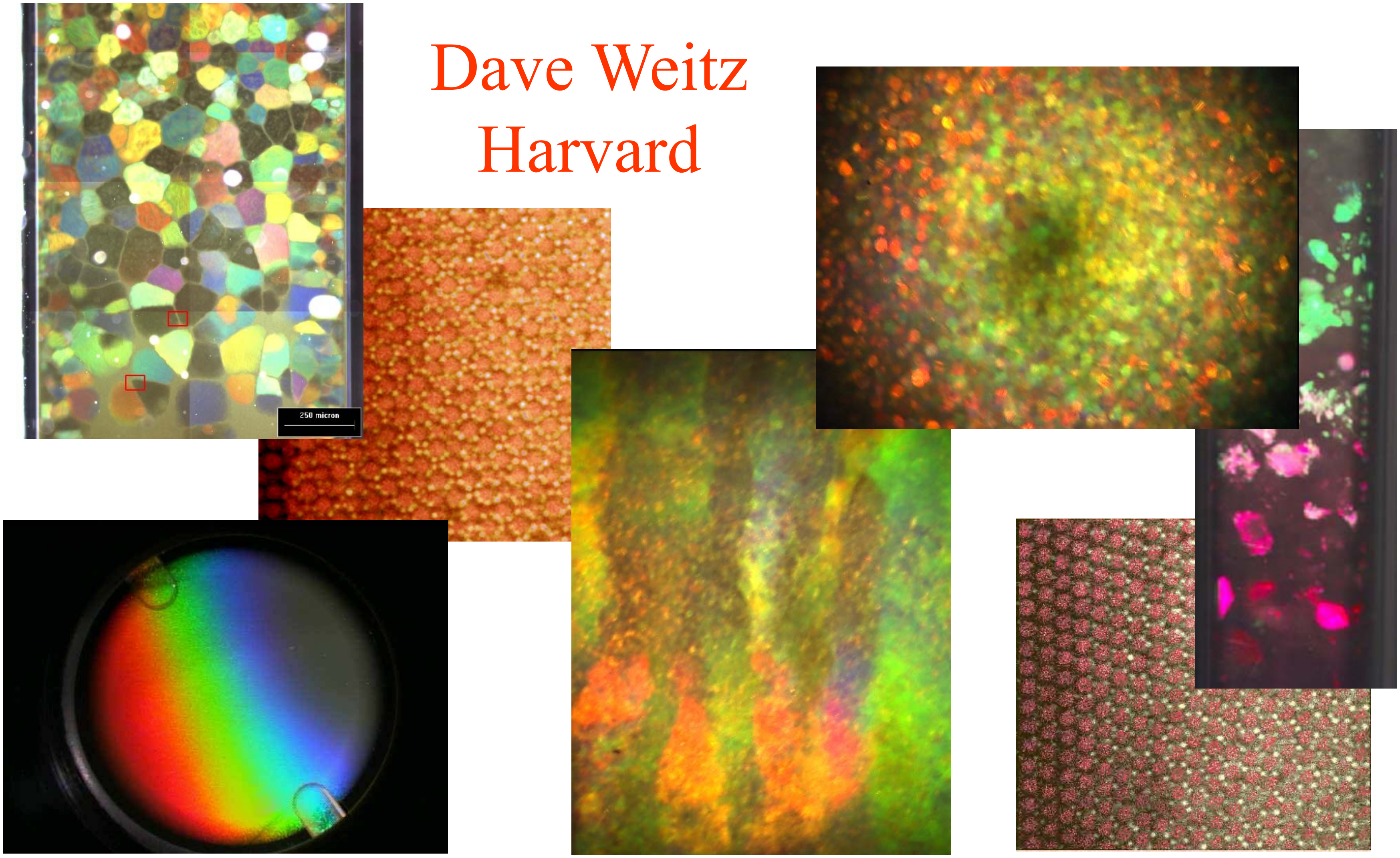
Experimental Colloids I



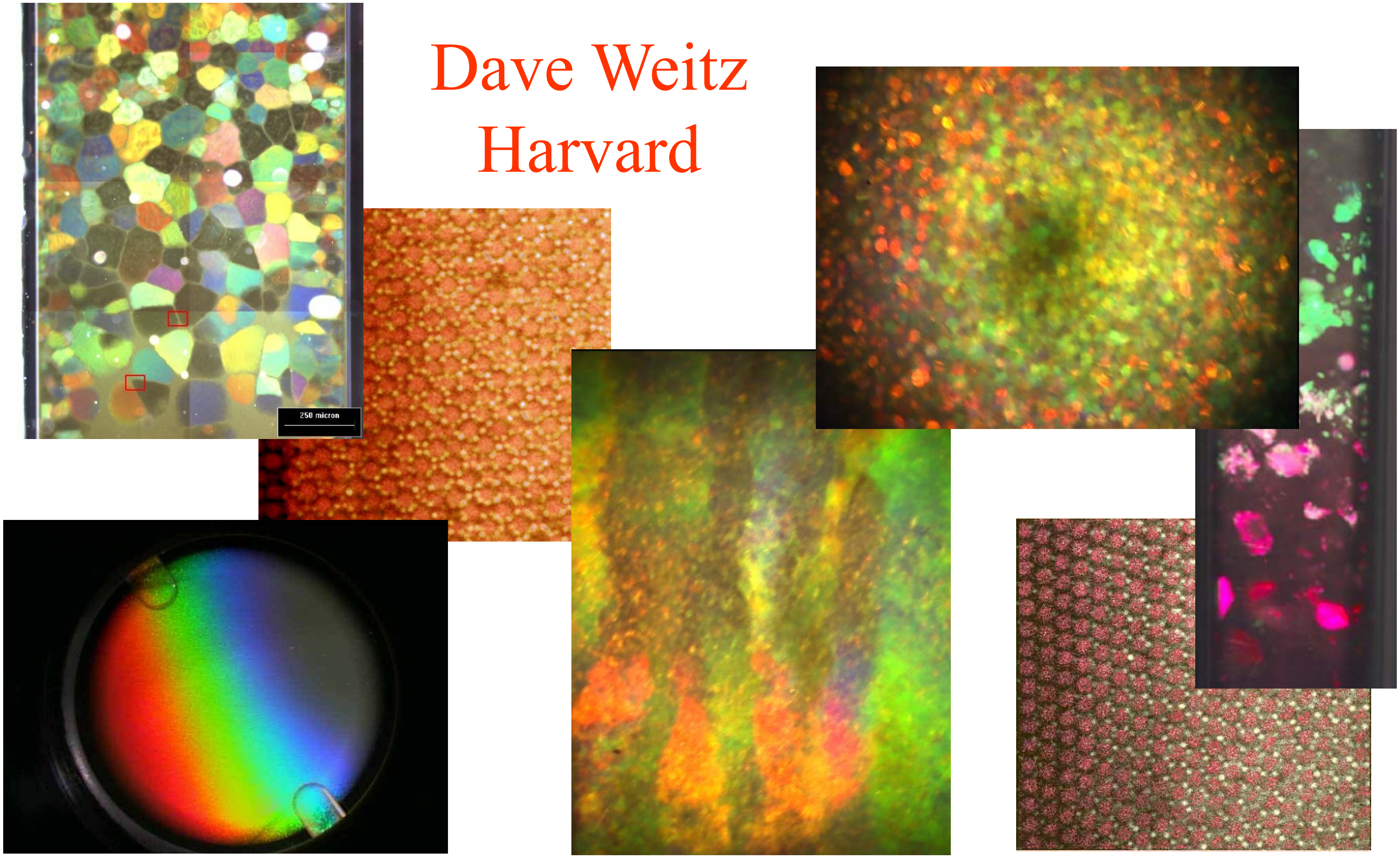
Dave Weitz
Harvard

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

Boulder Summer School
7/24/17

Experimental Colloids I (and I)

Dave Weitz
Harvard



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

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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 → 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

Colloidal particles

- Properties set by particle density
- Concentration of particles low compared to normal material
- Typical solid: ~10^{27} atoms/ m^3 (1 / nm^3)
- Colloids: ~10^{18} particles/ m^3 (1 / μm^3)
- Latent heat of phase transitions too small to measure
- Very low pressure: $\Pi = nk_BT$
- $\Pi \sim 10^{-18} \times 1.4 \times 10^{-23} \times 300 = 4 \times 10^{-3}$ Pa
- Gas: 3×10^{25} molecules/m^3 → 10^5 Pa = 1 atm

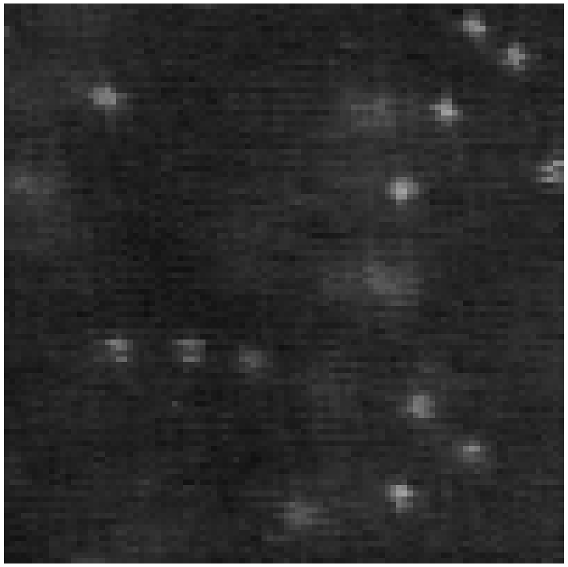
Soft Solids

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

Hard Materials	$\frac{\text{eV}}{\dot{\text{A}}^3}$	GPa
Soft Materials	$\frac{k_B T}{\mu\text{m}^3}$	1 Pa

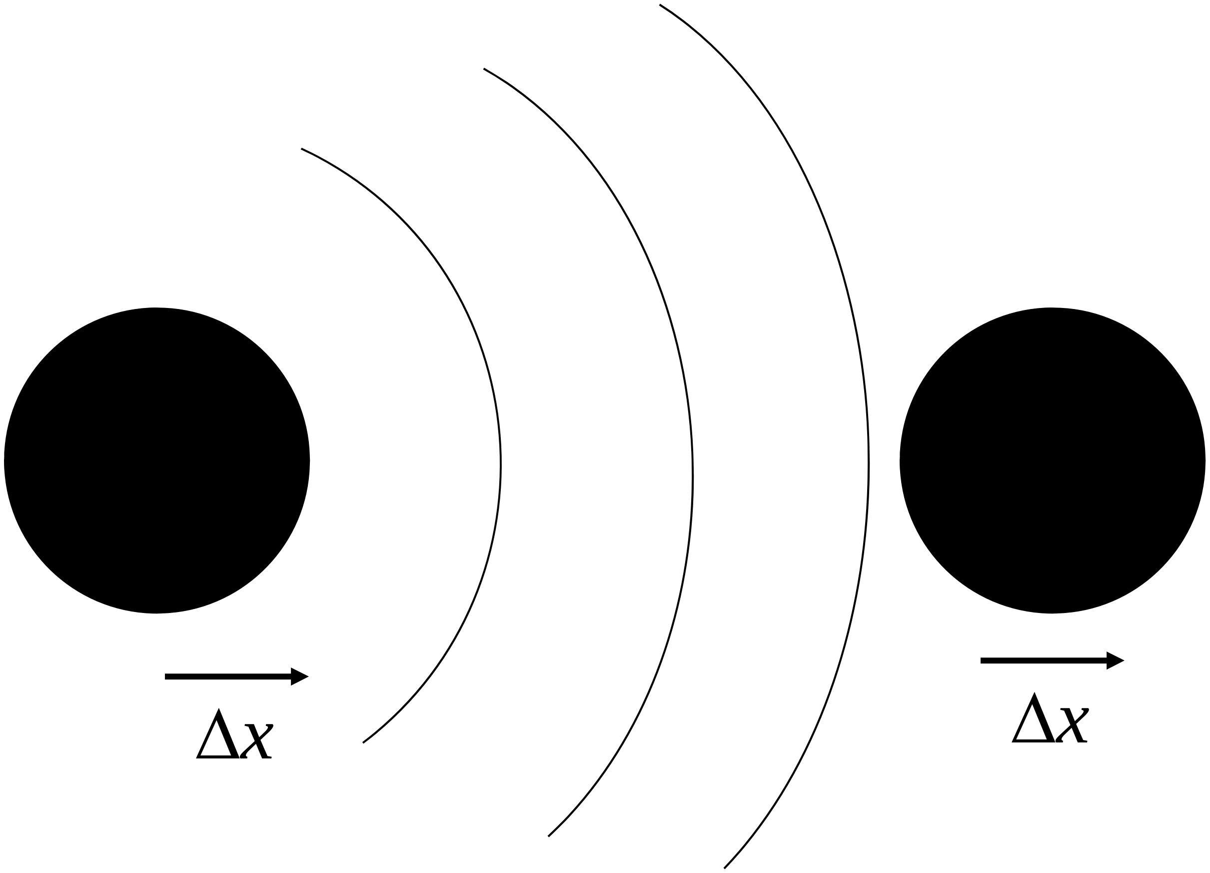
Soft materials invariably have a larger length scale

Continuous phase fluid



- Thermalization with fluid
- Equilibrates particles
- Brownian motion

Continuous phase fluid



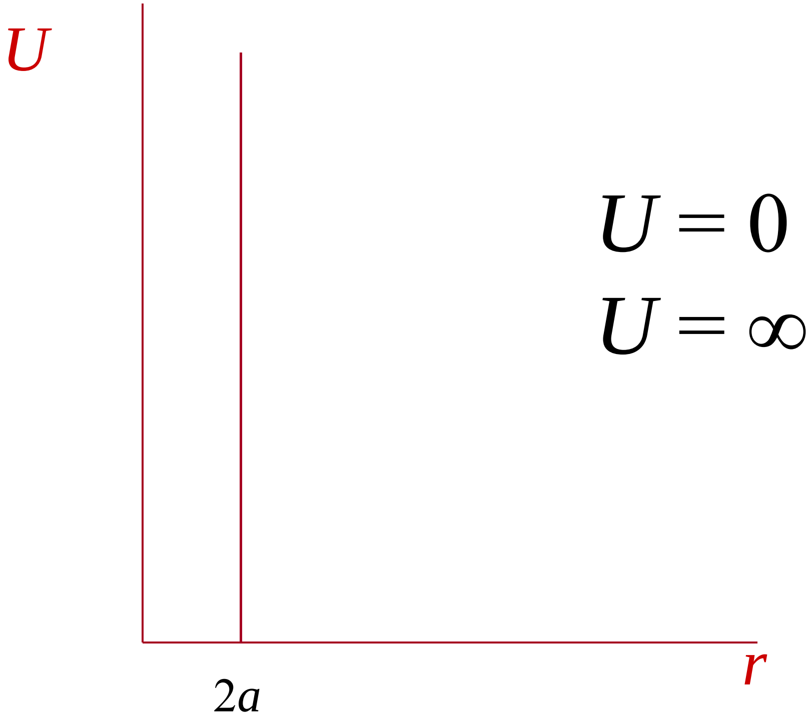
Hydrodynamic interactions

Colloidal particles

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

Colloidal Interactions

Hard-sphere interactions



$$\begin{aligned} U &= 0 \quad r > 2a \\ U &= \infty \quad r \le 2a \end{aligned}$$

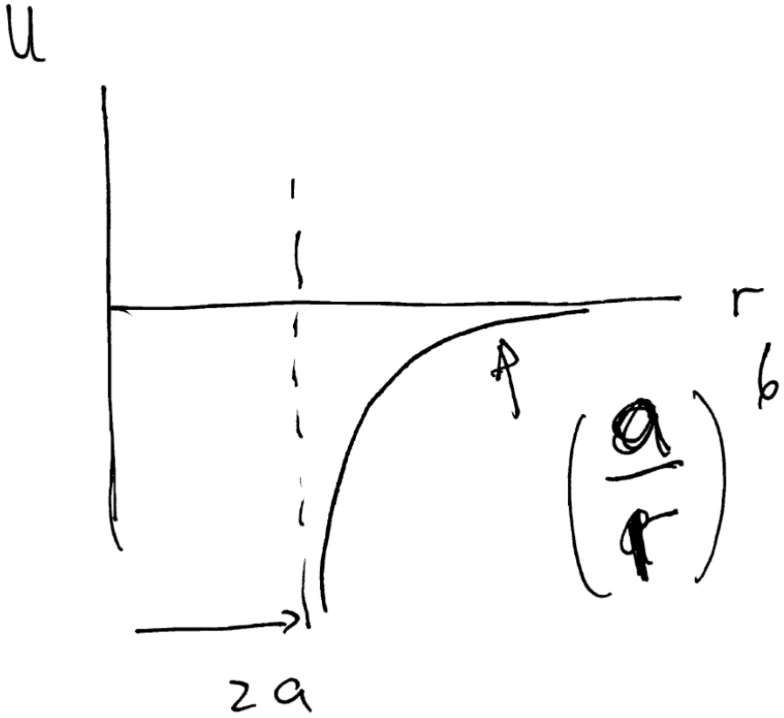
Only excluded volume

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

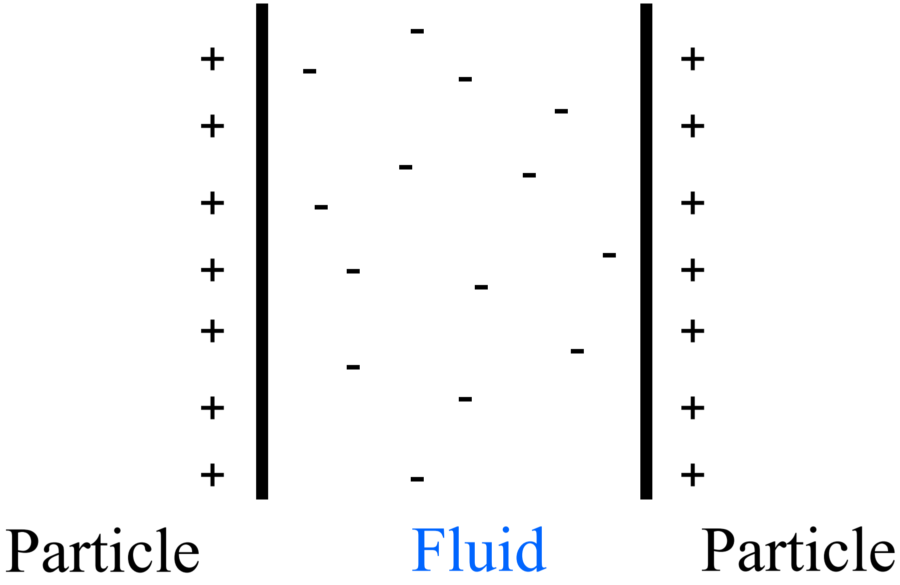
van der Waals interactions

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



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

Stabilizing interactions



Colloidal Interactions - Stabilization

- Screened Coulomb interaction

$$U_{\mathrm{R}} = 2\pi\varepsilon\psi_{\mathrm{o}}^{2}a(2a/R)\exp[-\kappa(R-2a)]$$

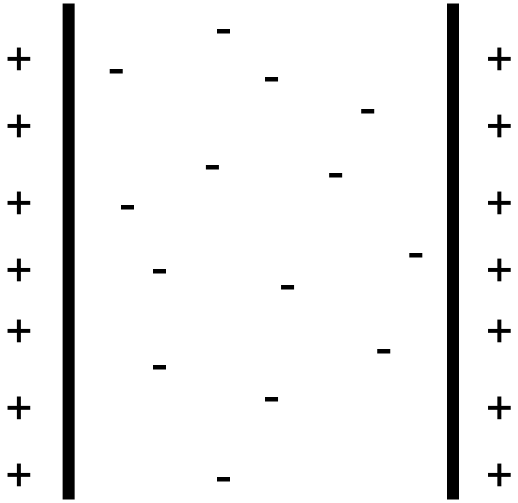
Surface potential

Inverse screening length

$$\kappa = (\varepsilon k_{\mathrm{B}}T/2z^{2}e^{2}n_{\mathrm{b}})^{-1/2}$$

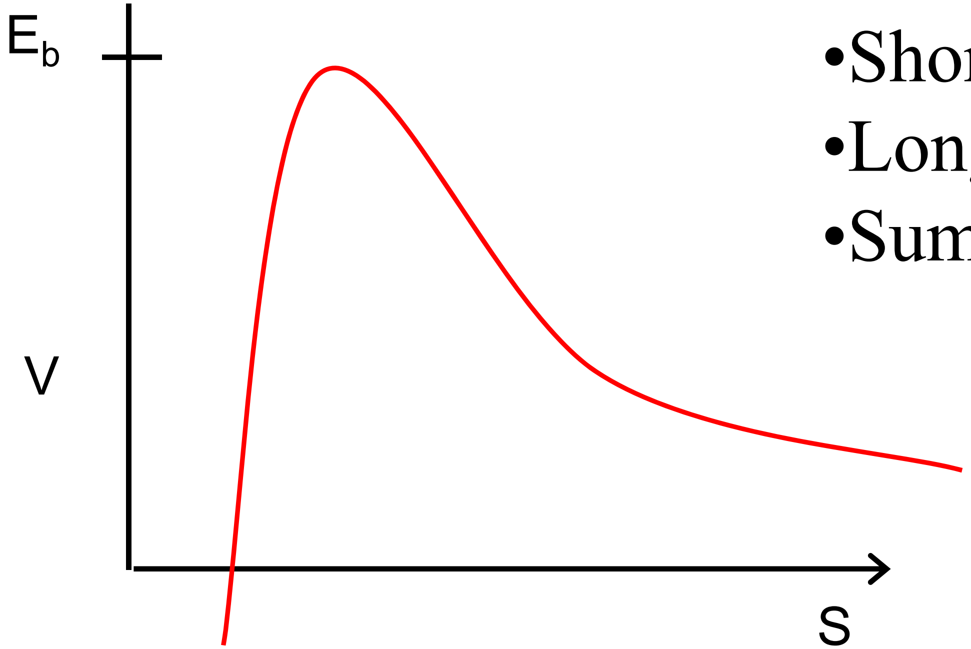
Ion density

Stabilizing interactions



Disjoining pressure:
Can’t compress ions

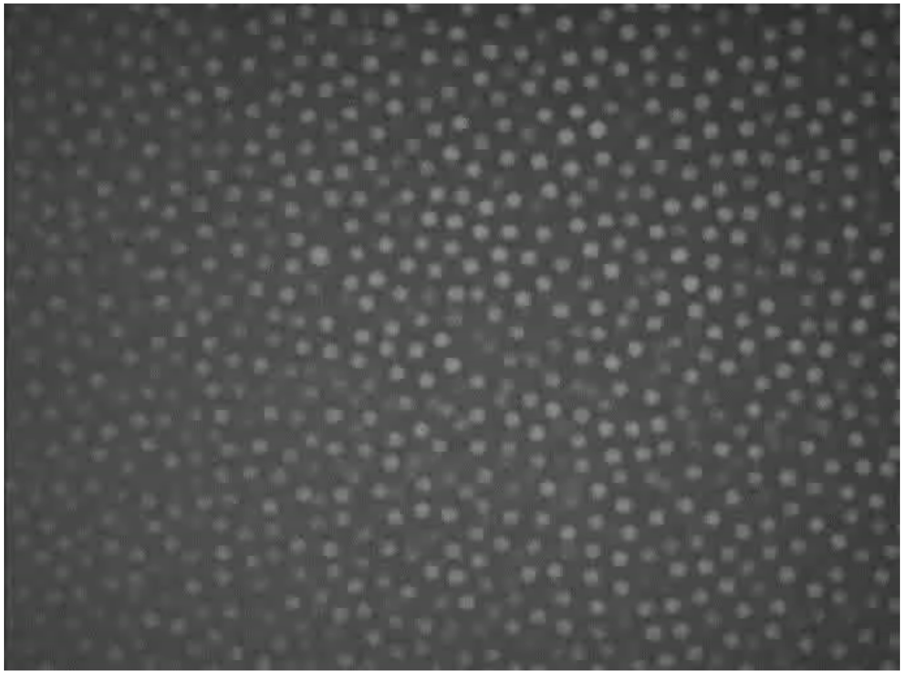
Colloidal interactions – stabilizing



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

$E_b > k_BT$ → Colloid stable against aggregation

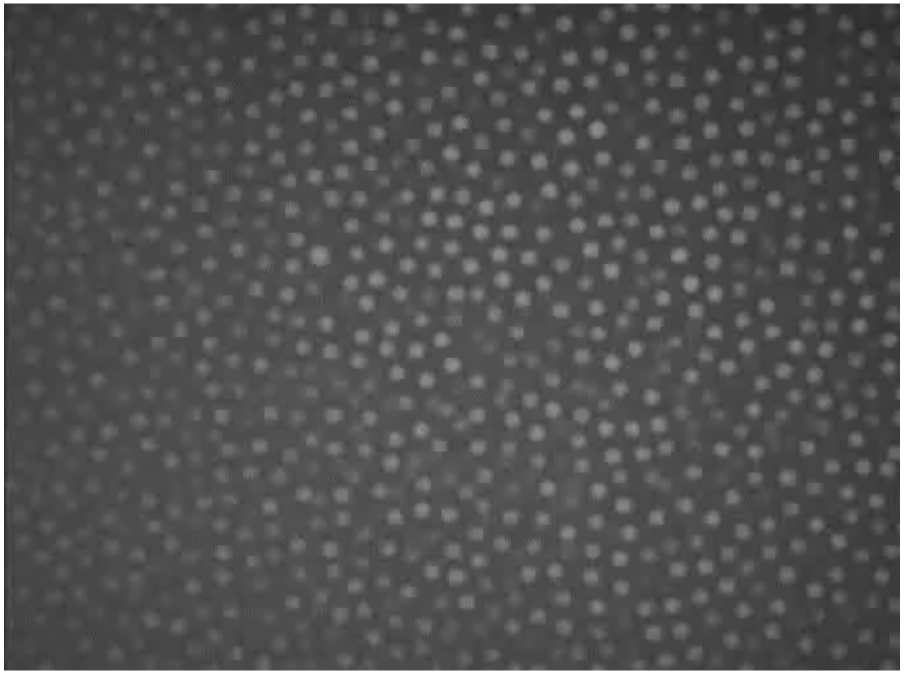
Repulsive Spheres



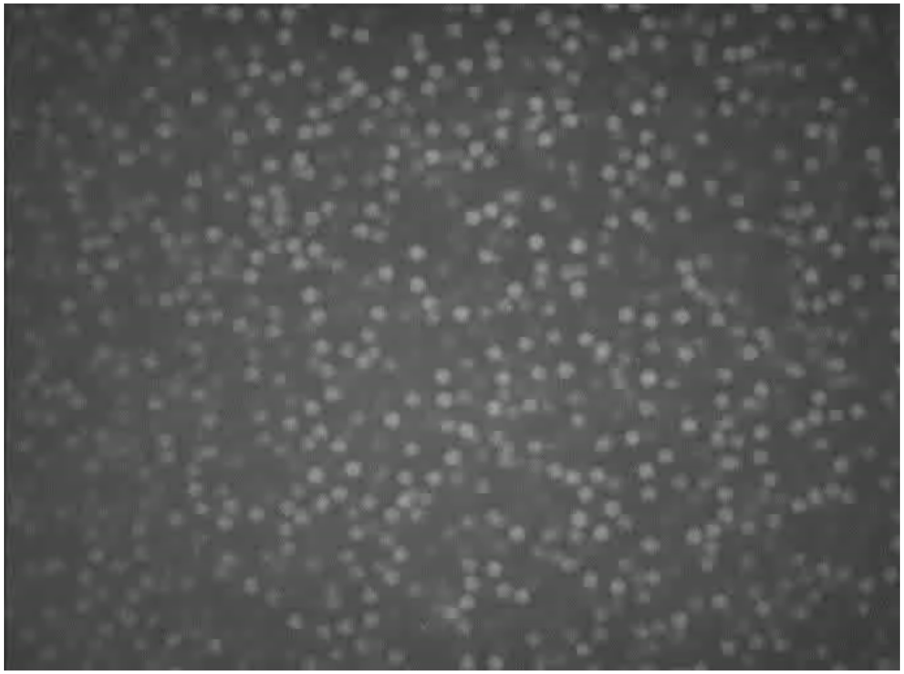
Repulsive interactions

Screen charges

No Salt



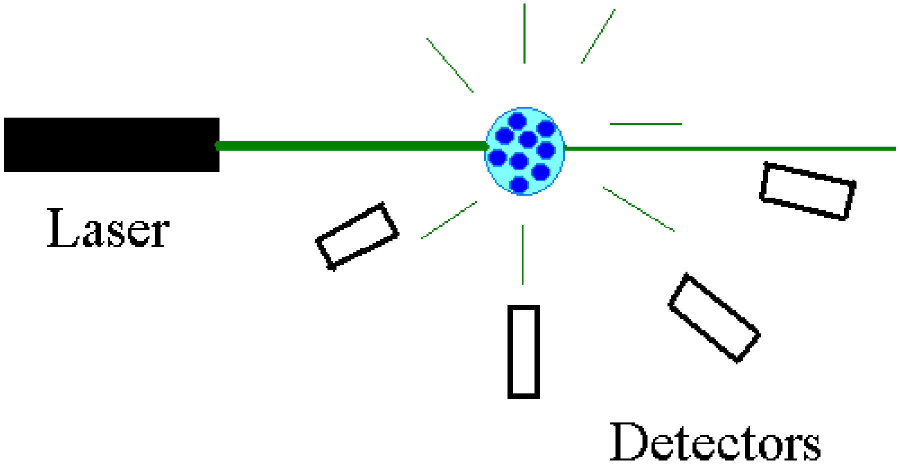
Salt

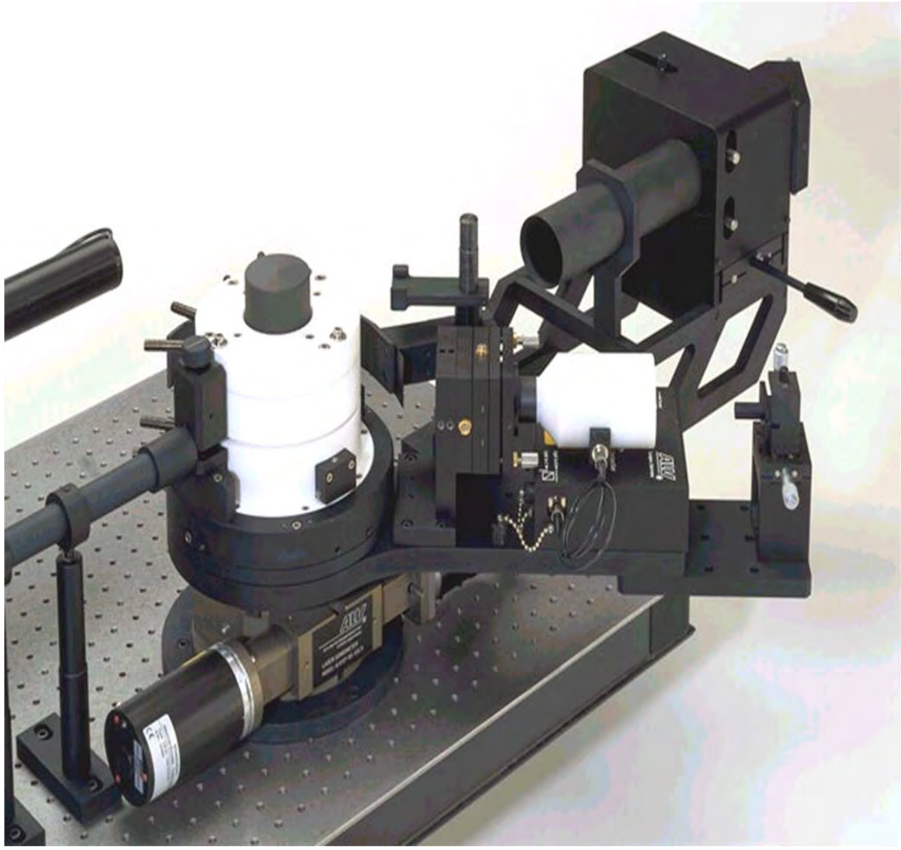


Experimental Techniques

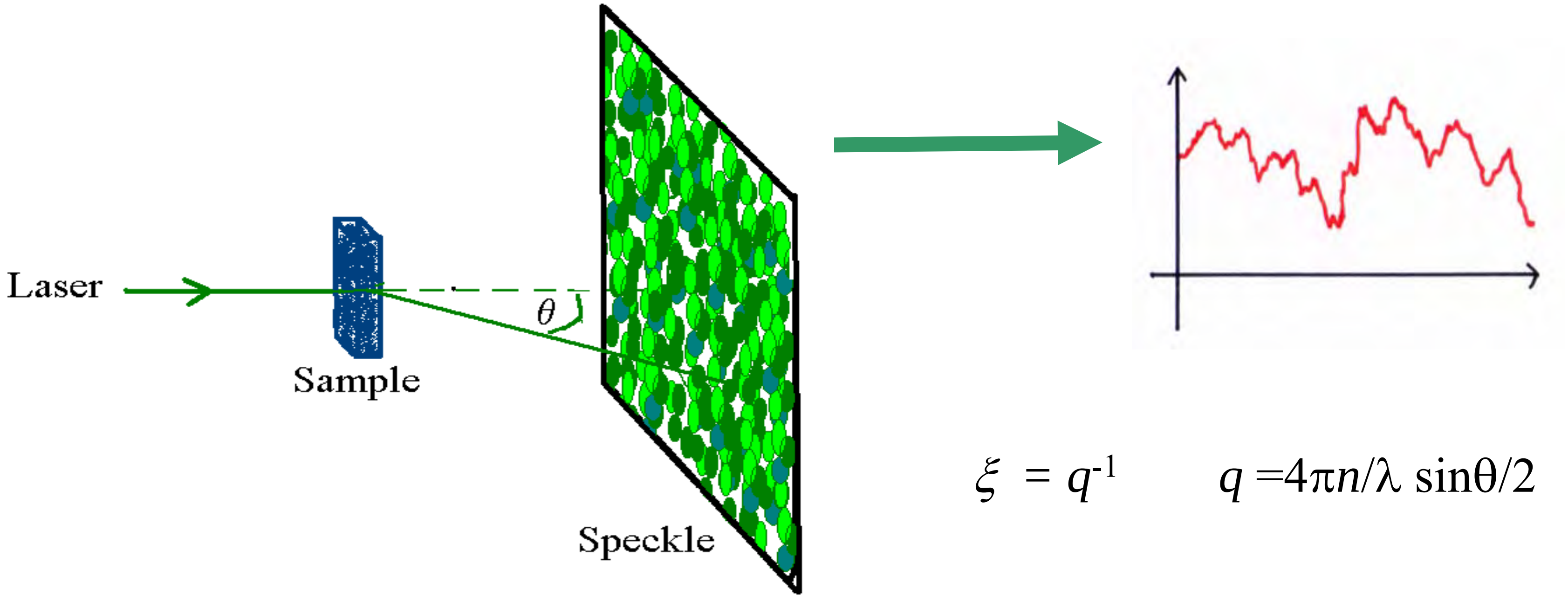
- Light scattering
  - Static light scattering
  - Dynamic light scattering
  - Ultra-small angle dynamic light scattering
  - Diffusing-wave spectroscopy
- Microscopy
- Rheology
  - microrheology

Dynamic Light Scattering





Structure and Dyanmics: Light Scattering

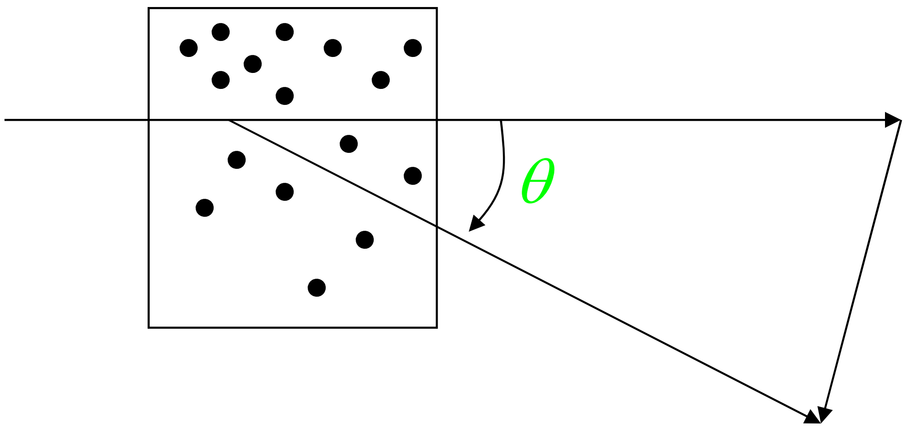


$\xi = q^{-1}$ $\quad$ $q = 4\pi n/\lambda \sin\theta/2$

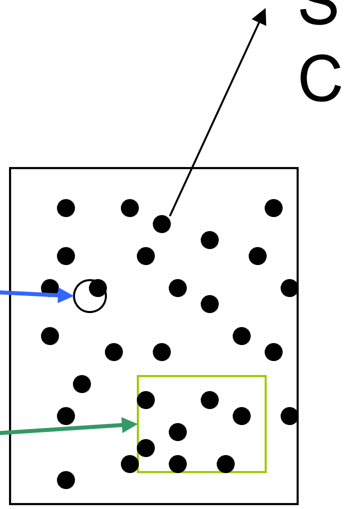
- SLS: $< I >$ vs. q ⟶ probe structure
- DLS: $< I(q,t)I(q,t+\tau) >$ ⟶ probe dynamics $f(q,\tau)$

Light Scattering

Probes characteristic sizes of colloidal particles



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



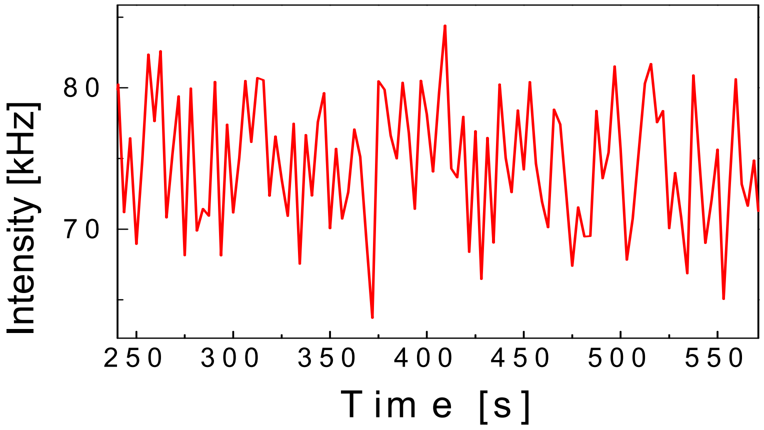
Speckle:
Coherence area

DYNAMIC LIGHT
SCATTERING:
Single speckle

STATIC LIGHT
SCATTERING:
Many speckles

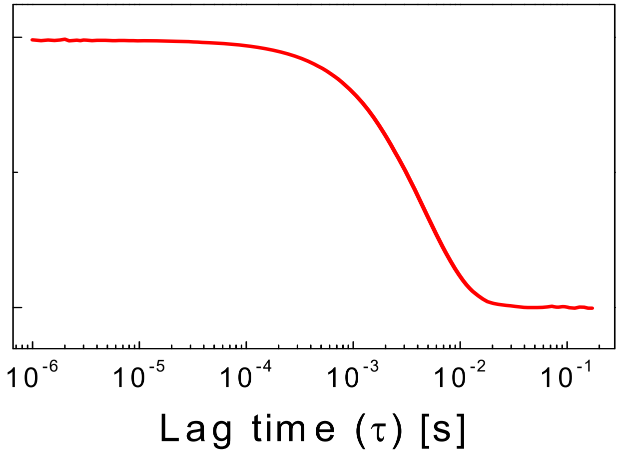
Dynamic Light Scattering

Measure temporal intensity fluctuations



Obtain an intensity autocorrelation function

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



Dynamic Light Scattering

Measure temporal correlation function of scattered light:
Intermediate structure factor

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

$$\langle E(0)E(t)\rangle = \left\langle A^2 \sum_{m,n} e^{i\vec{q}\bullet\{\vec{r}_m(0)-\vec{r}_n(t)\}} \right\rangle$$

Time average over all particles

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

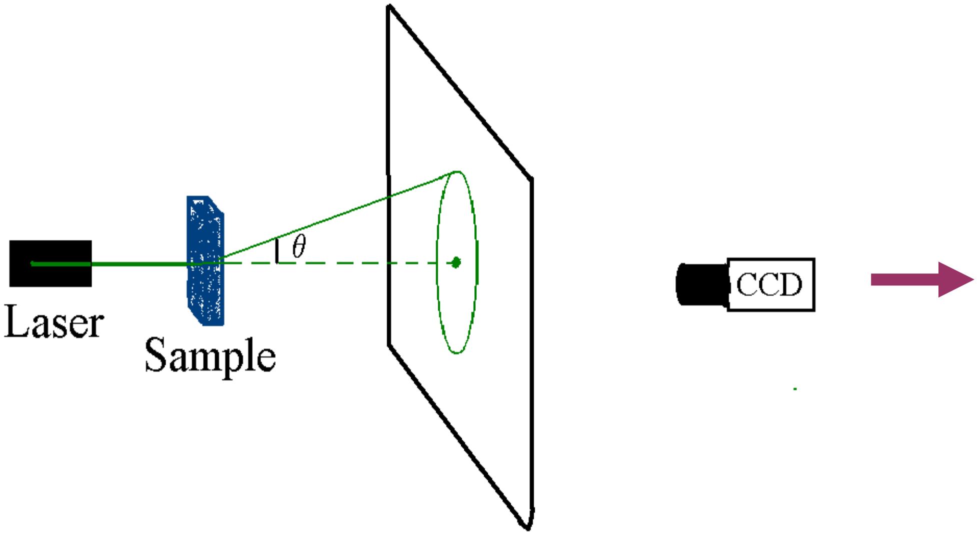
Correlations only between the same particles
Cumulant expansion: $\Delta r^2(t) \sim Dt$

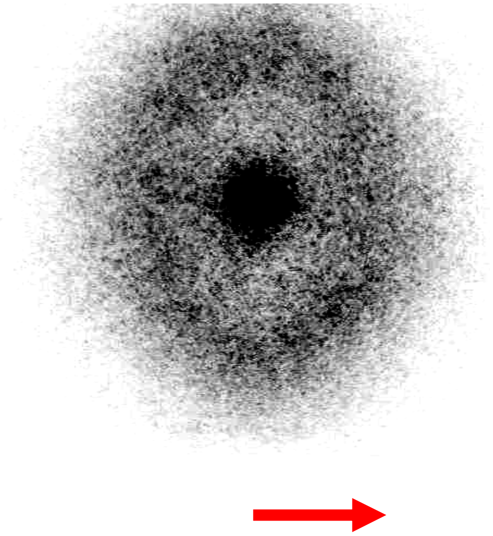
$$\sim e^{-q^2 Dt}$$

Physics: How to change the phase of the field by π
Each particle must move by $\sim\lambda$

Ultra Small Angle Light Scattering

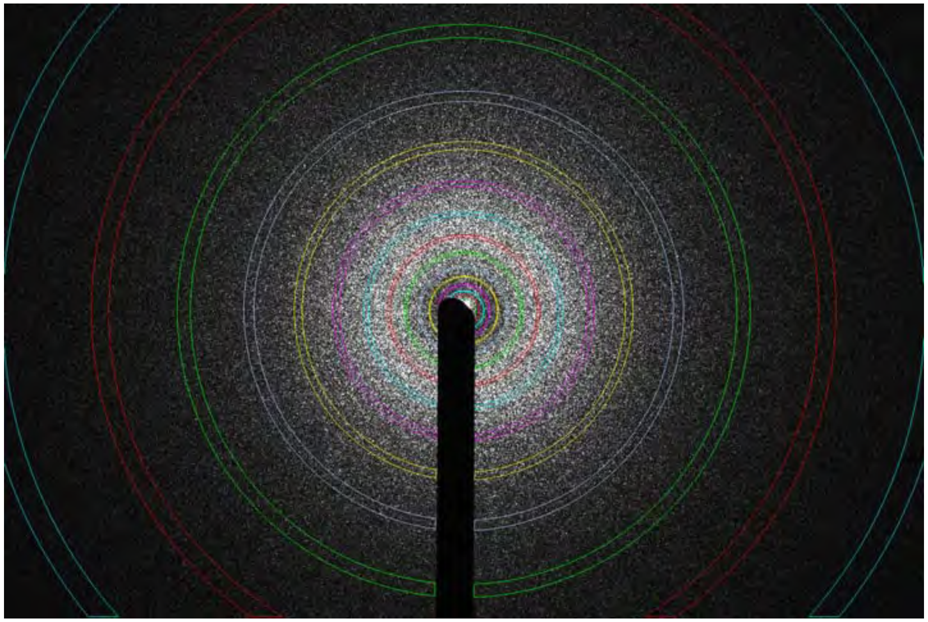
Probe Structure





L. Cipelletti

Multispeckle Detection



0.07 deg to 5.0 deg

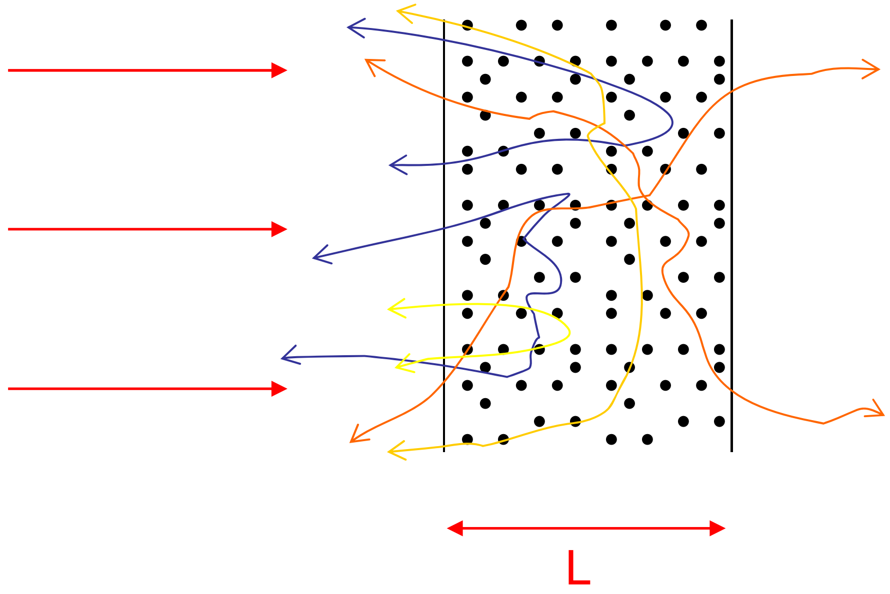
$100\ \mathrm{cm}^{-1} < q < 7000\ \mathrm{cm}^{-1}$

Average over constant *q*:

- non-ergodic samples
- avoid excessive time averaging

Diffusing Wave Spectroscopy: Very strong scattering

TRANSMISSION

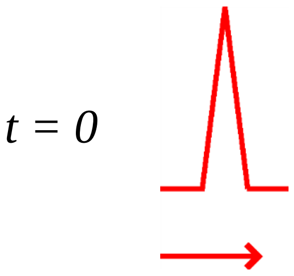


MOST LIGHT IS SCATTERED BACK

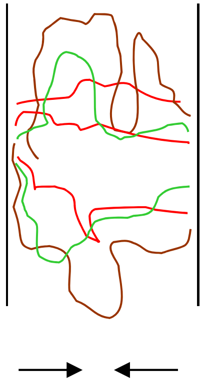
→ MILK IS WHITE!!

D. Pine, P. Chaikin, E. Herbolzheimer

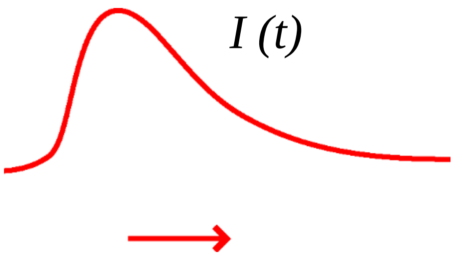
P(s): DIFFUSION EQUATION



PRL **60**, 1134 (88)



$z_0 = \gamma \ell^*$

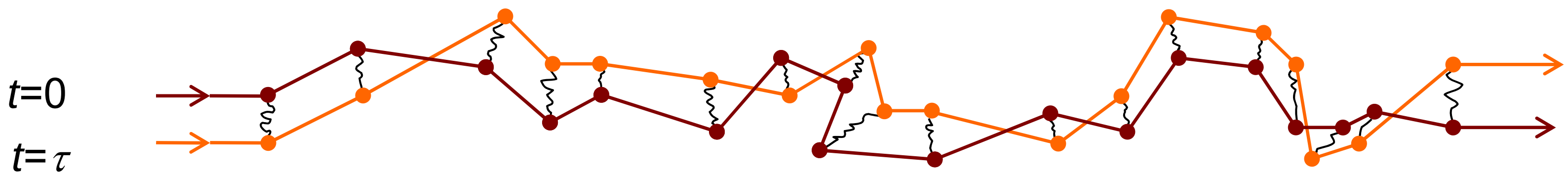


I(t) ~ # PATHS OF LENGTH $s = ct$

→ **P(s)**

SINGLE PATH

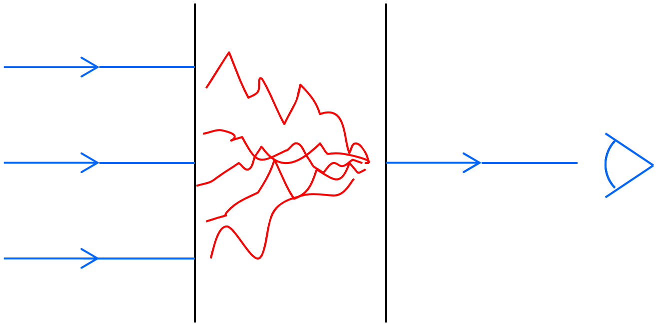
[MARET & WOLFE]



n SCATTERING EVENTS

$s = n\ell$ → PATH LENGTH

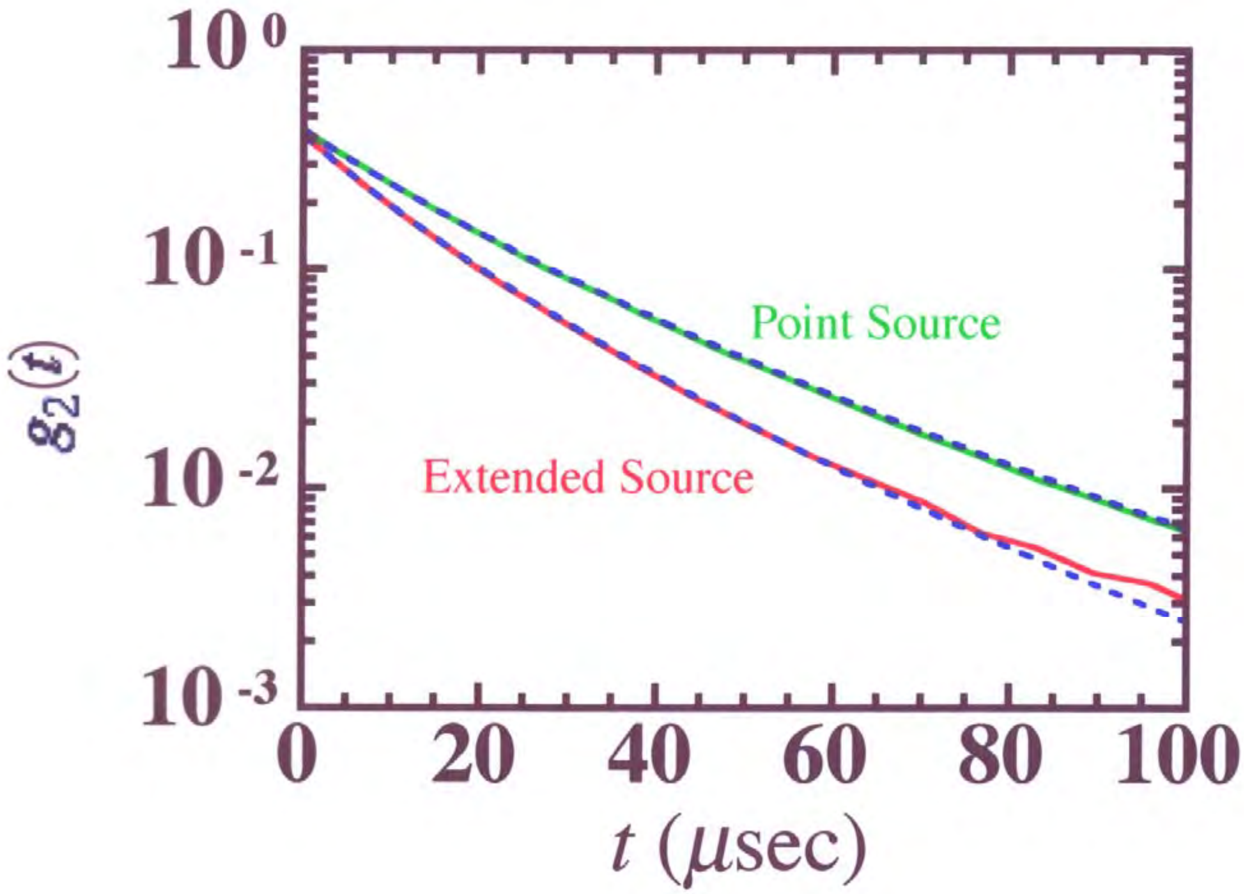
EXTENDED SOURCE



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

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

TRANSMISSION



$$d = 0.6\mu\text{m}$$

$$\phi = 2\%$$

DWS PROBES MOTION ON *SHORT* LENGTH SCALES

PHASE OF PATH CHANGES WHEN PATH LENGTH CHANGES BY
~1 WAVELENGTH

$$\lambda \sim 5000\ \text{Å}$$

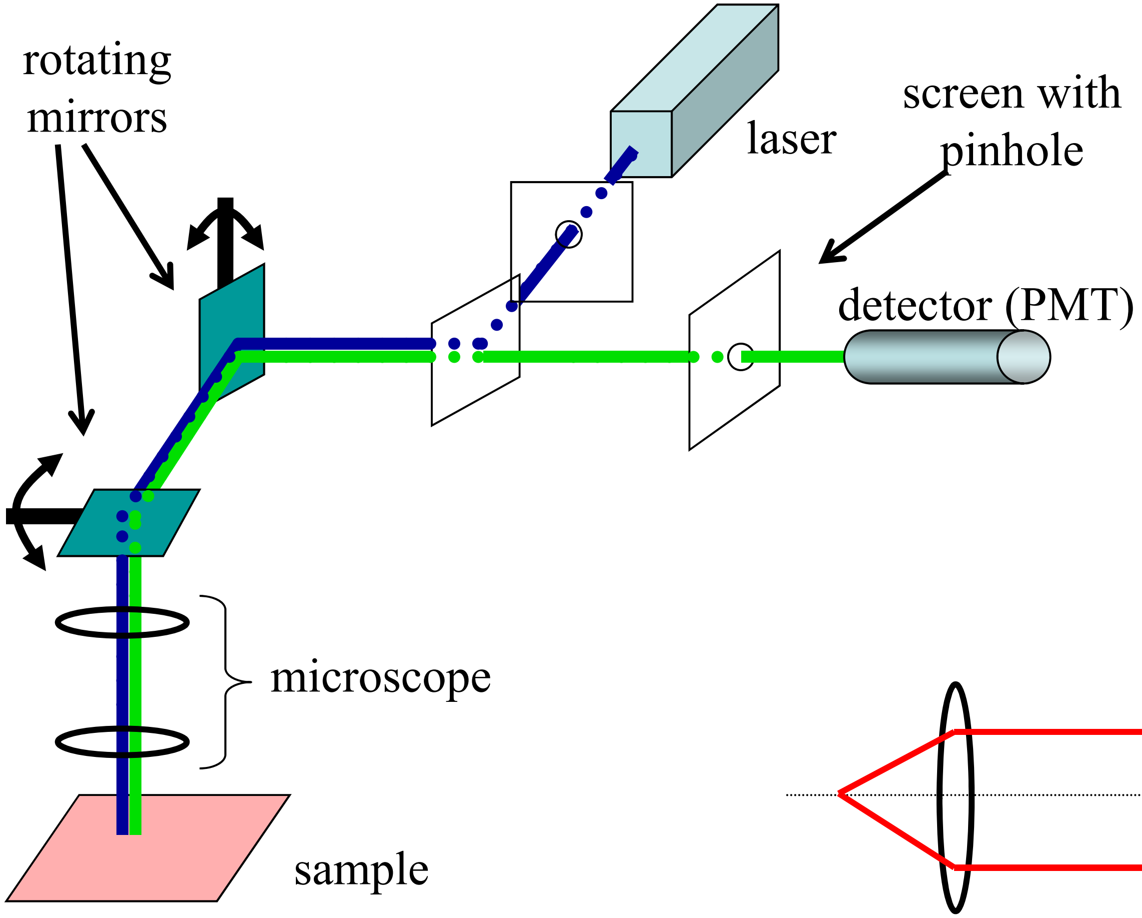
BUT: LIGHT IS SCATTERED FROM MANY PARTICLES

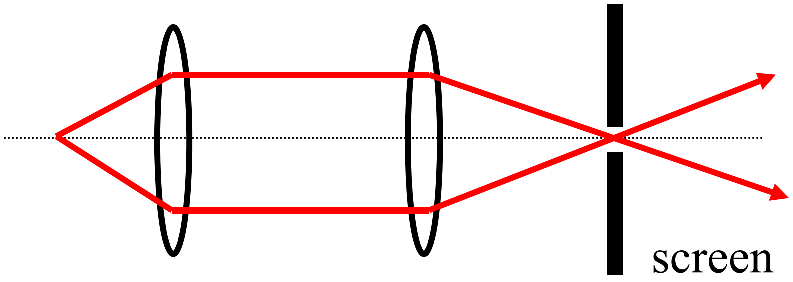
$$\left(\text{Estimate:}\qquad \left(\frac{L}{\ell^*}\right)^2 \approx \left(\frac{10^3}{10}\right)^2 \approx 10^4\right)$$

∴ MOTION OF EACH **INDIVIDUAL** PARTICLE CAN BE **MUCH** LESS

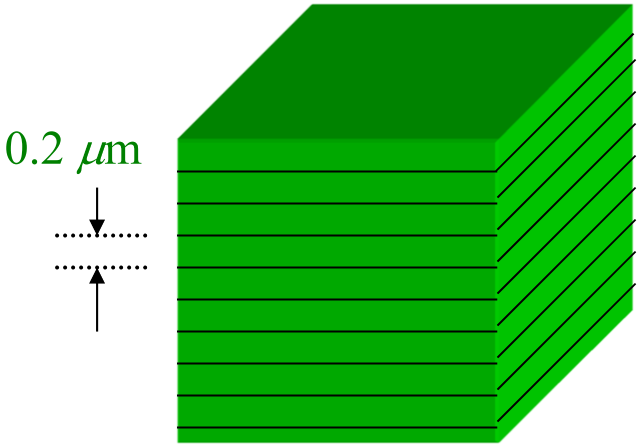
→ CAN MEASURE PARTICLE MOTION ON SCALE OF
~ 5 Å

Confocal Microscopy

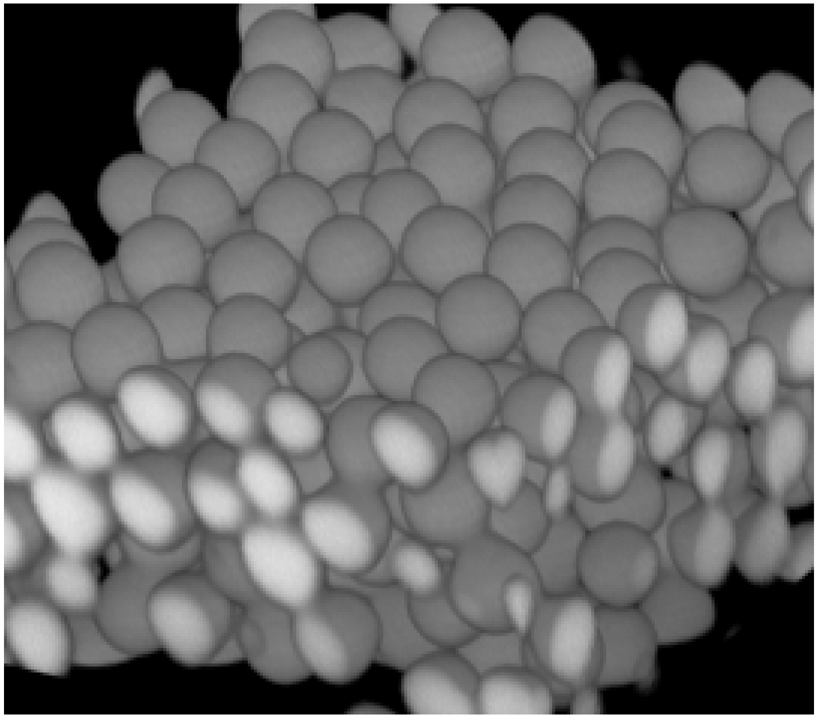




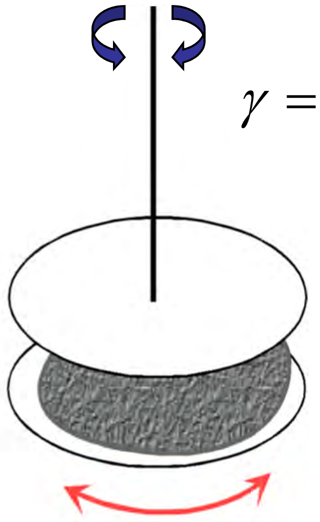
Confocal microscopy for 3D pictures



Scan many slices,
reconstruct 3D image



Rheology



$$\gamma = \gamma_o \sin(\omega t)$$

$$\sigma = \sigma_o \sin(\omega t + \delta)$$

$$\sigma = E\gamma$$

Elasticity

$$\sigma = \eta\dot{\gamma}$$

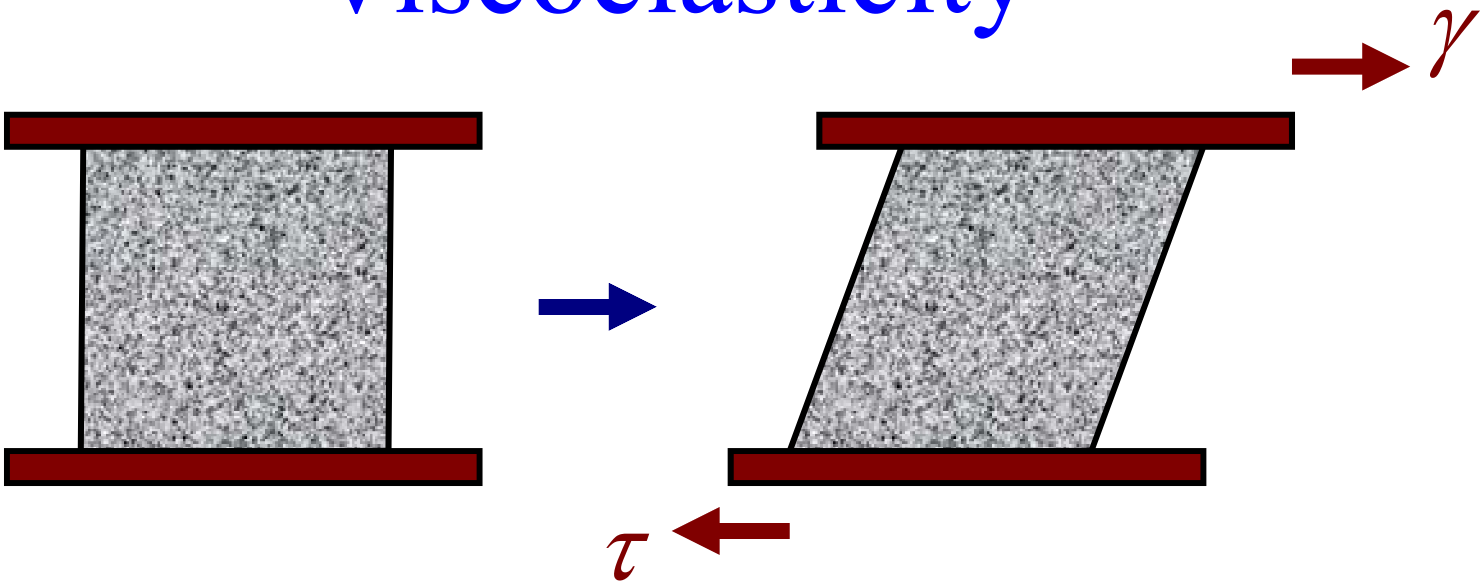
Viscosity

$$\sigma = \sigma_o(\cos\delta \sin\omega t + \sin\delta \cos\omega t)$$

G’ G”

Mechanical Properties of Soft Materials:

Viscoelasticity



Solid: $\tau = G\gamma$

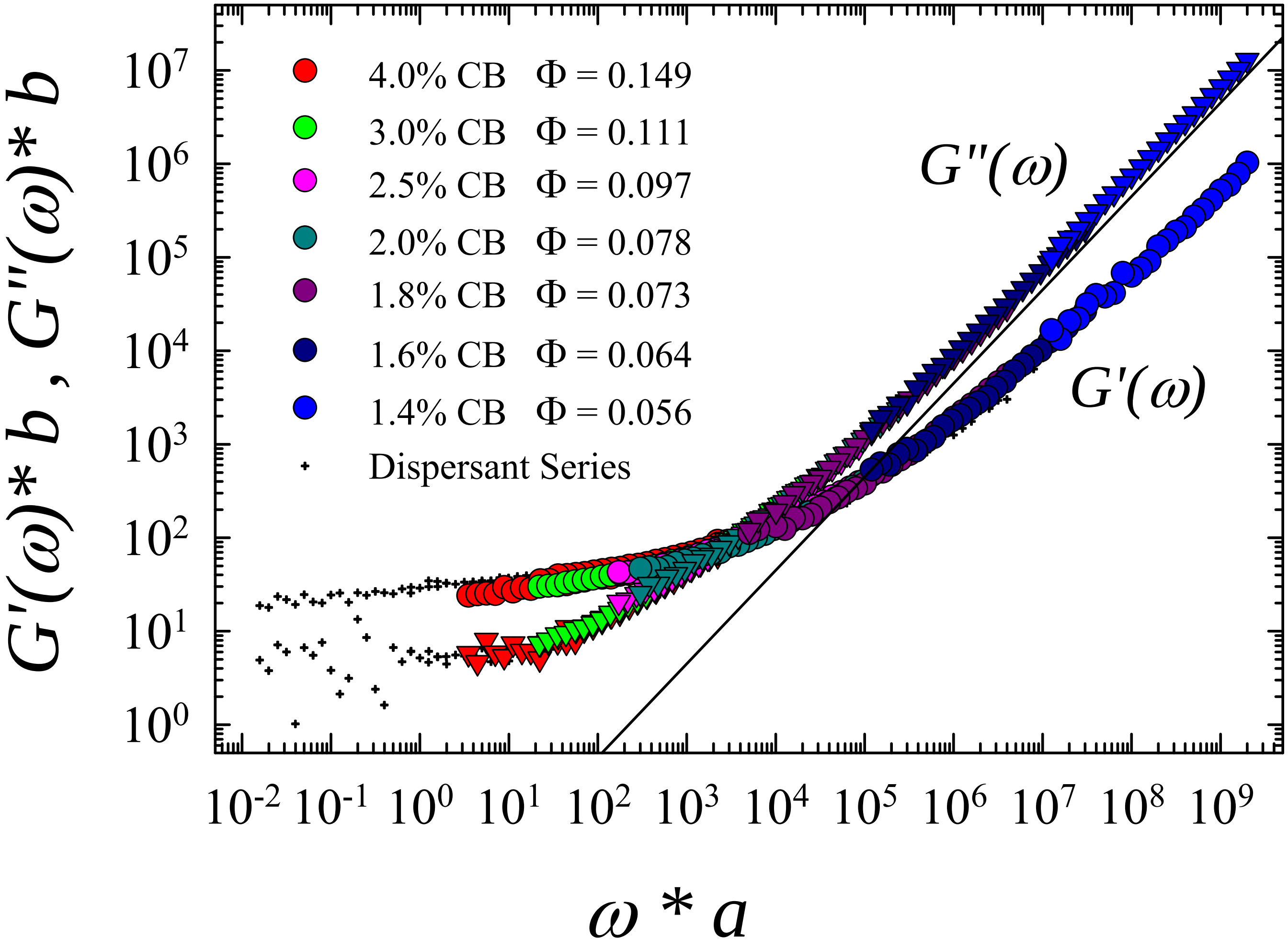
Fluid: $\tau = \eta\dot{\gamma}$

$$\xrightarrow{\gamma = \gamma_0 e^{i\omega t}} \quad \tau = \left[G'(\omega) + iG''(\omega) \right] \gamma$$

Elastic

Viscous

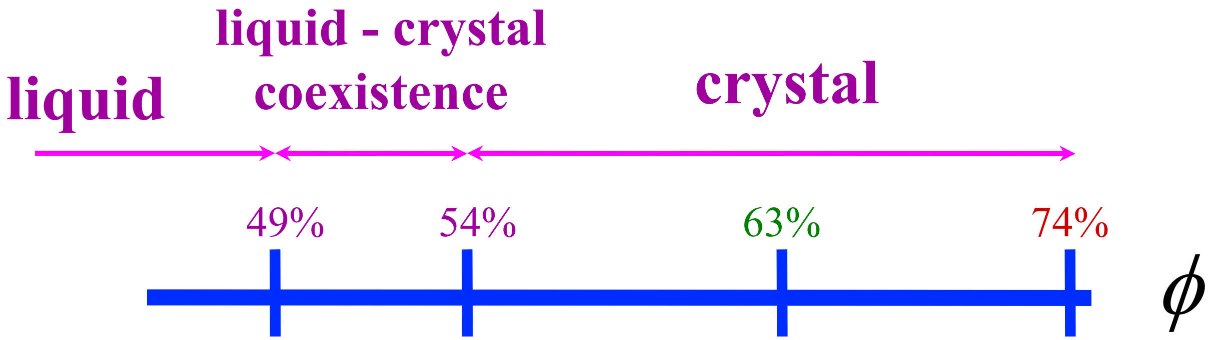
Rheology of soft materials



Scaling plot

Hard Sphere Phase Diagram

Volume Fraction Controls Phase Behavior



liquid

liquid - crystal coexistence

crystal

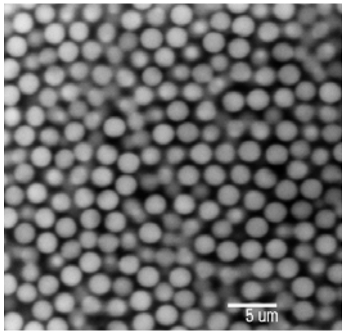
49%

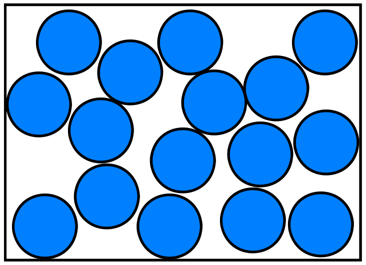
54%

63%

74%

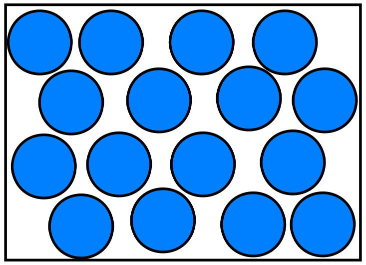
ϕ





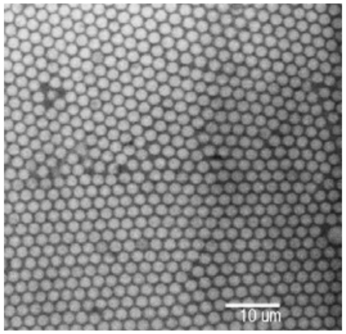
maximum packing

$\phi_{RCP} \approx 0.63$



maximum packing

$\phi_{HCP} = 0.74$



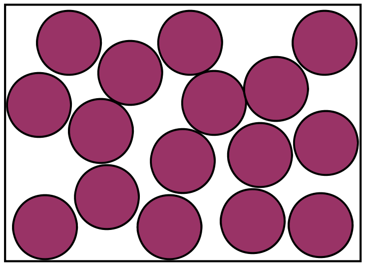
Increase ϕ => Decrease Temperature

$$F = \overset{0}{\cancel{U}} - TS$$

Entropy Drives Crystallization

Entropy => Free Volume

$$F = \cancelto{0}{U} - TS$$

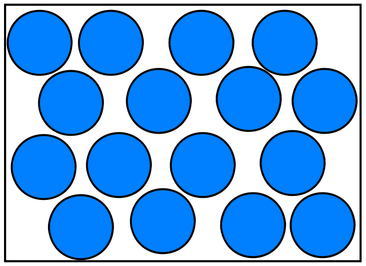


Disordered:

- Higher configurational entropy
- Lower local entropy
- Higher Energy

maximum packing

$\phi_{RCP} \approx 0.63$



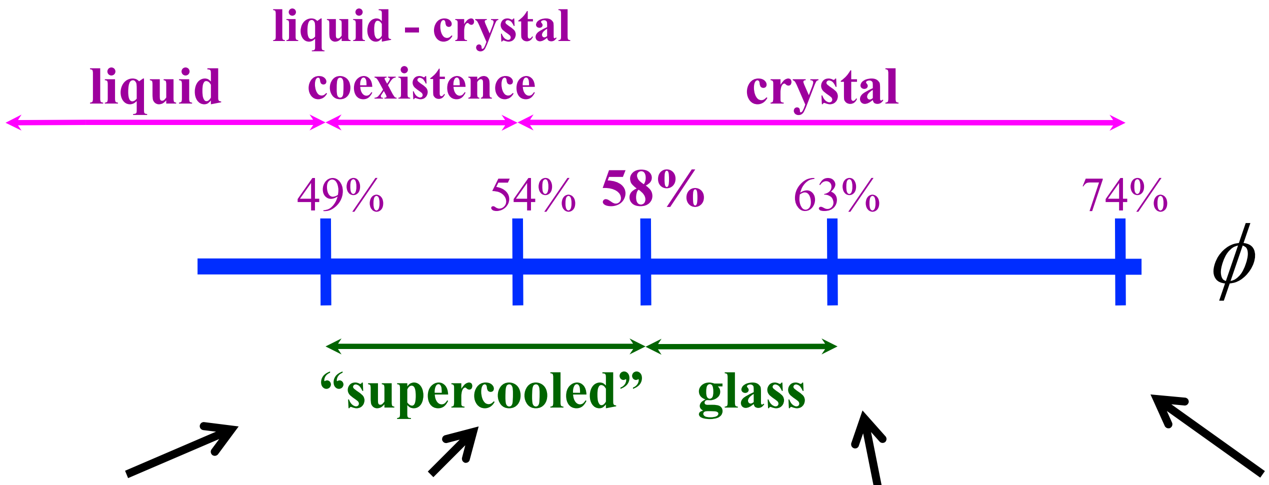
Ordered:

- Lower configurational entropy
- Higher local entropy
- Lower Energy

maximum packing

$\phi_{HCP} = 0.74$

Metastable Hard Sphere Phases



liquid - crystal coexistence

liquid

crystal

49%

54%

58%

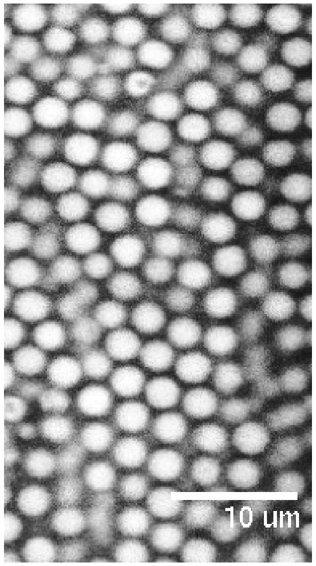
63%

74%

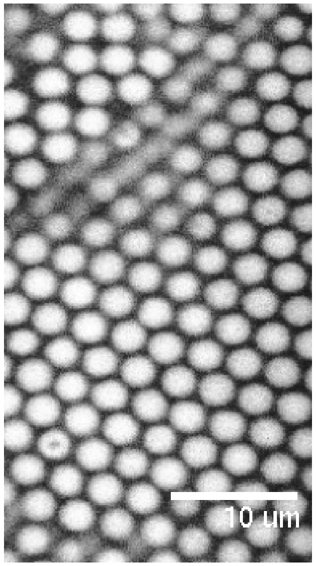
ϕ

“supercooled”

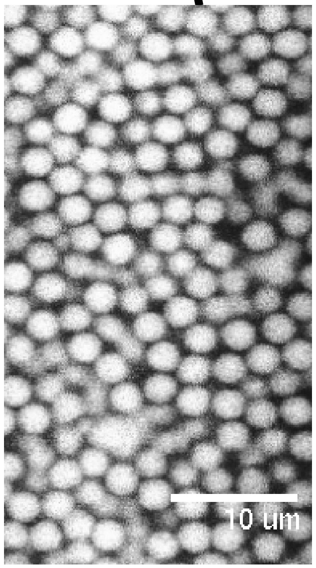
glass



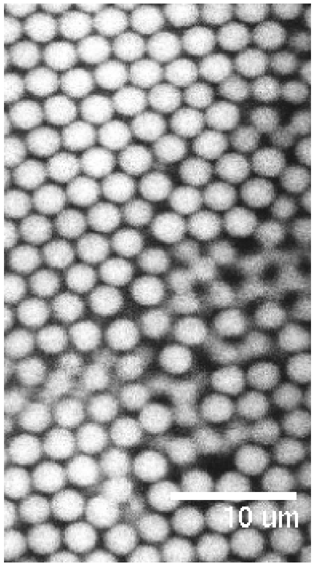
$\phi_{\text{liquid}} \approx 0.48$



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

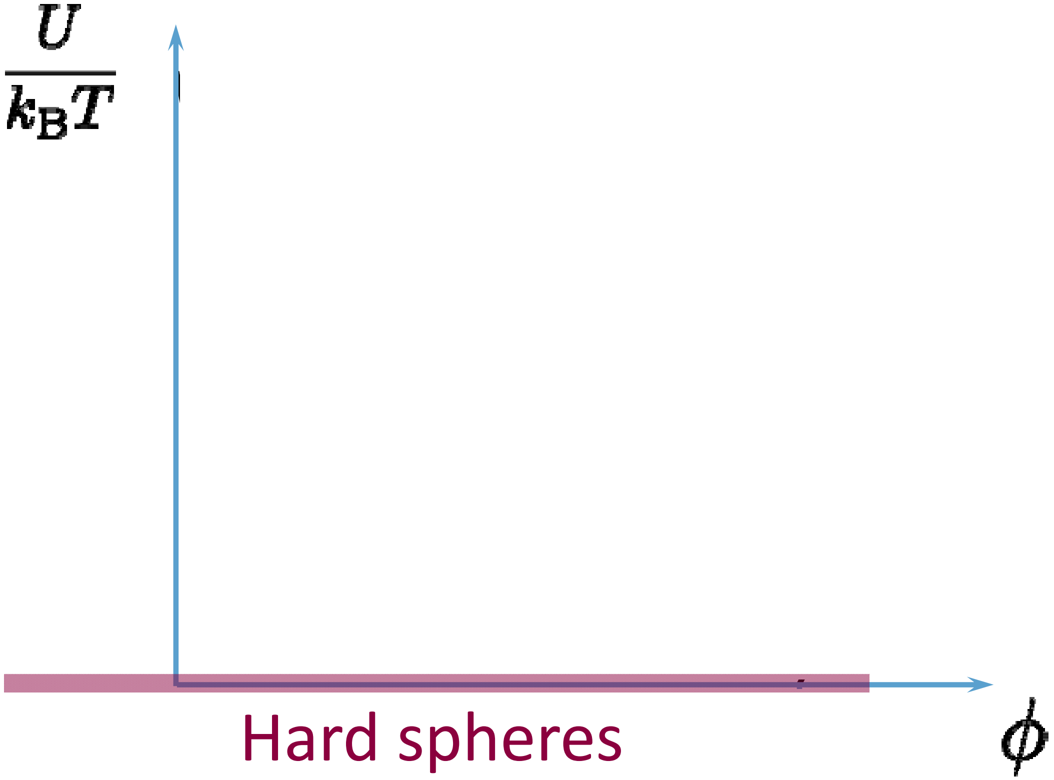


Maximum packing
$\phi_{\text{RCP}} \approx 0.63$



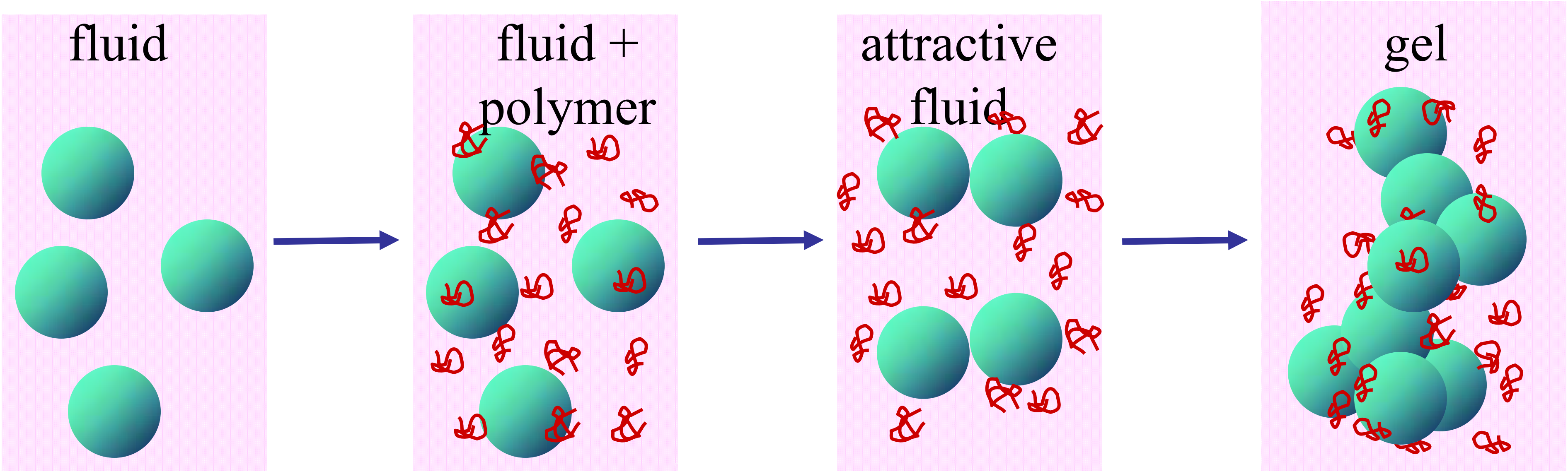
Maximum packing
$\phi_{\text{HCP}} = 0.74$

State diagram for colloidal particles



Controlled Attraction of Colloidal Particles

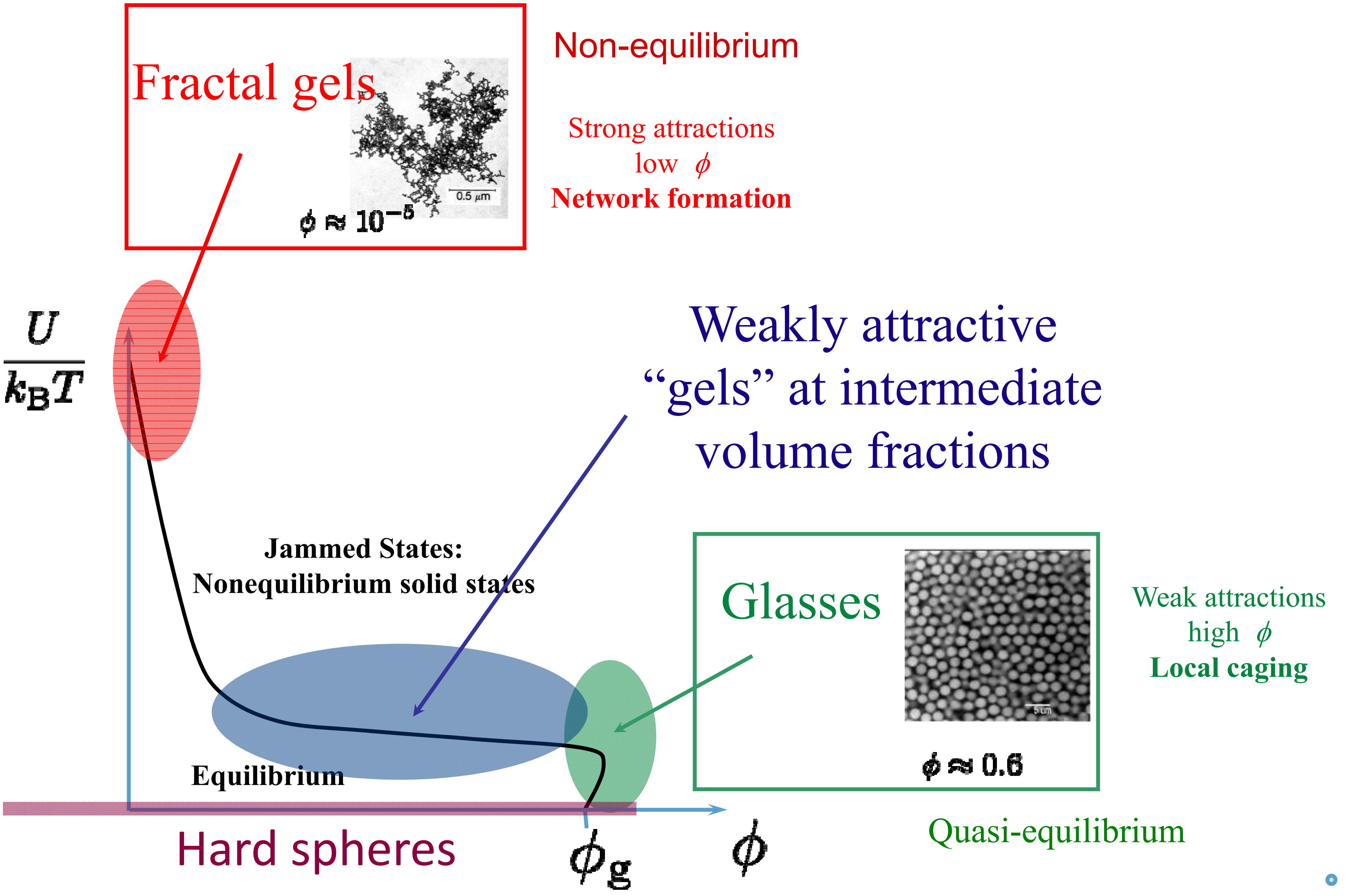
Depletion attraction



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

T. Dinsmore

State diagram for colloidal particles



Fractal gels

Non-equilibrium

Strong attractions
low ϕ
Network formation

Weakly attractive
"gels" at intermediate
volume fractions

Jammed States:
Nonequilibrium solid states

Glasses

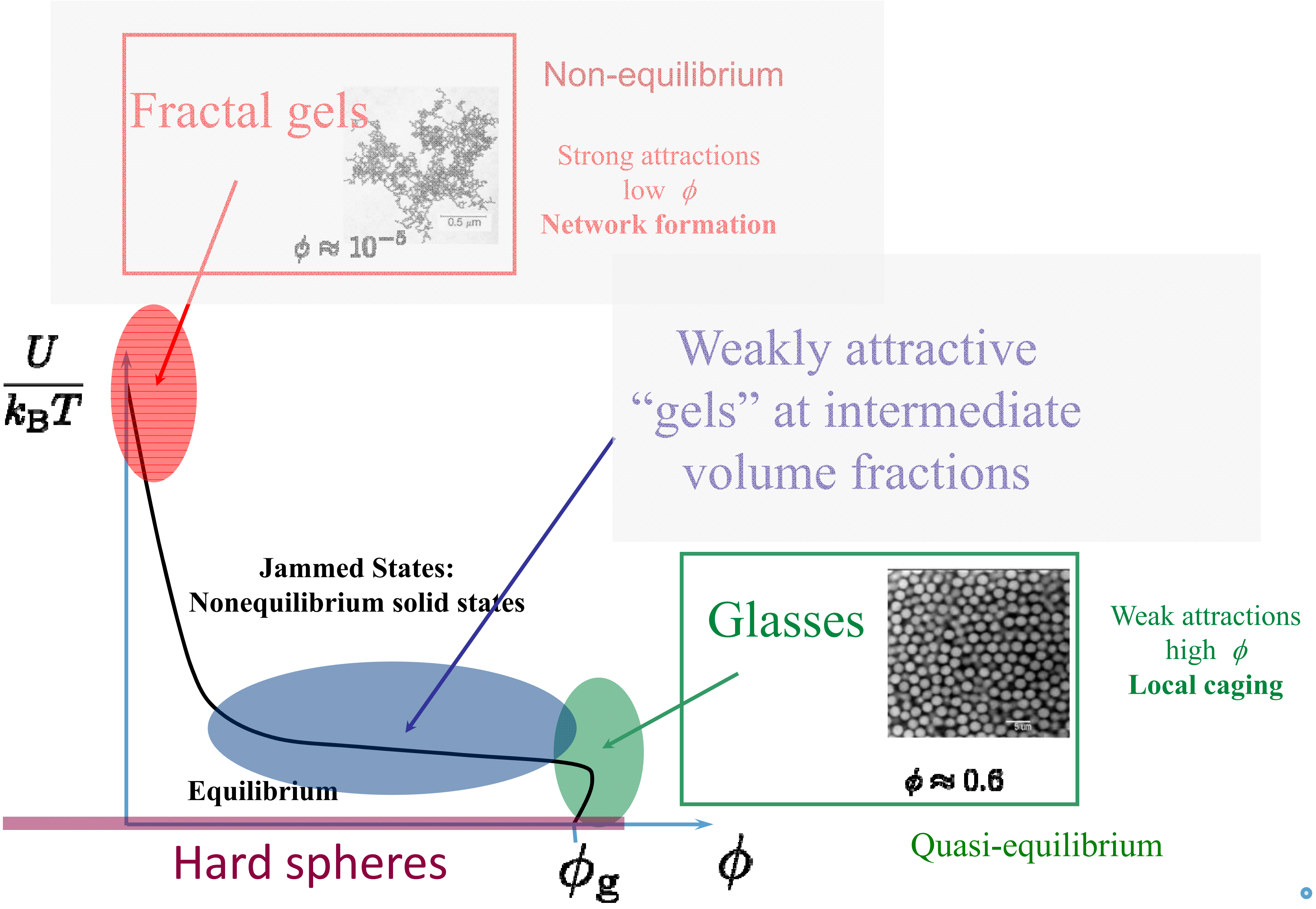
Weak attractions
high ϕ
Local caging

Equilibrium

Hard spheres

Quasi-equilibrium

State diagram for colloidal particles



Fractal gels

$\phi \approx 10^{-5}$

Non-equilibrium

Strong attractions
low ϕ
Network formation

Weakly attractive
“gels” at intermediate
volume fractions

Jammed States:
Nonequilibrium solid states

Glasses

$\phi \approx 0.6$

Weak attractions
high ϕ
Local caging

Equilibrium

Hard spheres

Quasi-equilibrium

Hard spheres: ϕ-dependent structure factor

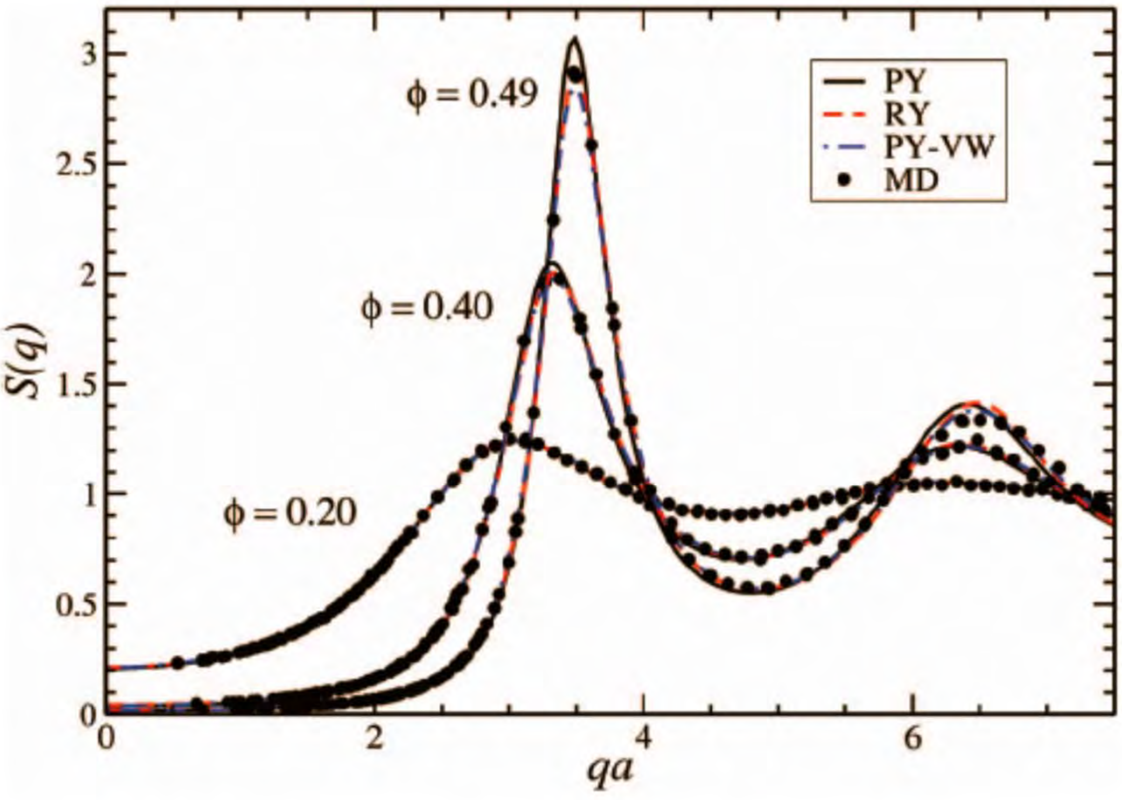
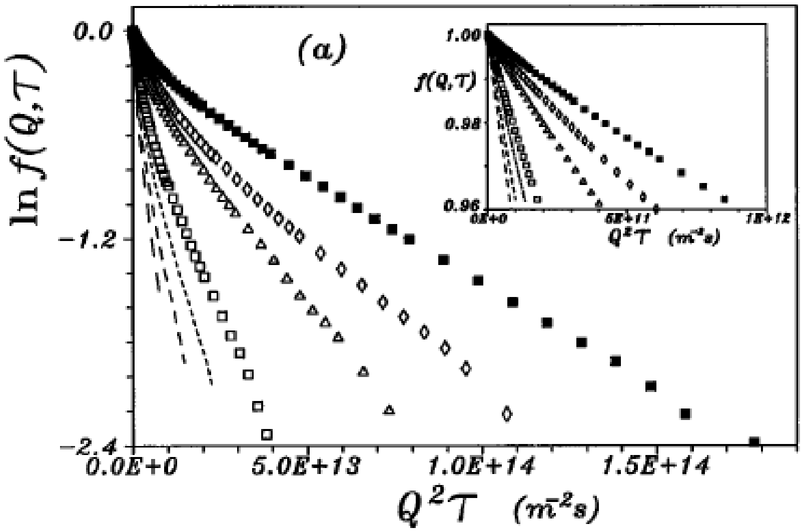


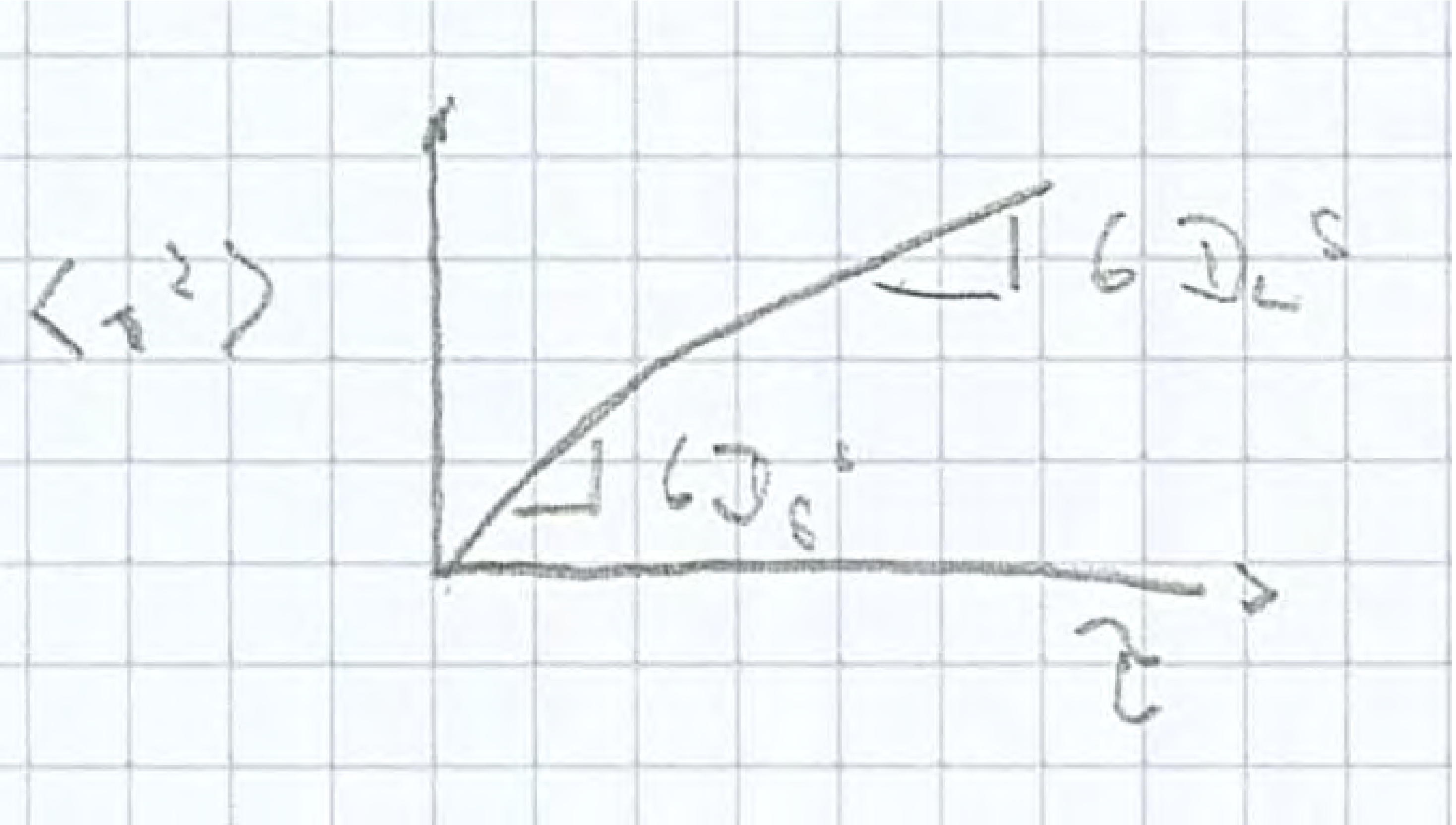
FIG. 1. (Color) Static structure factor of a hard-sphere suspension at various volume fractions ϕ as indicated. Comparison between MD simulation data and RY, PY, and PY-VW integral equation schemes.

ϕ-dependent relaxation



Short-time and long time relaxation processes

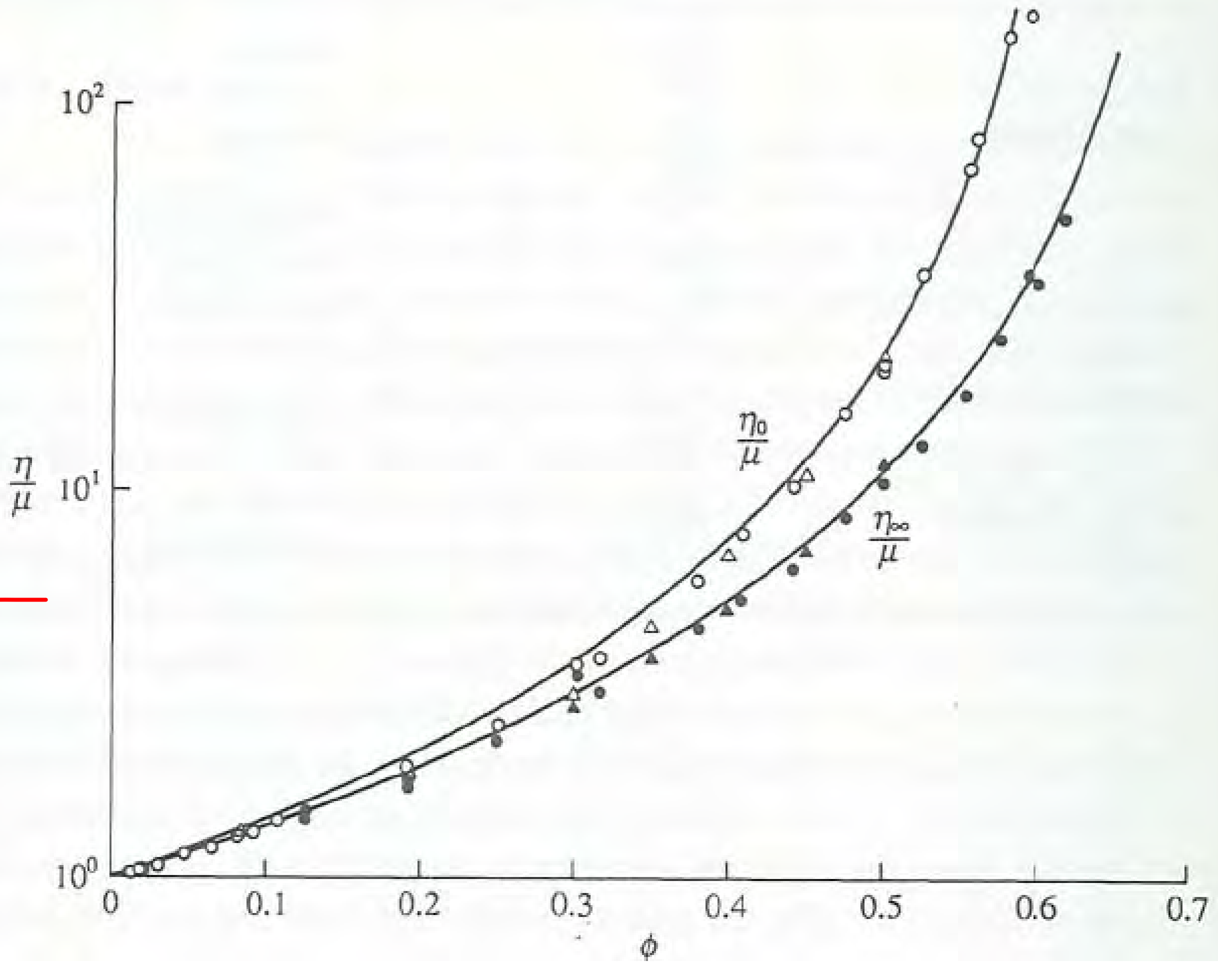
ϕ-dependent relaxation



Slopes give relaxation rates → effective diffusion coefficients

ϕ-dependence of viscosity

Comparison of frequency dependent data



ϕ-dependence of short-time diffusion coefficient
→ Correlates with viscosity

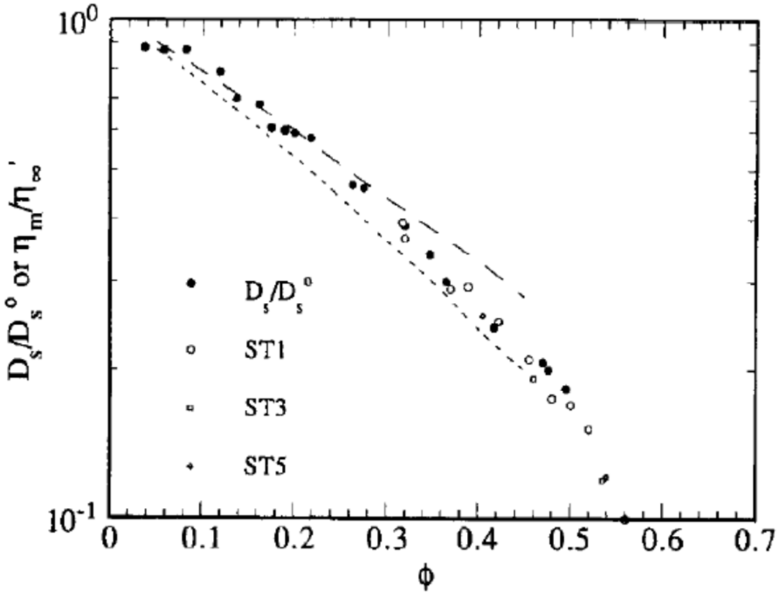
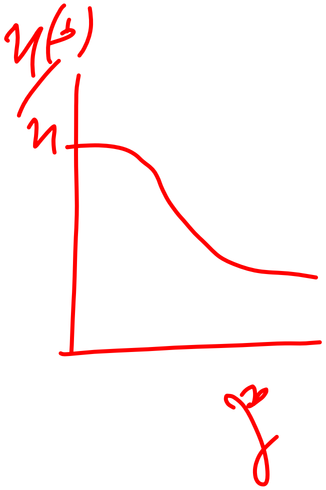
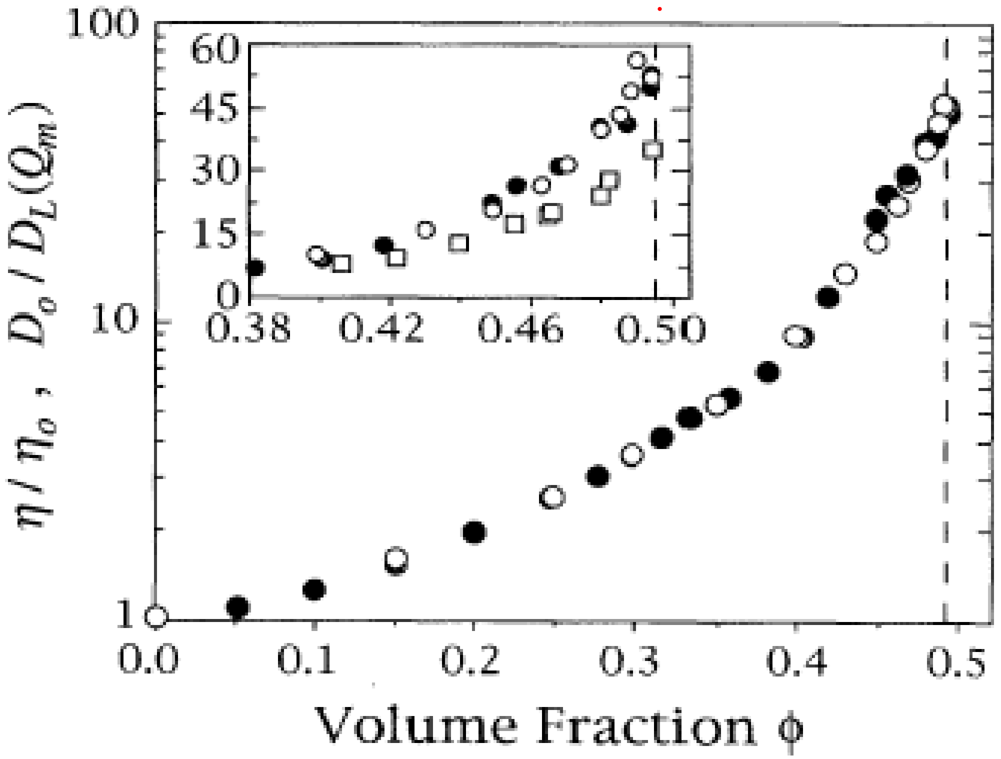
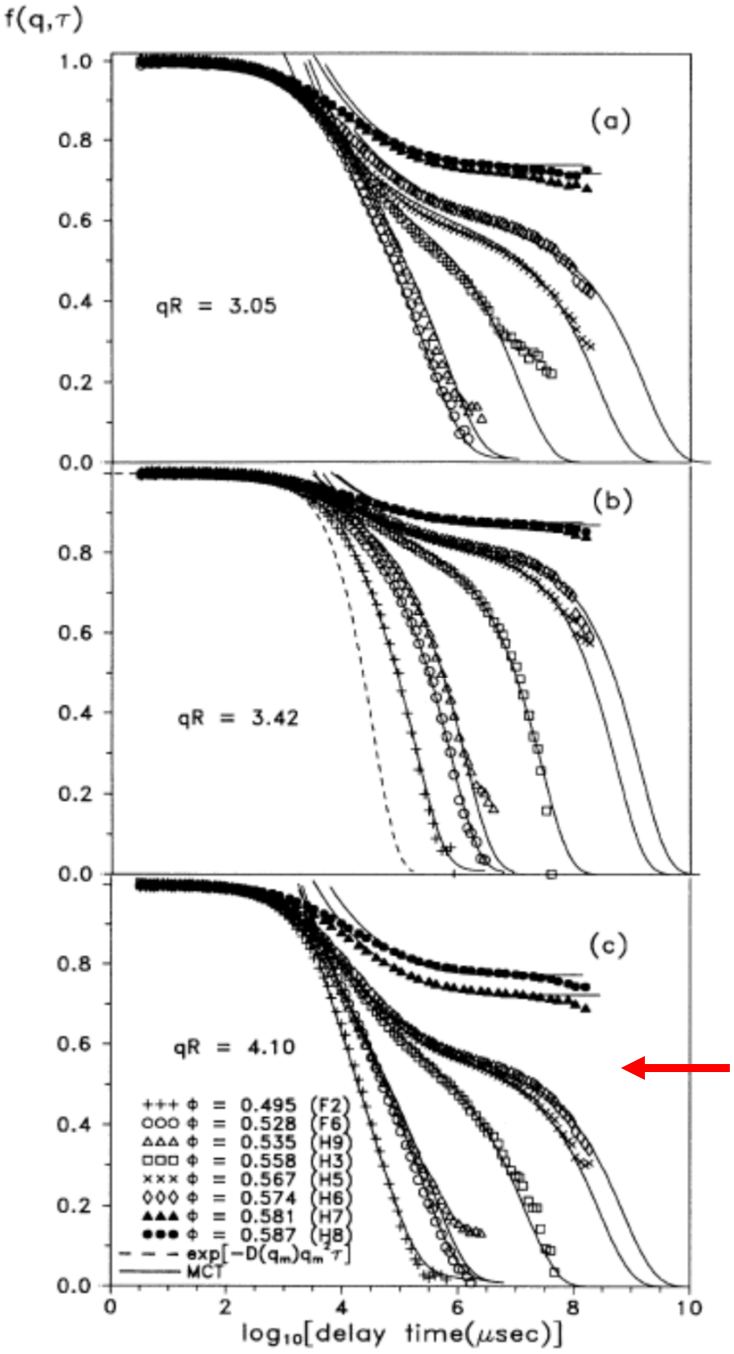


FIG. 4. The relationship between the reduced short-time self-diffusion coefficient $D_s(\phi)/D^0$ and ϕ (van Megan and Underwood, 1990) and that between the reciprocal of the relative high-frequency viscosity η_m/η'_∞ and ϕ for each of our suspensions. The long dashed and short dashed lines are, respectively, the theoretical prediction of Beenakker and Mazur (1984) and Beenakker (1984).

ϕ-dependence of long-time diffusion coefficient → Correlates with viscosity







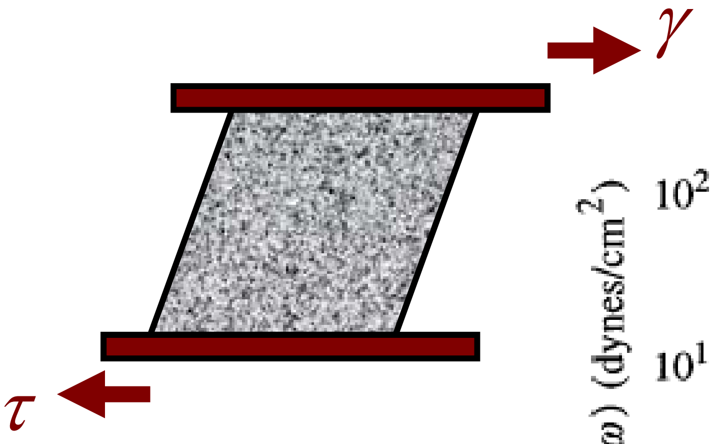
Increasing ϕ : Approach to the glass transition:

ϕ-dependent relaxation

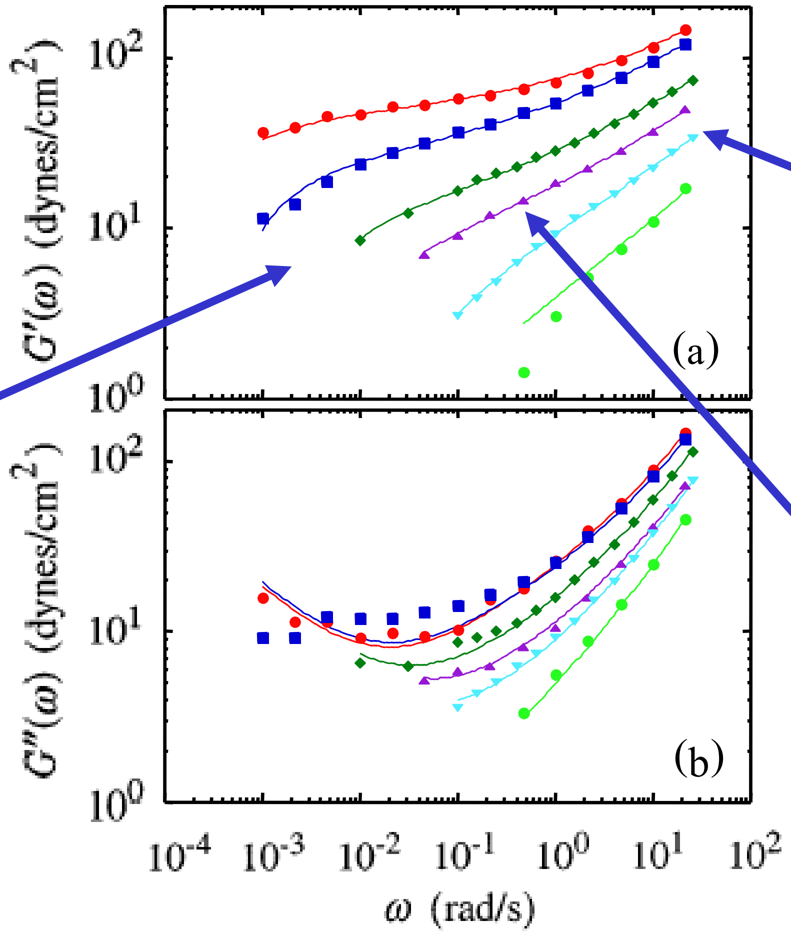
q-dependent relaxation

What is the nature of the relaxation?

Viscoelasticity of Hard Spheres



ϕ~0.45-0.56

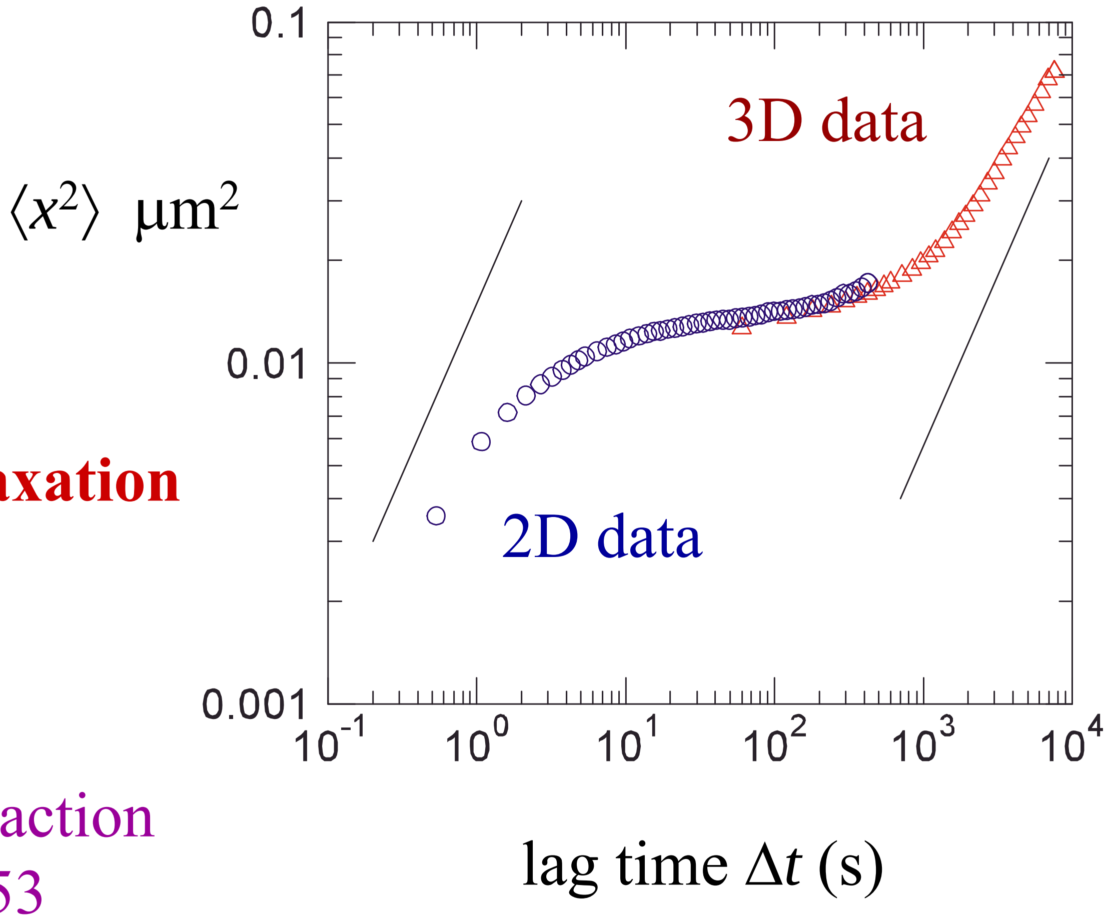


Low frequency
relaxation

High frequency
response
Fluid contribution

Glassy plateau

Mean square displacement – Confocal Microscopy



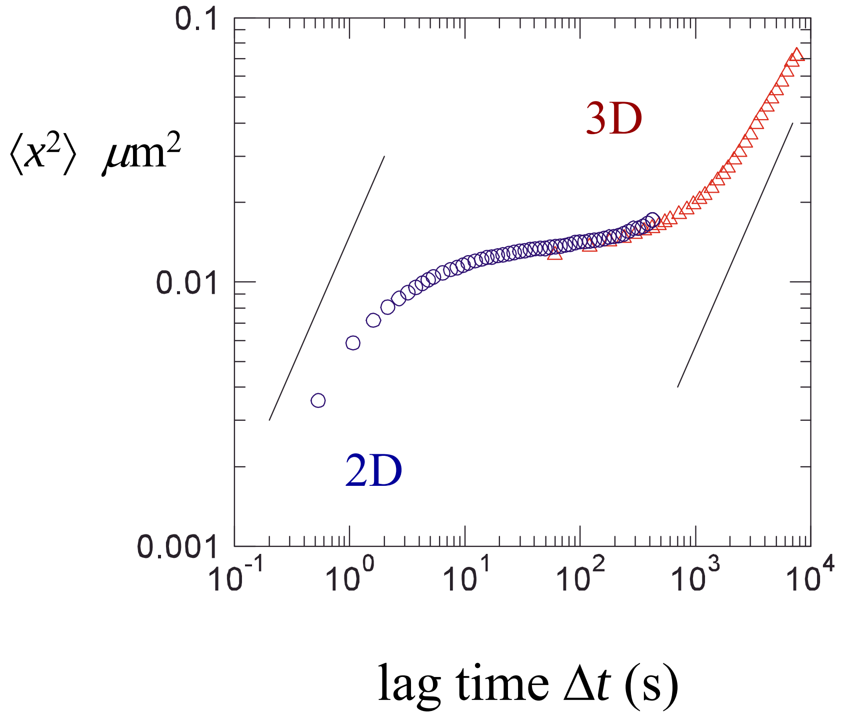
***α*-relaxation**

***β*-relaxation**

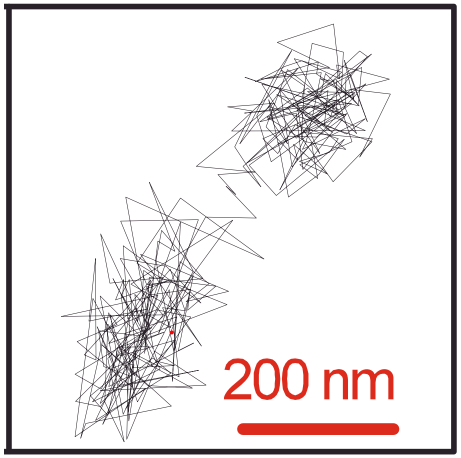
Volume fraction
ϕ=0.53
"supercooled fluid"

Mean-squared displacement

ϕ=0.53 -- “supercooled fluid”

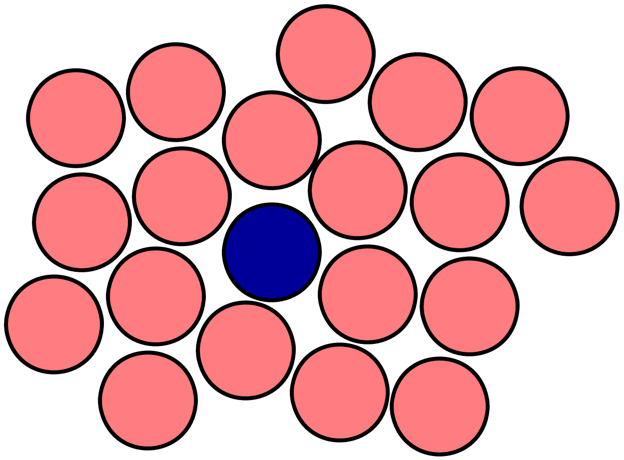


- Short times: particles stuck in “cages”
- Long times: cages rearrange

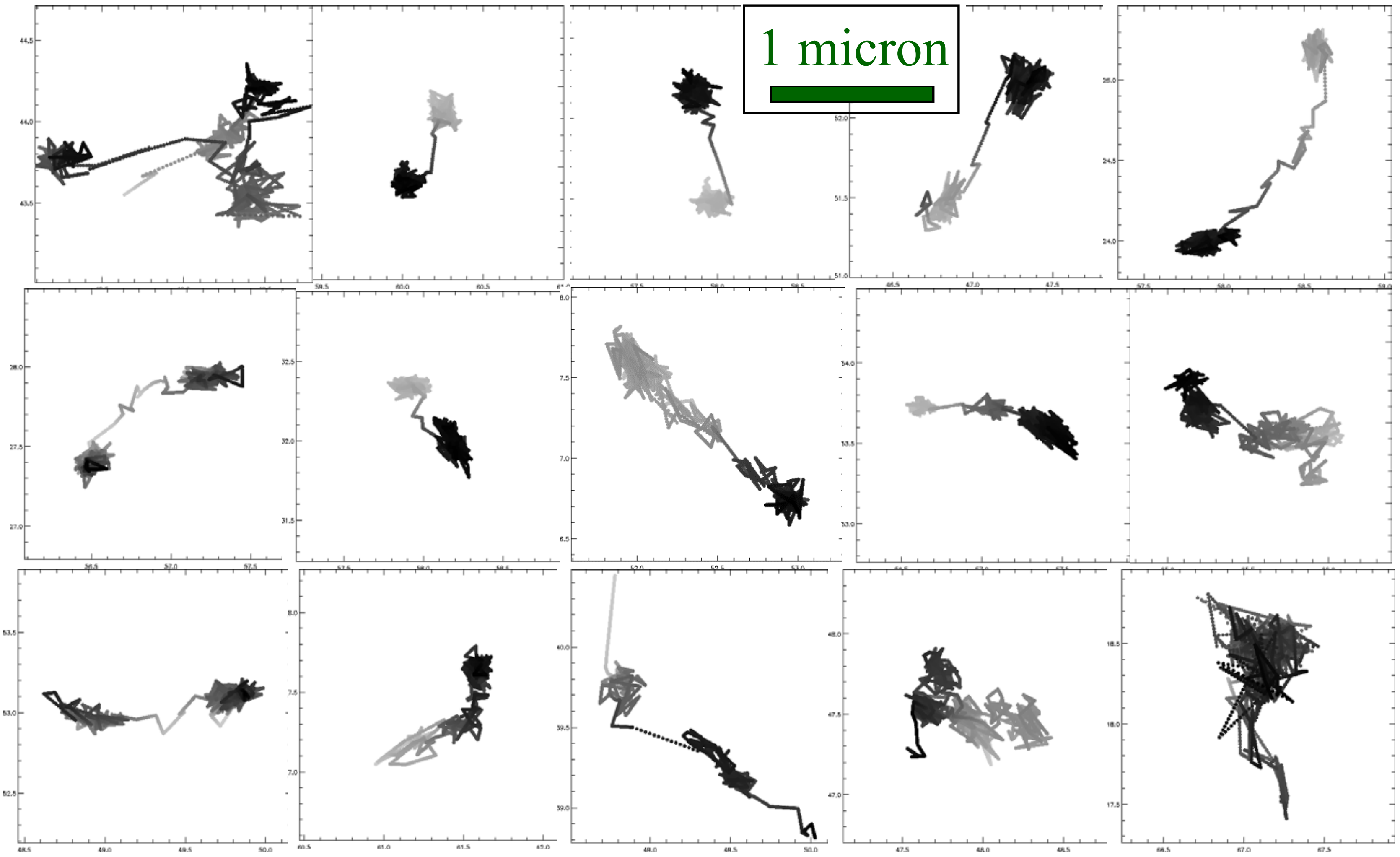


ϕ=0.56, 100 min
(supercooled fluid)

Cage trapping:

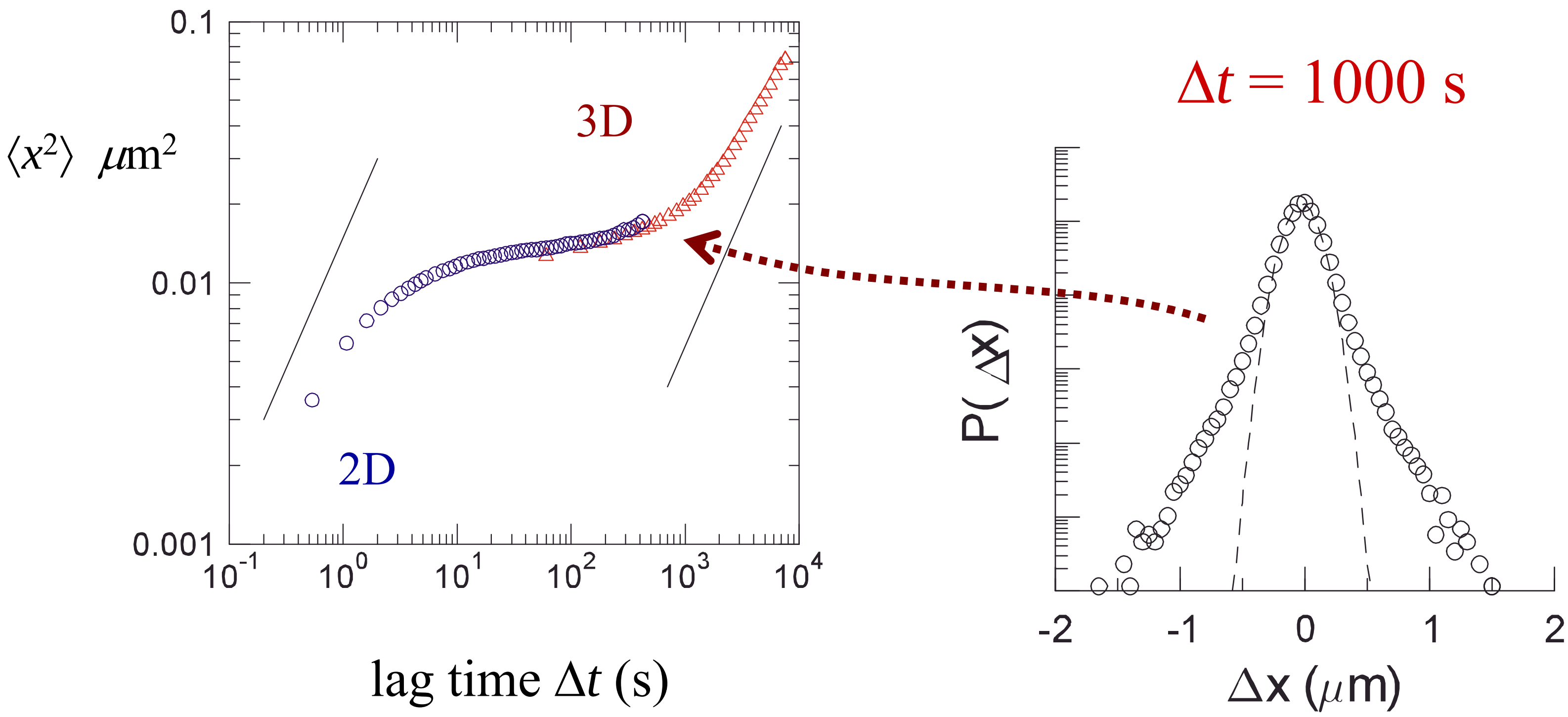


Trajectories of “fast” particles, ϕ=0.56



shading indicates depth

Displacement distribution function

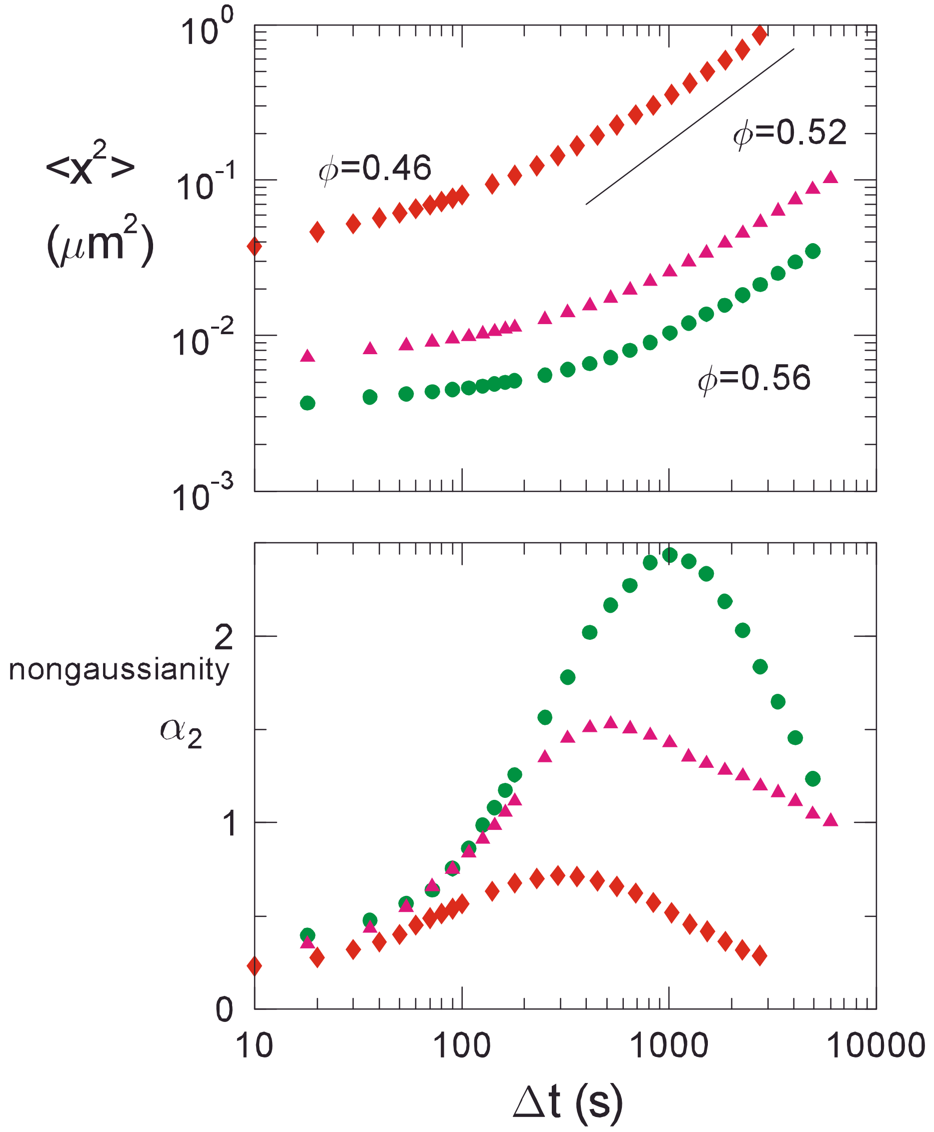


$\phi = 0.53$: “supercooled fluid”

Nongaussian Parameter

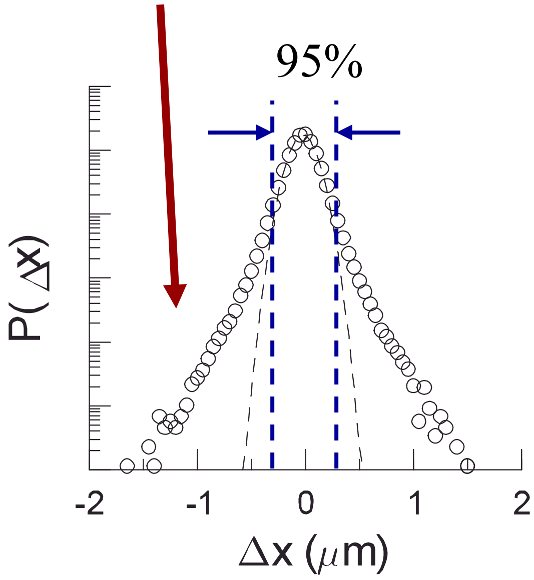
$$\boxed{\alpha_2 = \frac{\langle x^4 \rangle}{3\langle x^2 \rangle^2} - 1}$$

Choose Time with Maximum Non-Gaussian Parameter



Time Scale and Length Scale

top 5% = tails
of Δ*x* distribution



ϕ=0.53, supercooled fluid

Time scale:

Δ*t**   when nongaussian parameter α_2 largest

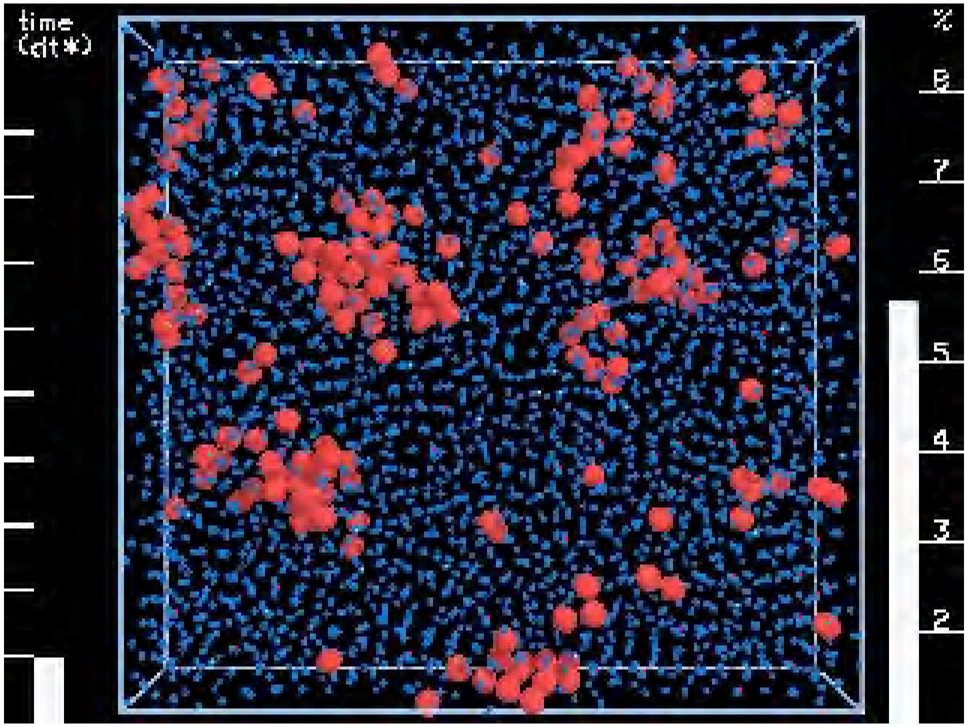
Length scale:

Δ*r**   on average, 5% of particles have Δ*r*(Δ*t**) > Δ*r**

≈ cage rearrangements

Structural Relaxations in a Supercooled Fluid

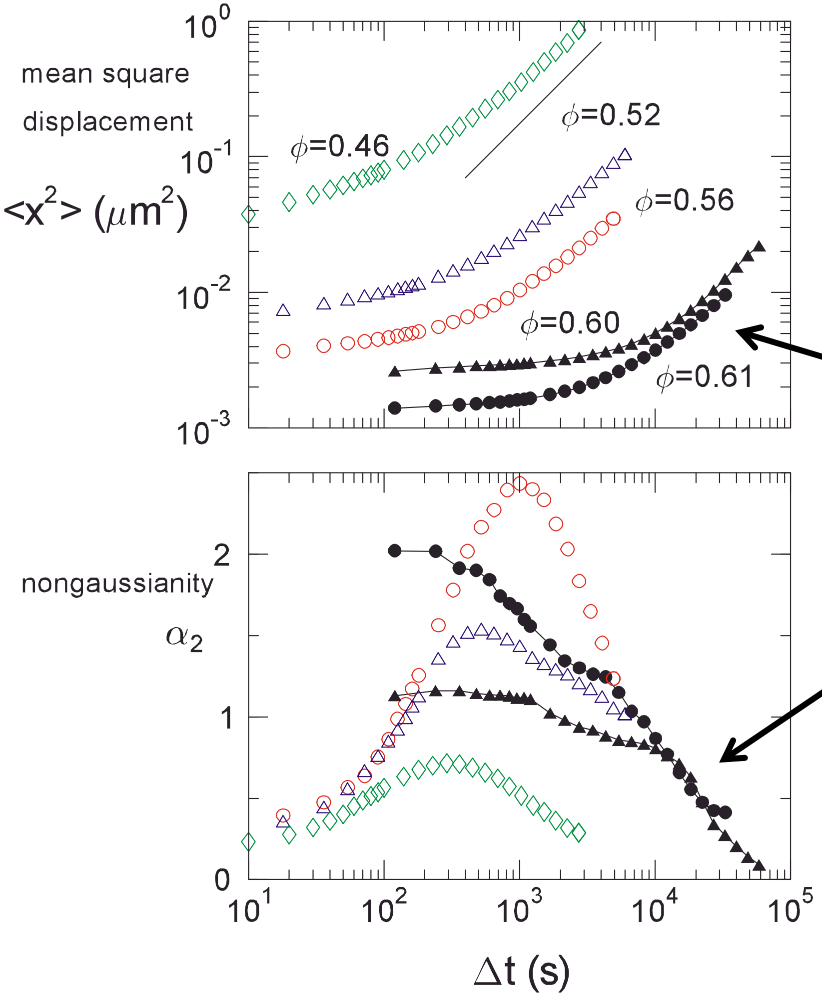
time



Number of relaxing particles

Relaxing particles are highly correlated spatially

Non-Gaussian parameter for glasses

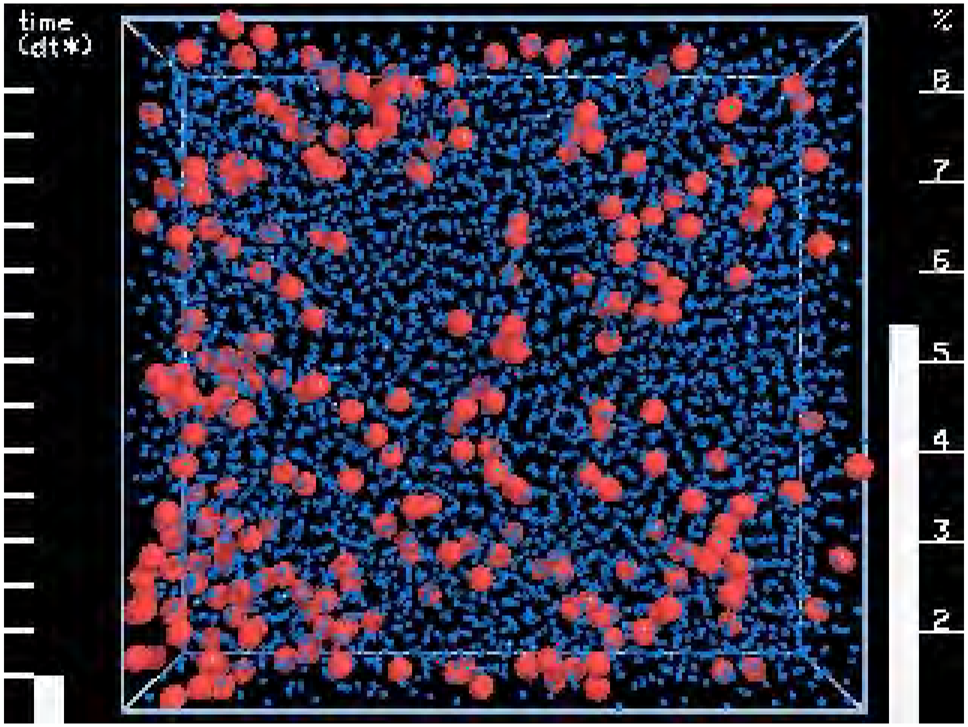


glasses

No well-defined peak

Structural Relaxations in a Glass

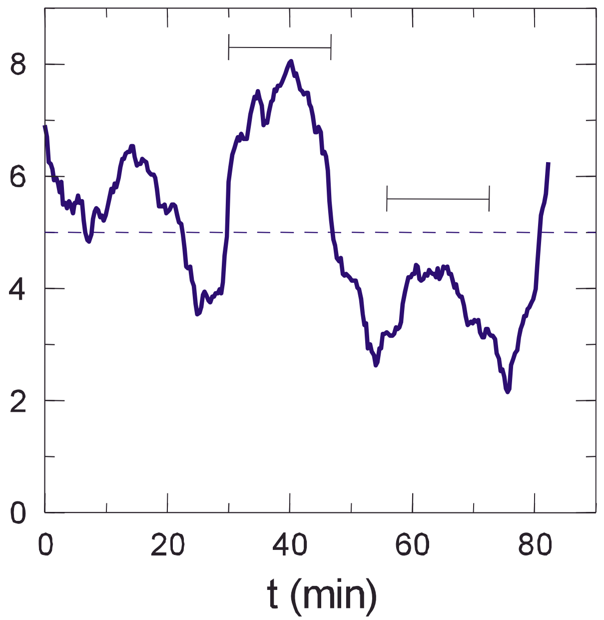
time

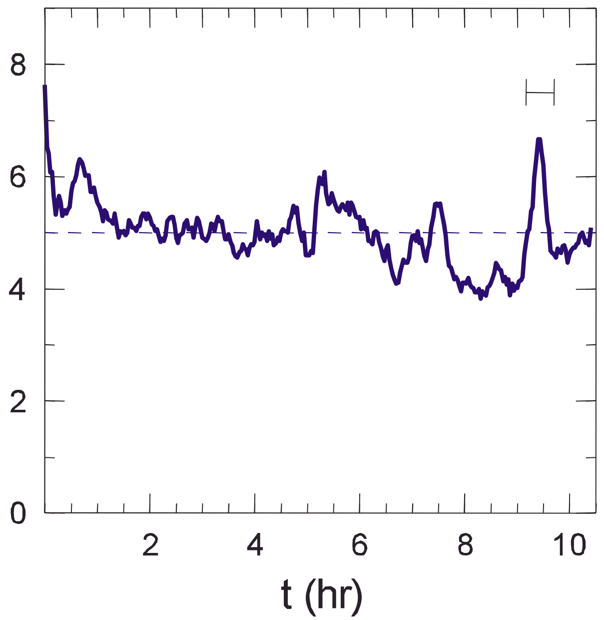


Number of relaxing particles

Relaxing particles are NOT correlated spatially

Fluctuations of fast particles

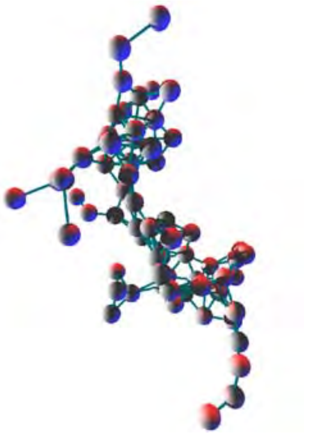




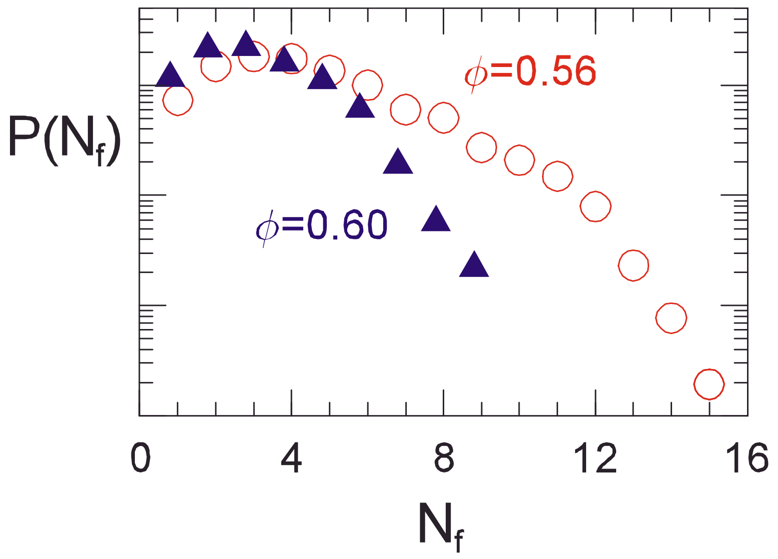
Supercooled fluid $\phi = 0.56$

Glass $\phi = 0.61$

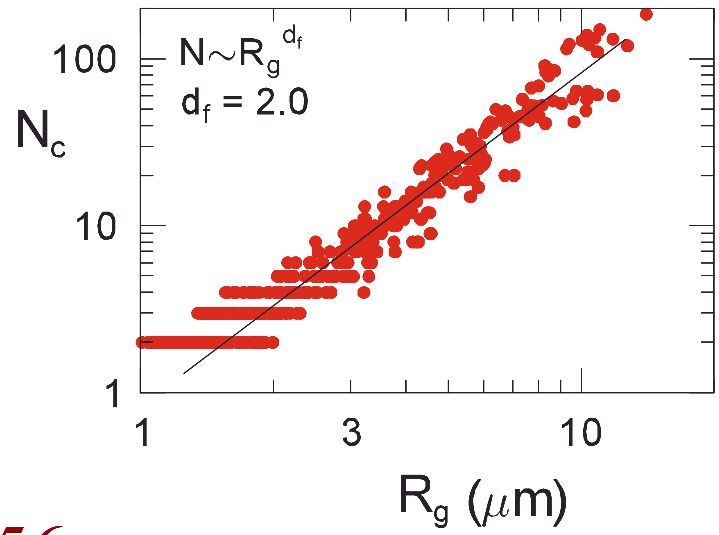
Cluster Properties



Number N_f of fast neighbors to a fast particle:



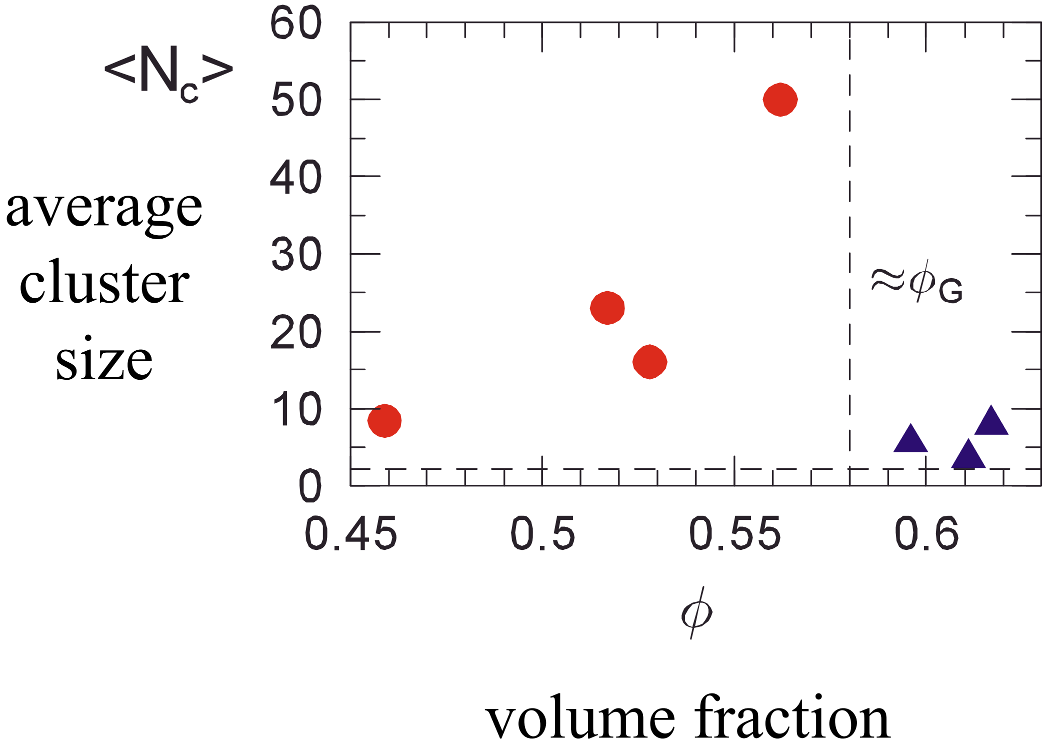
Fractal dimension:



$\phi = 0.56$

supercooled fluid

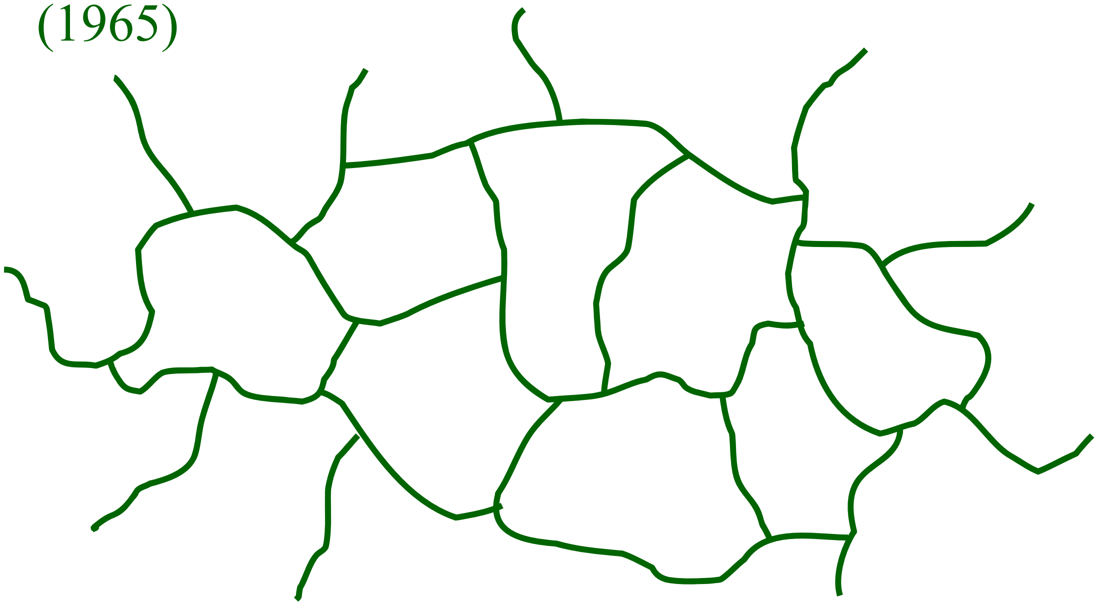
Relaxation events are spatially correlated



Cluster size grows as glass transition is approached

Dynamical Heterogeneity:
possible *dynamic* length scale

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



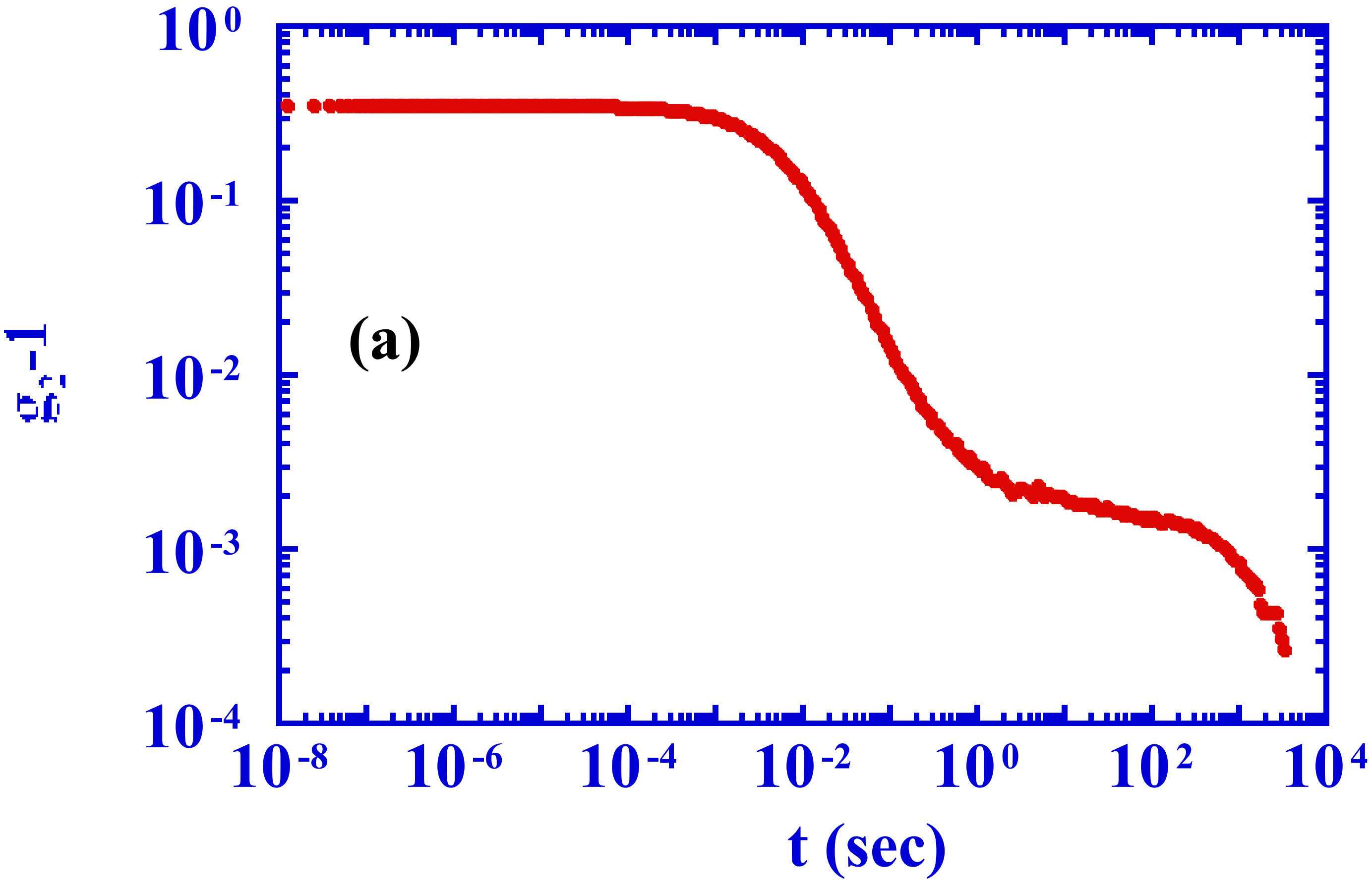
Simulations:
- **Glotzer, Kob, Donati, et al (1997, Lennard-Jones)**

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

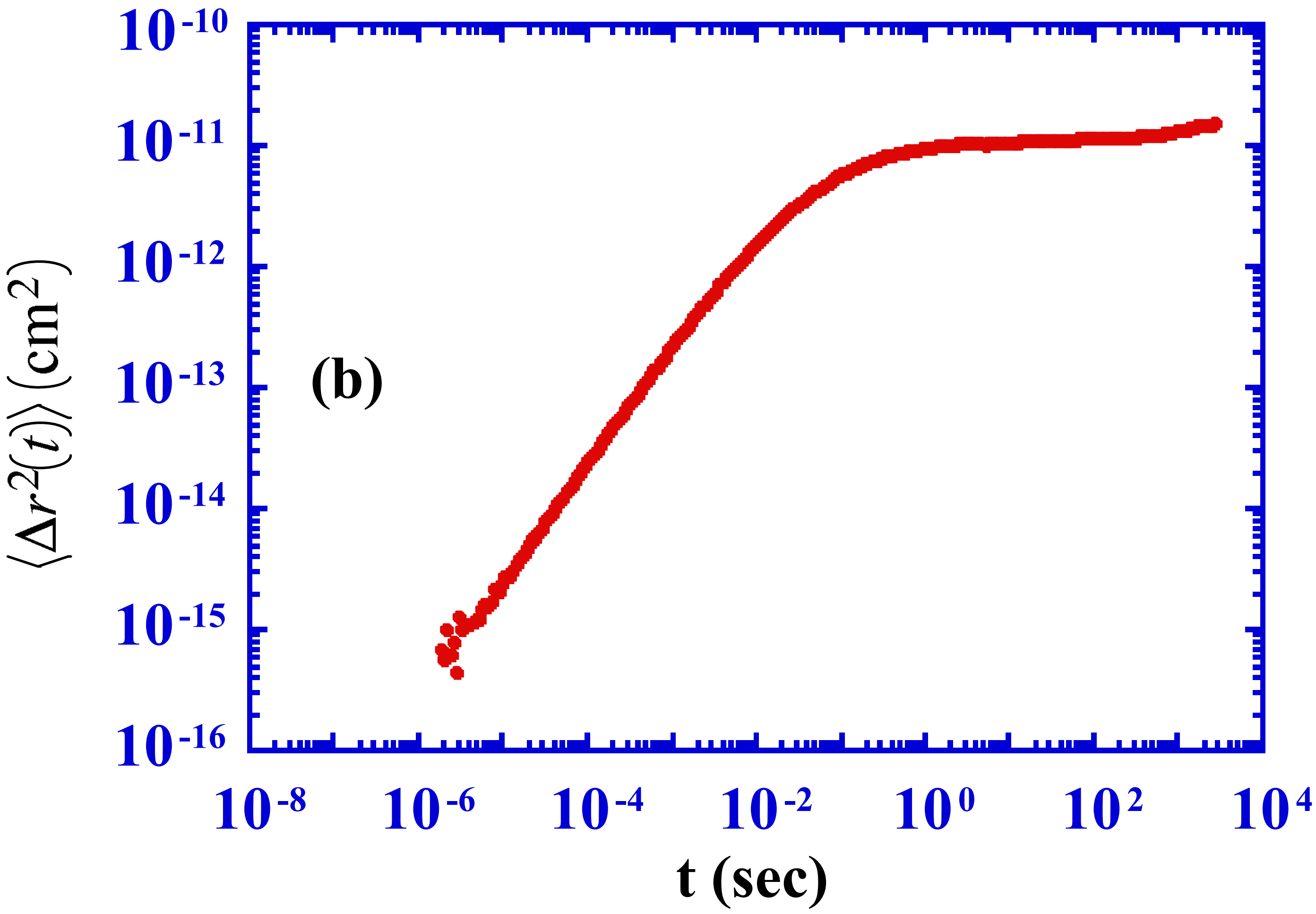
NMR experiments:
- Schmidt-Rohr & Spiess (1991, polymers)

Boulder summer school experiments

DWS from hard spheres



Mean-squared displacement



Microrheology

Measure mean square displacement of probe particles:

Light scattering:

- Dynamic light scattering
  - Motion over larger lengths - lower frequencies
- Diffusing Wave Spectroscopy
  - Motion over smaller lengths - higher frequencies

Calculate Modulus

- Generalized Stokes-Einstein equation

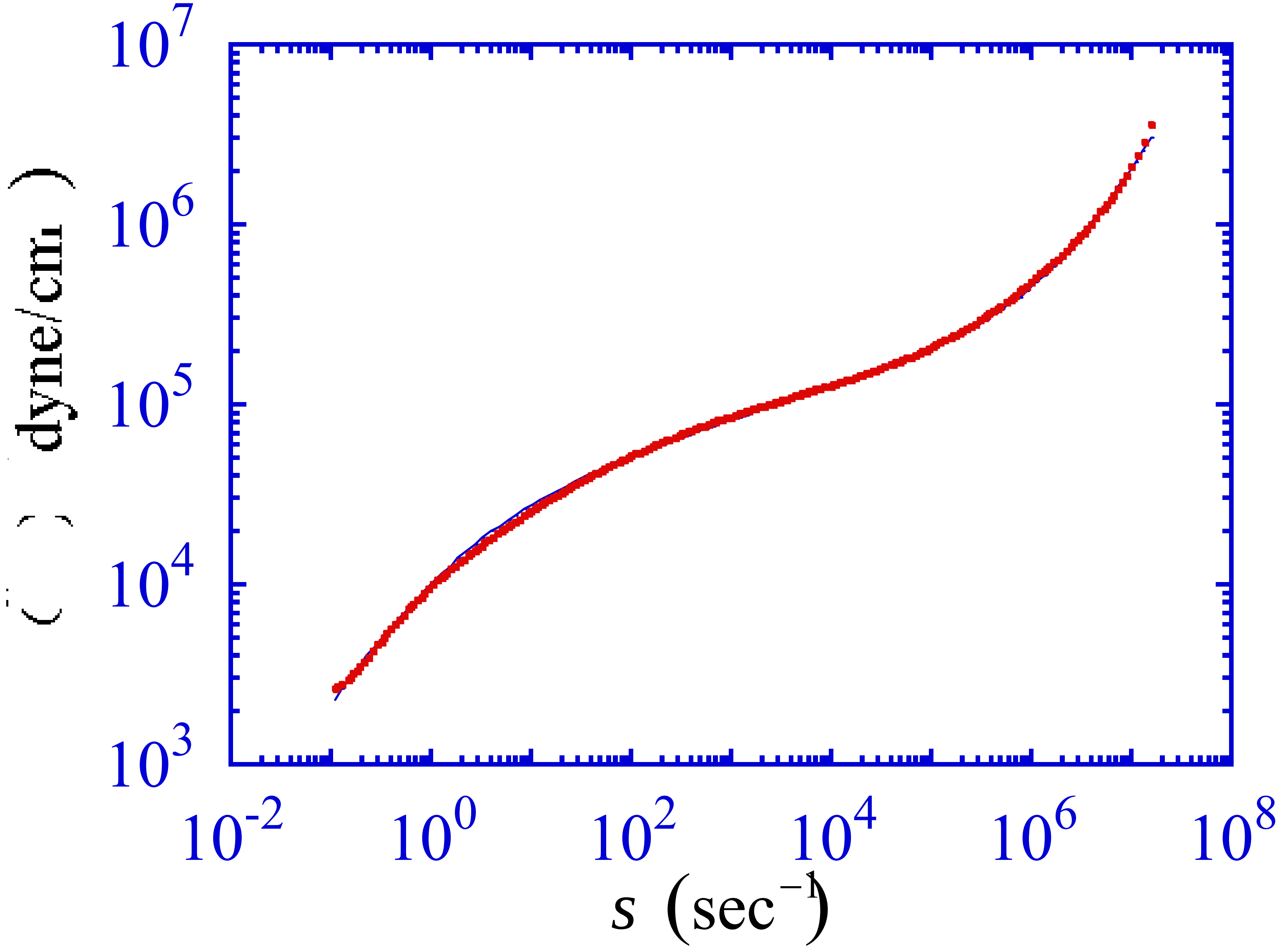
$$G(s) = \frac{k_B T}{\pi a s \left\langle \Delta r^2(s) \right\rangle_{\max}}$$

Transform to storage and loss moduli

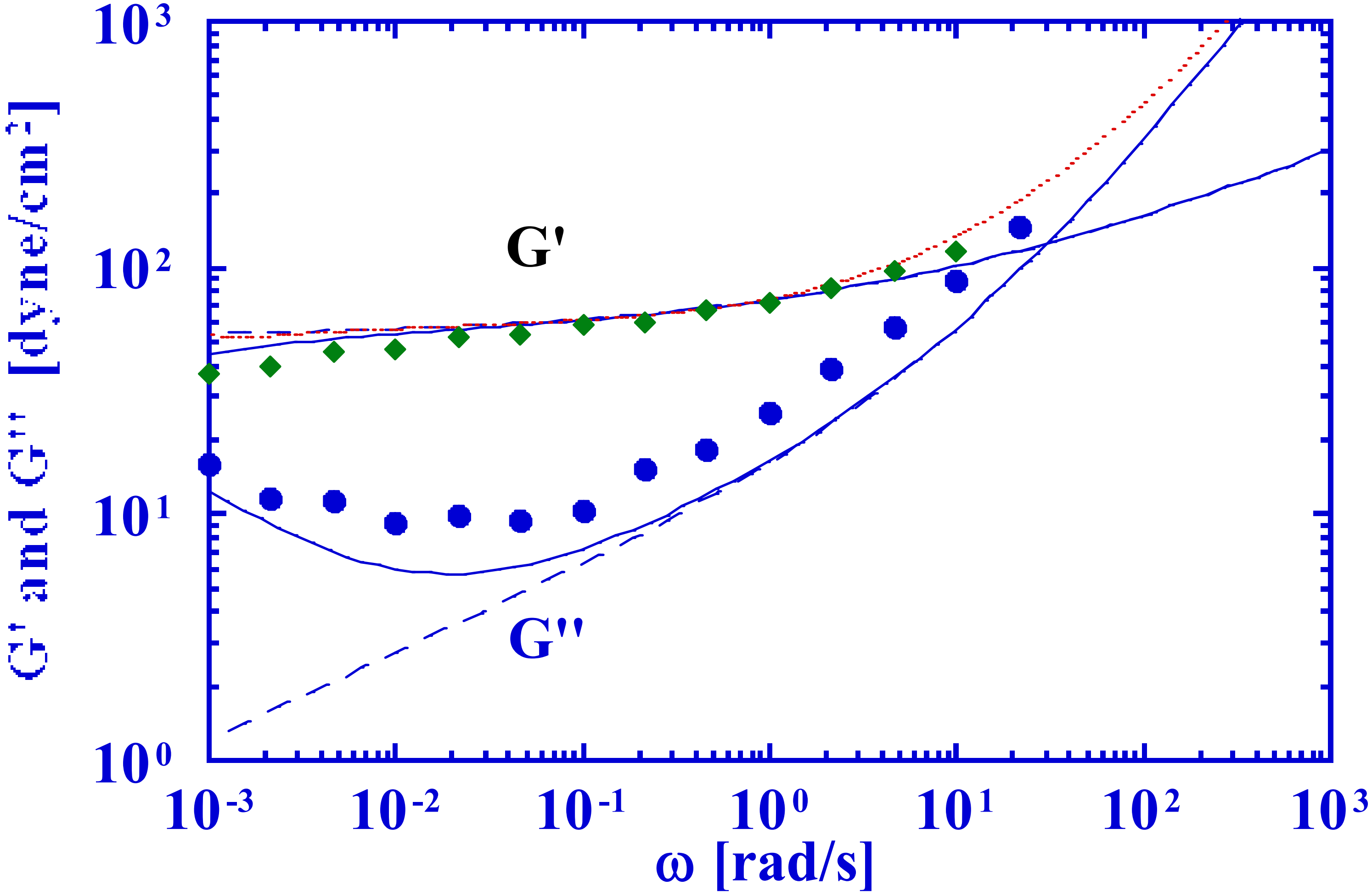
- Analytic continuation: $s = i\omega$

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

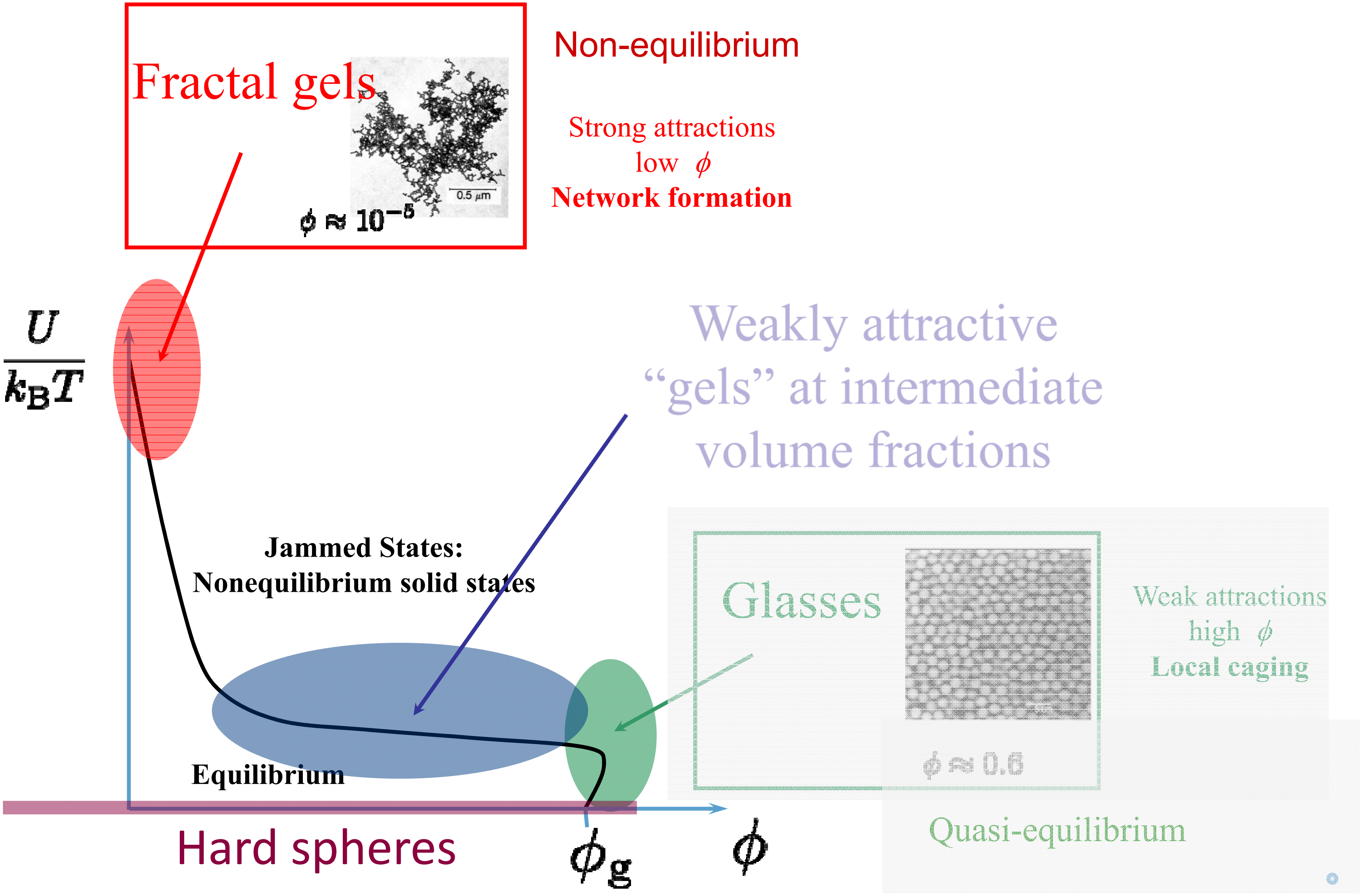
“Complex” modulus



Light scattering rheology



State diagram for colloidal particles



Fractal gels

Non-equilibrium

Strong attractions
low ϕ
Network formation

Weakly attractive "gels" at intermediate volume fractions

Jammed States:
Nonequilibrium solid states

Glasses

Weak attractions
high ϕ
Local caging

Quasi-equilibrium

Equilibrium

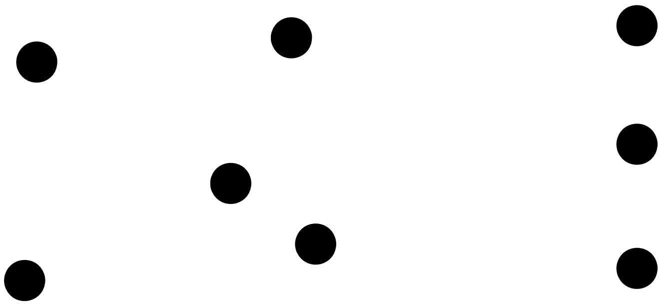
Hard spheres

Colloidal Stability

Partial Stability
→ Many collisions to stick

No Stability
→ Sticks every collision

Dilute, stable suspension

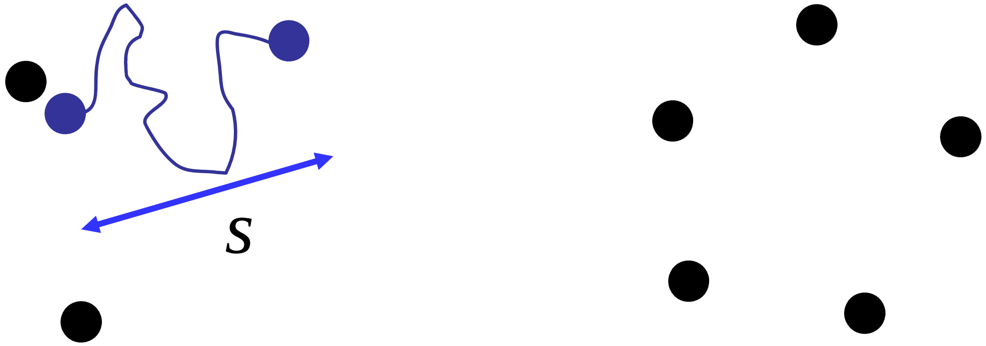


R

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

ϕ

Destablize

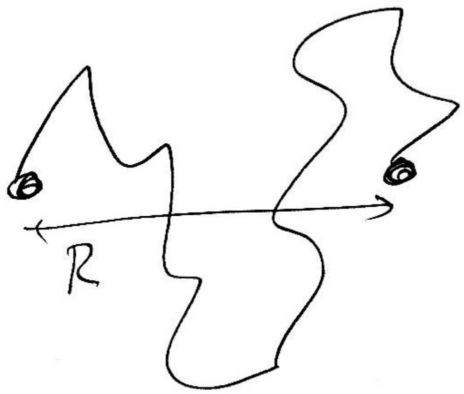


$$s \sim c^{-1/3}$$

$$\tau \sim \frac{s^2}{D} \sim \frac{1}{DC^{2/3}}$$

WRONG!

Irreversible aggregation



Vo~~l~~lume : $s a^2$

contour length : $s = \#\,\text{steps} \times \text{step length}$

$$= \left(\frac{R}{a}\right)^2 a$$

$$= \frac{R^2}{a}$$

Volume: $R^2 a$

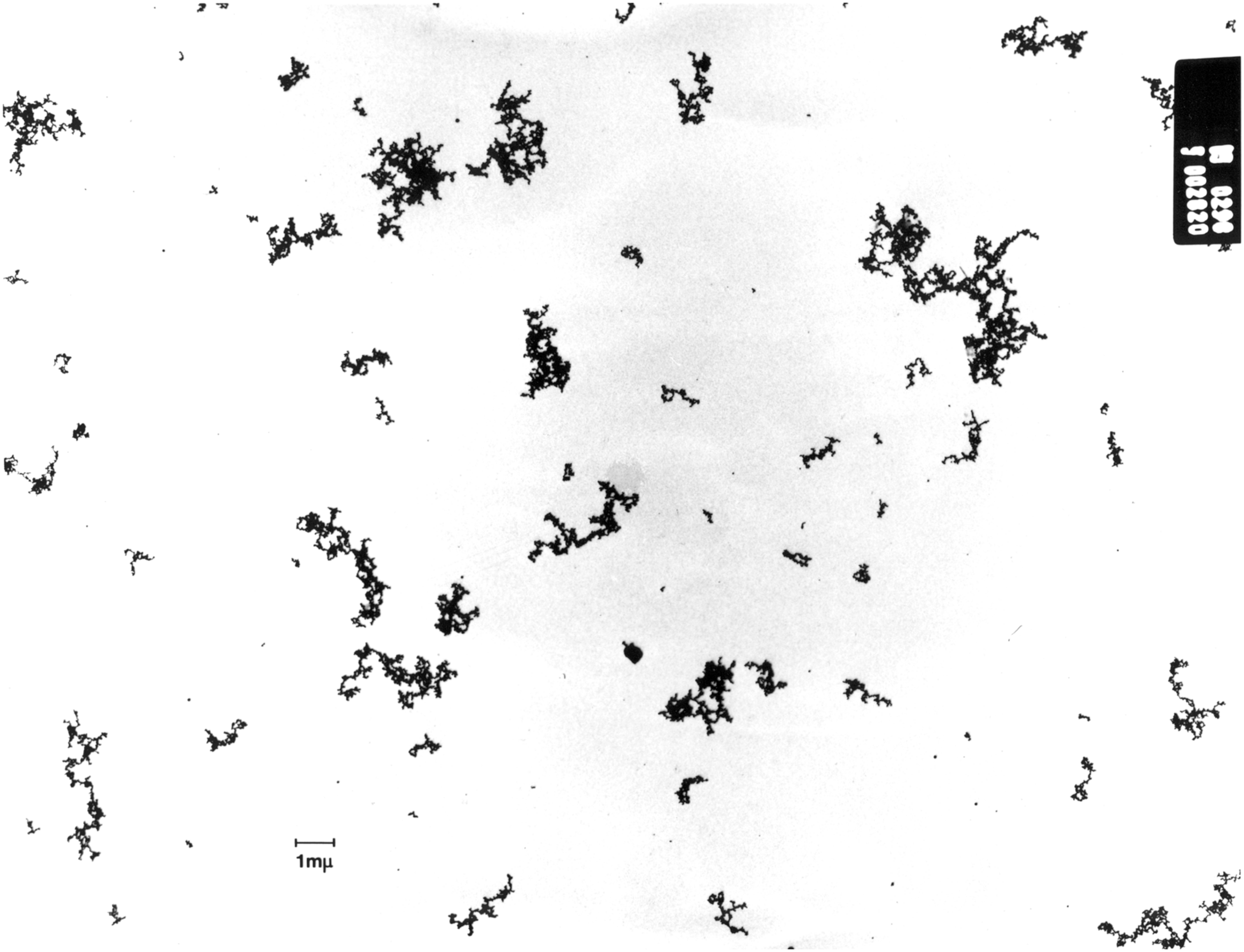
time: $\dfrac{R^2}{D}$

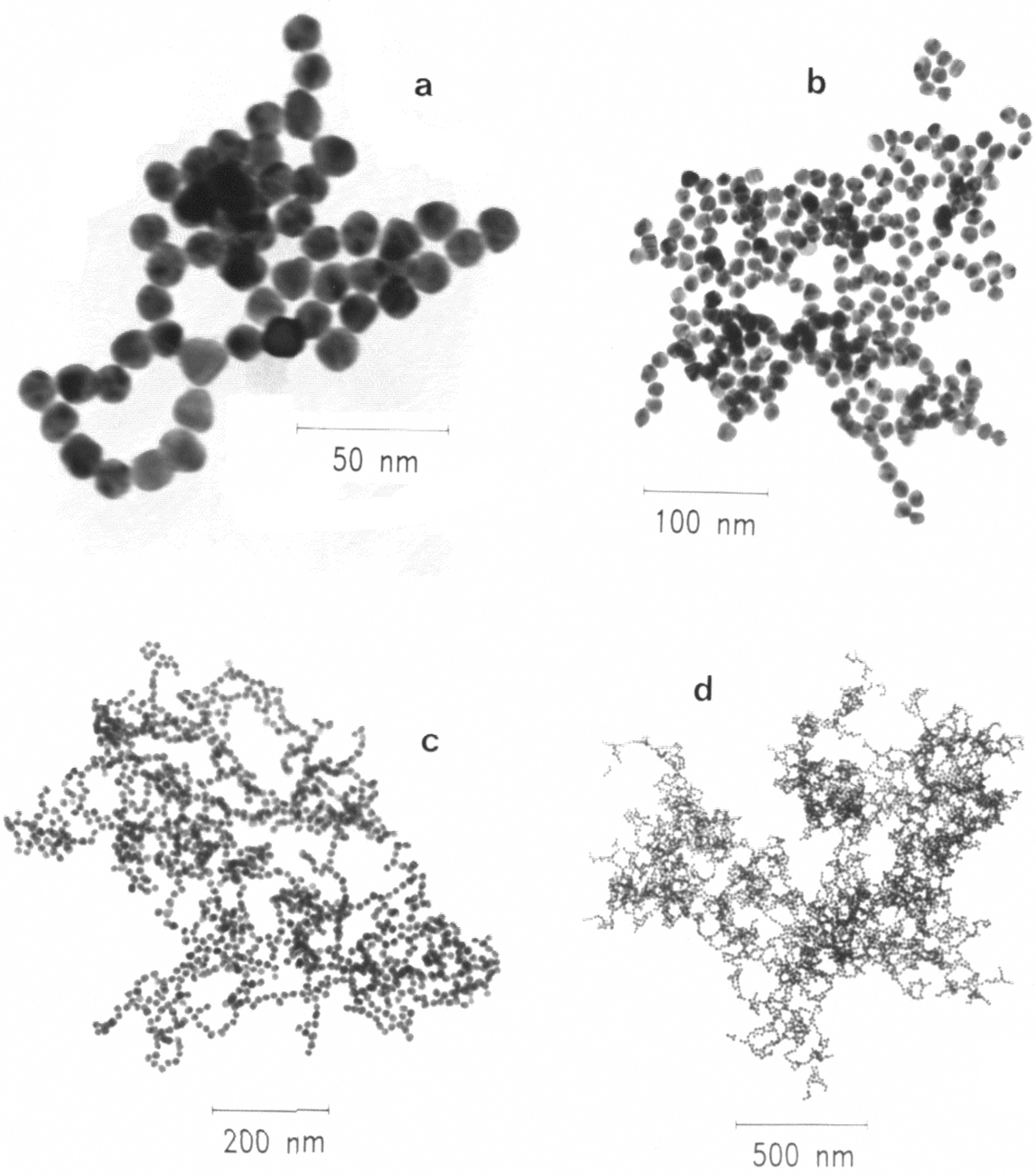
volume / time $= Da$

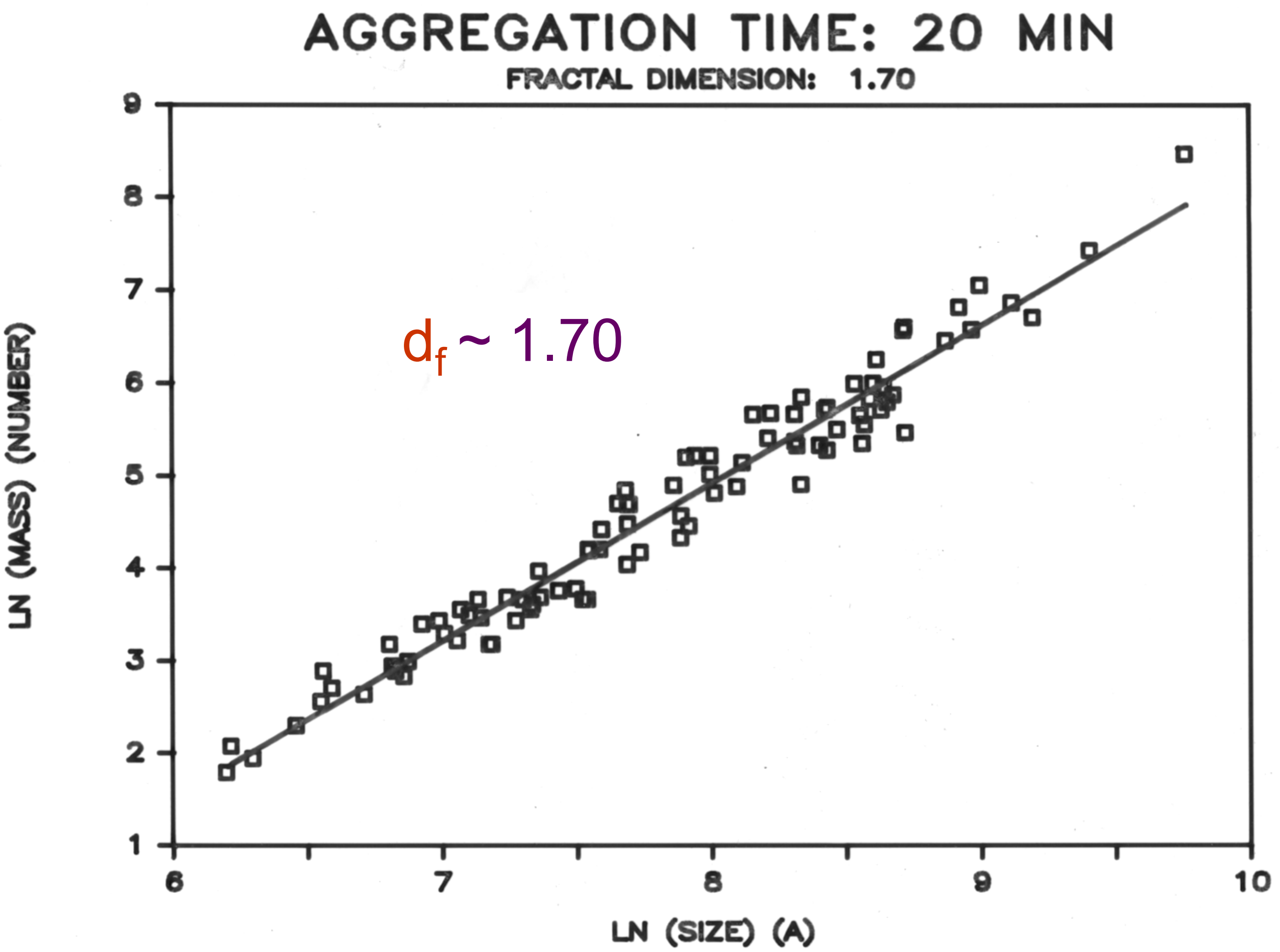
Volume required $= \dfrac{1}{c}$

$$t = \frac{1}{caD}$$

Rate: $\tau^{-1} = caD$


1mμ


a
50 nm
b
100 nm
c
200 nm
d
500 nm


AGGREGATION TIME: 20 MIN
FRACTAL DIMENSION: 1.70
LN (MASS) (NUMBER)
LN (SIZE) (A)
1
2
3
4
5
6
7
8
9
6
7
8
9
10

$d_f \sim 1.70$

FRACTAL:

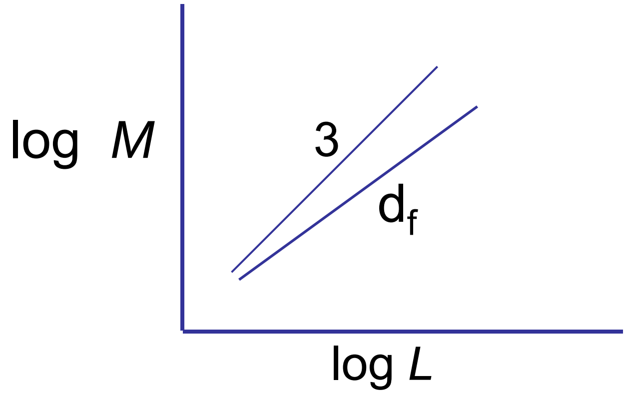
- SELF-SIMILAR

  NO CHARACTERISTIC LENGTH SCALE

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

d_f: FRACTAL DIMENSION

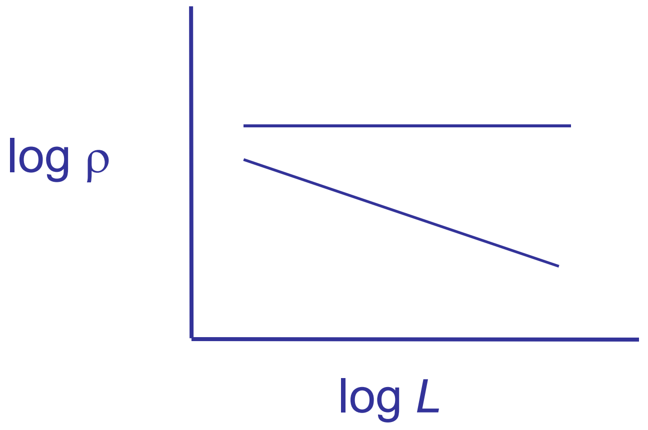
NON-INTEGRAL



$d_f < d$

DENSITY: <u>DECREASES</u> WITH SIZE

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

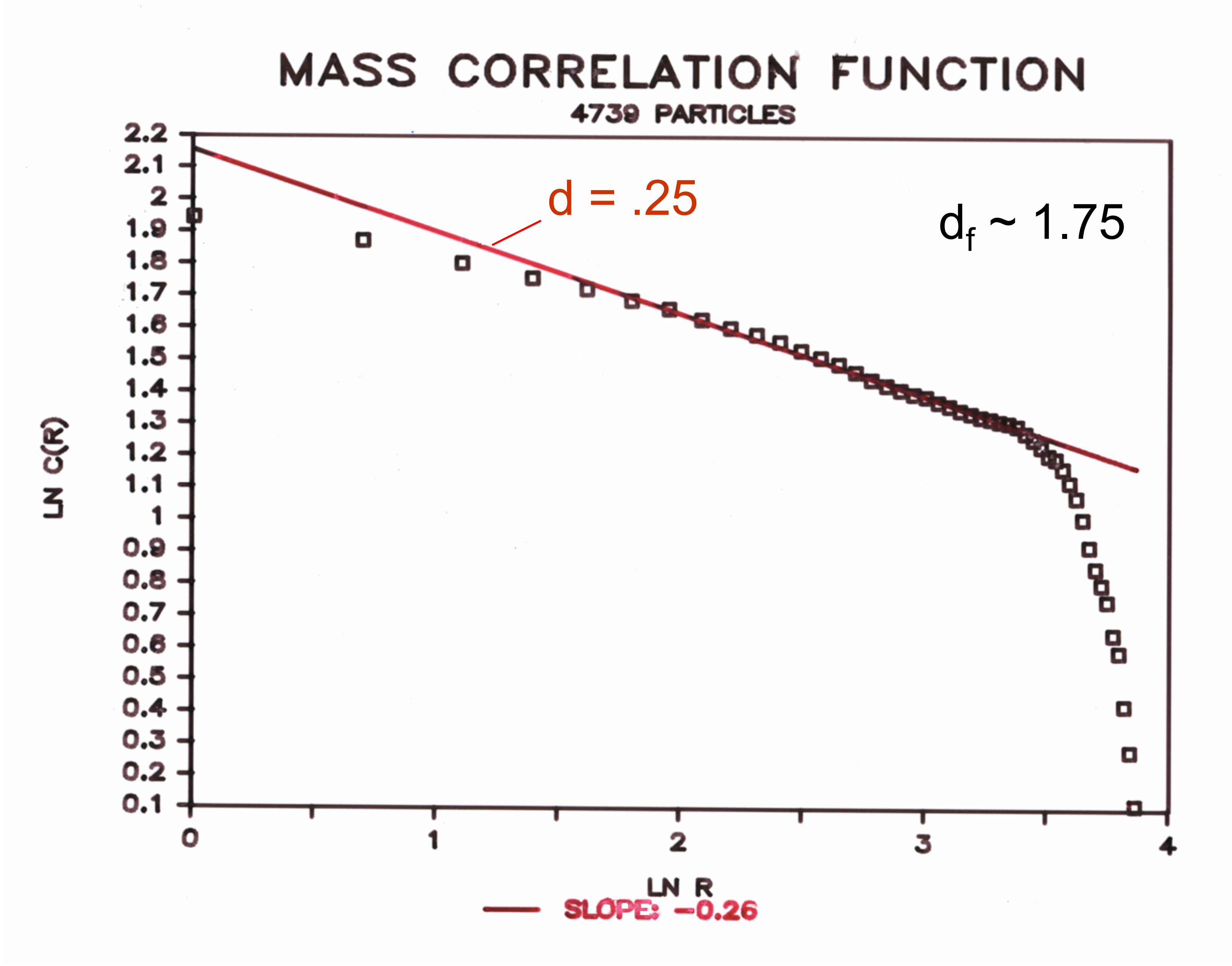


← FRACTAL

MASS CORRELATIONS:

3d: $c(r) \sim \frac{1}{r^{3-d_{f3}}}$

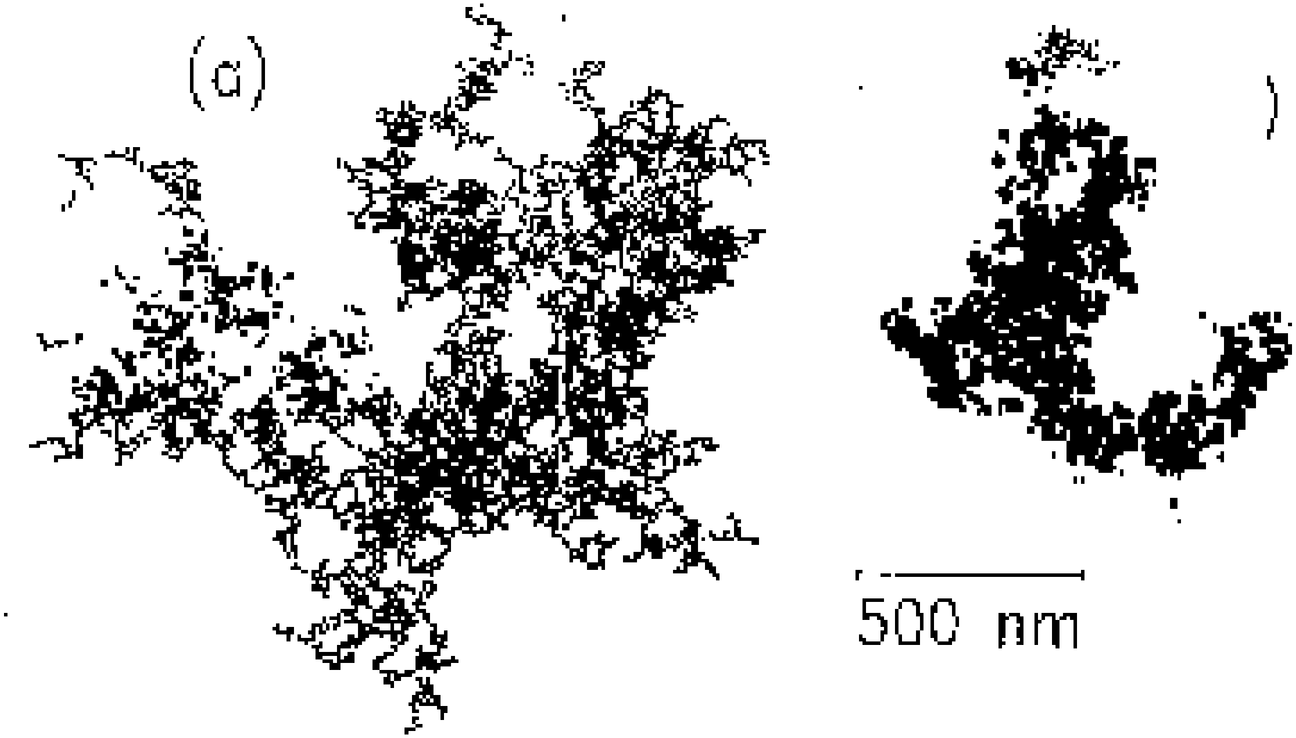
2d: $c(r) \sim \frac{1}{r^{2-d_f}}$



d = .25

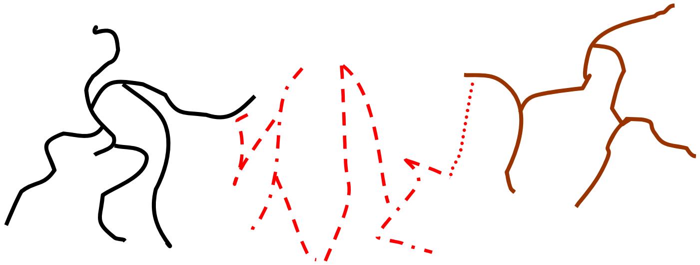
$d_f \sim 1.75$

Colloidal Aggregation

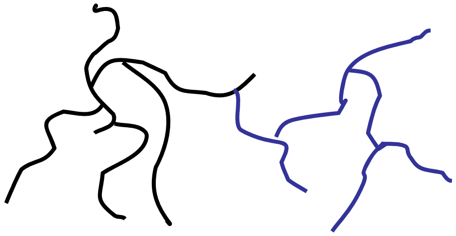


Colloidal Gold

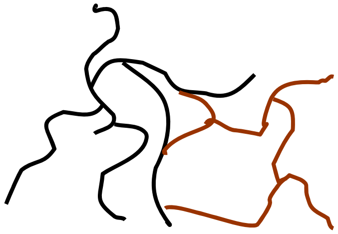
DIFFUSION – REACTION – *LIMITED AGGREGATION*



DIFFUSE MOTION



DIFFUSION-LIMITED
STICKS WHERE IT FIRST TOUCHES



REACTION-LIMITED
MUST COLLIDE MANY TIMES
DIFFUSIVE MOTION NOT IMPORTANT.

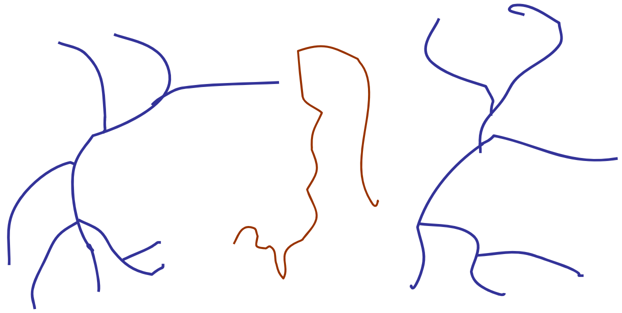
DIMENSIONS:

d: Euclidean dimension of space
$d = 3$ real space
$d = 2$ surface

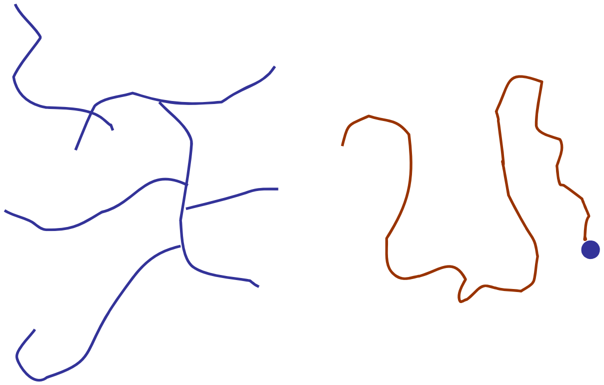
d_f: Fractal dimension
Amount of volume occupied by a space filling object
is $M \sim R^{d_f}$

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



$$d_f^1 + d_f^2 + d_t = 1.75 + 1.75 + 2 > 3.$$

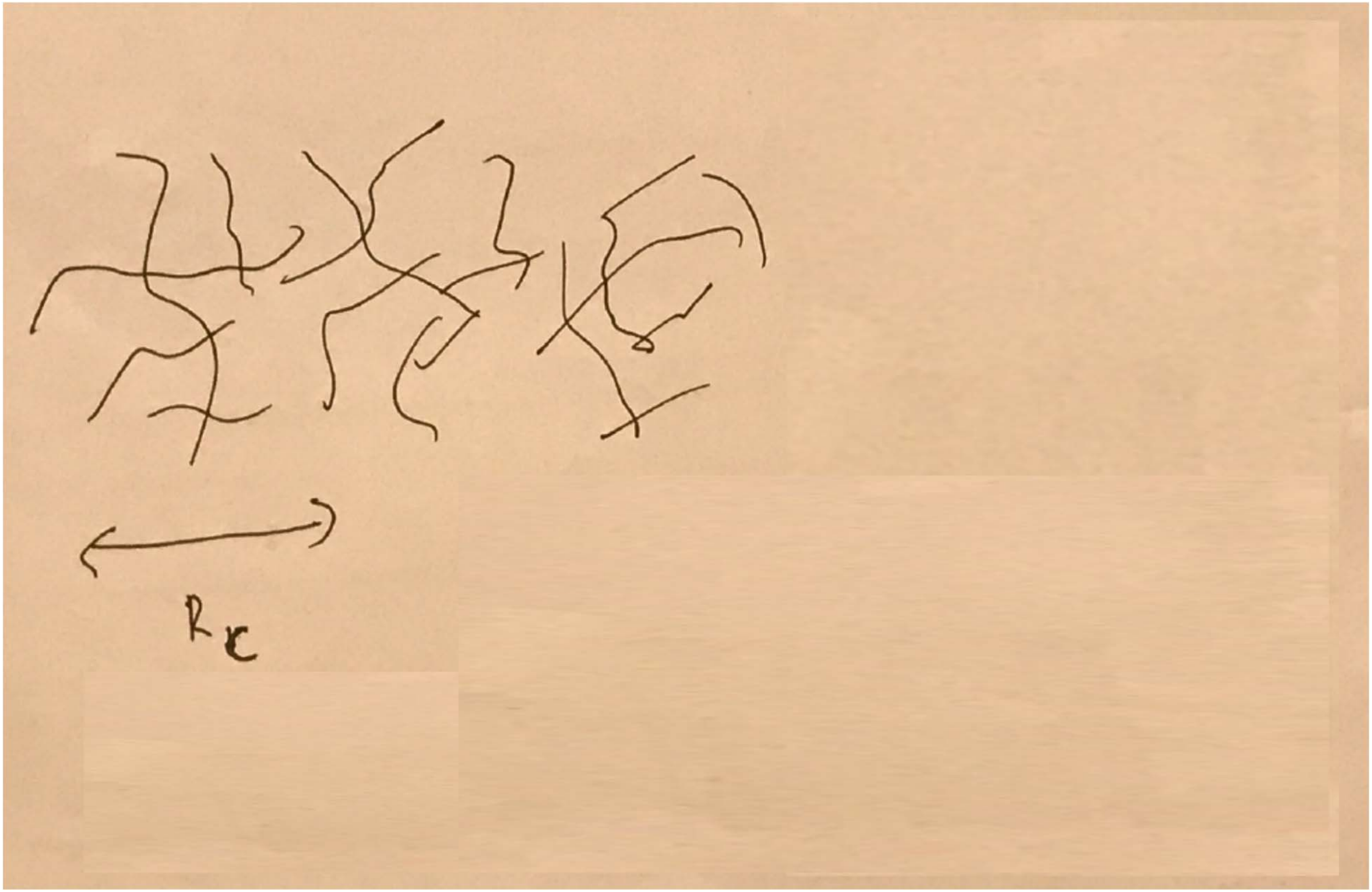


$$d_f^1 + d_f^2 + d_t = 1.75 + 0 + 2 > 3.$$

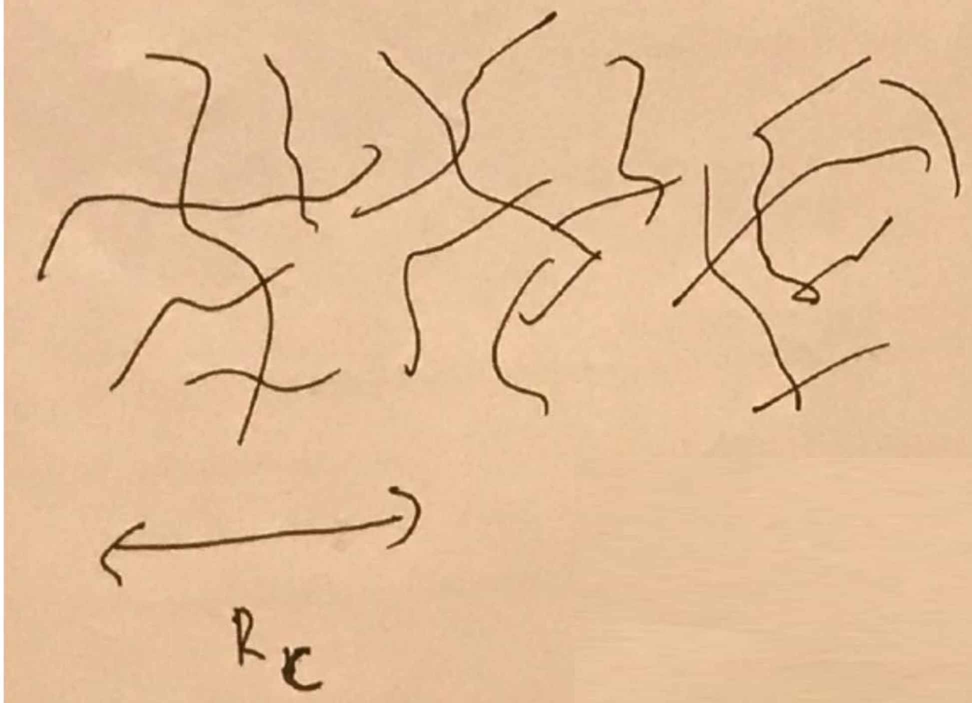
NO INTERPENETRATION
BUT CLUSTERS STICK WITH OTHER CLUSTERS

$\therefore d_f \sim 1.8$ in 3-d.

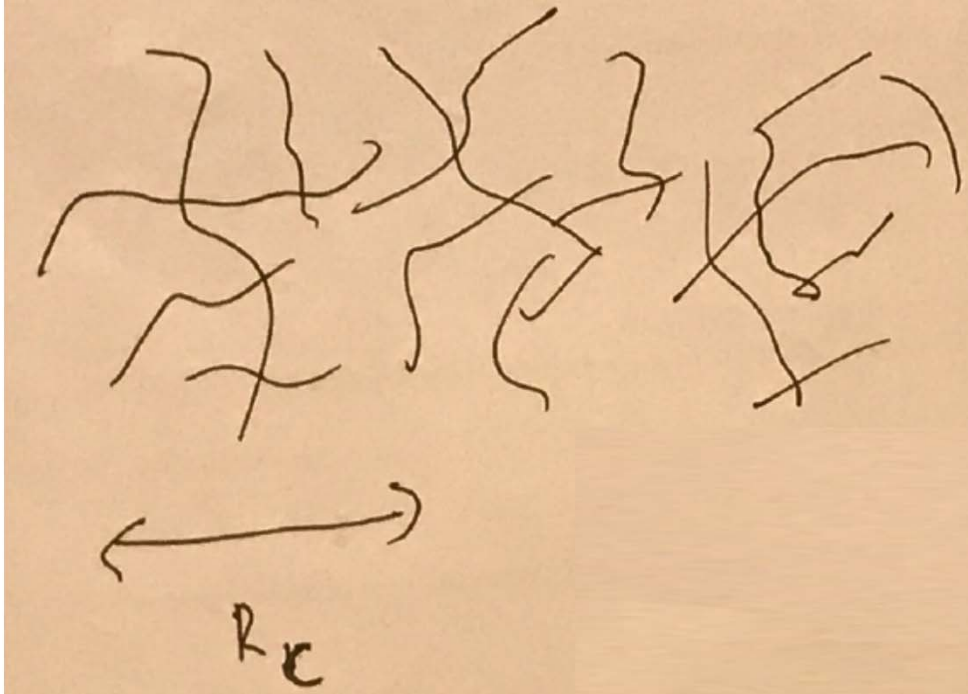
Brown bag calculation



Gelation of fractal clusters

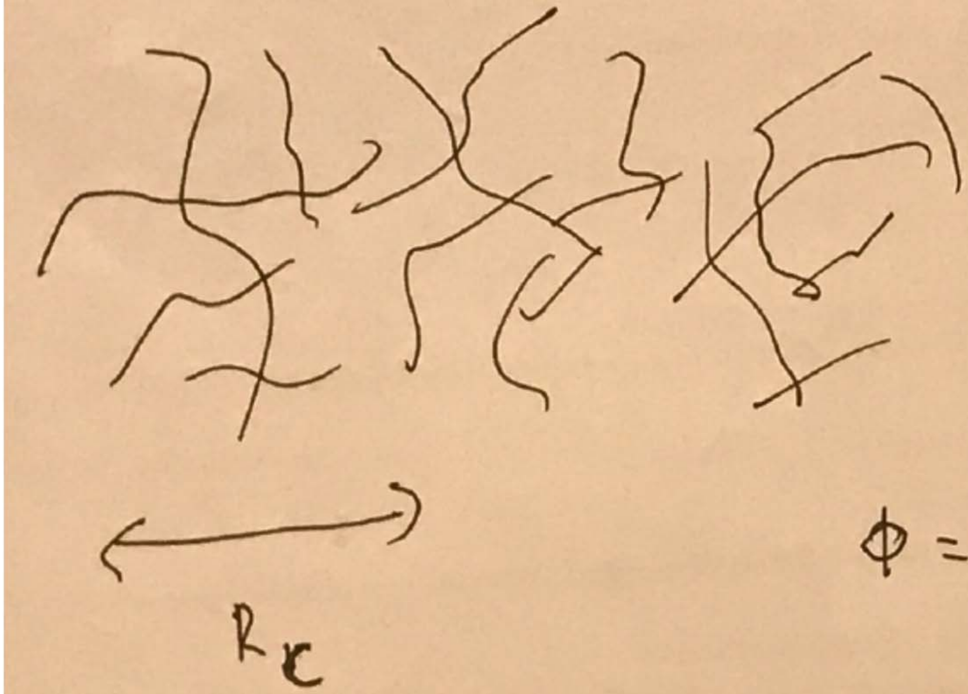


Gelation of fractal clusters



$$N_c = \left(\frac{R_c}{a}\right)^{d_f}$$

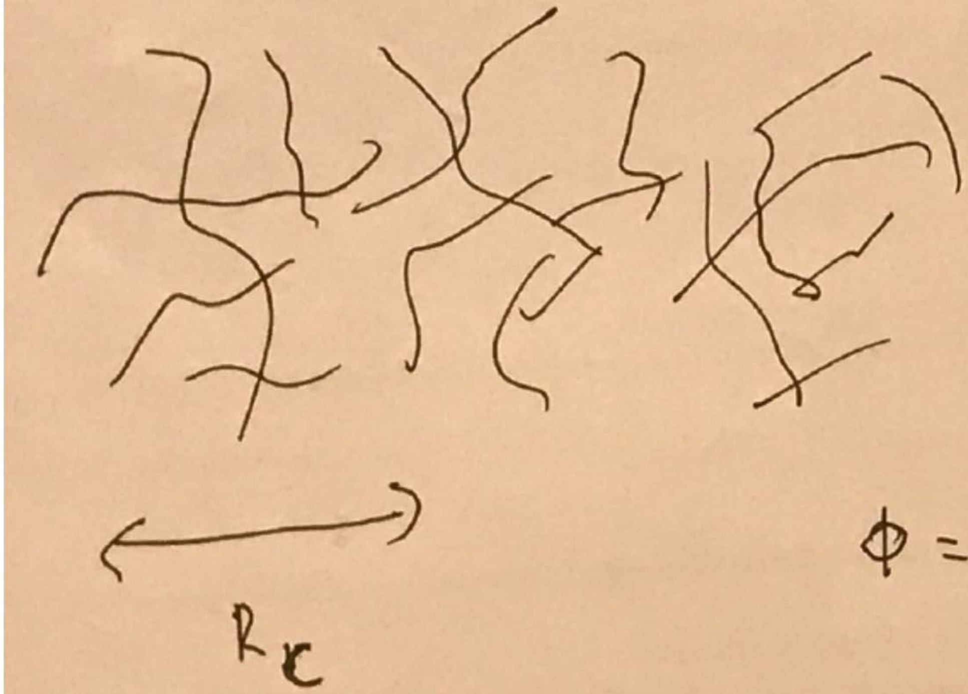
Gelation of fractal clusters



$$N_c = \left(\frac{R_c}{a}\right)^{d_f}$$

$$\Phi = \frac{N_c}{\left(\frac{R_c}{a}\right)^3} = \left(\frac{R_c}{a}\right)^{d_f - 3}$$

Gelation of fractal clusters



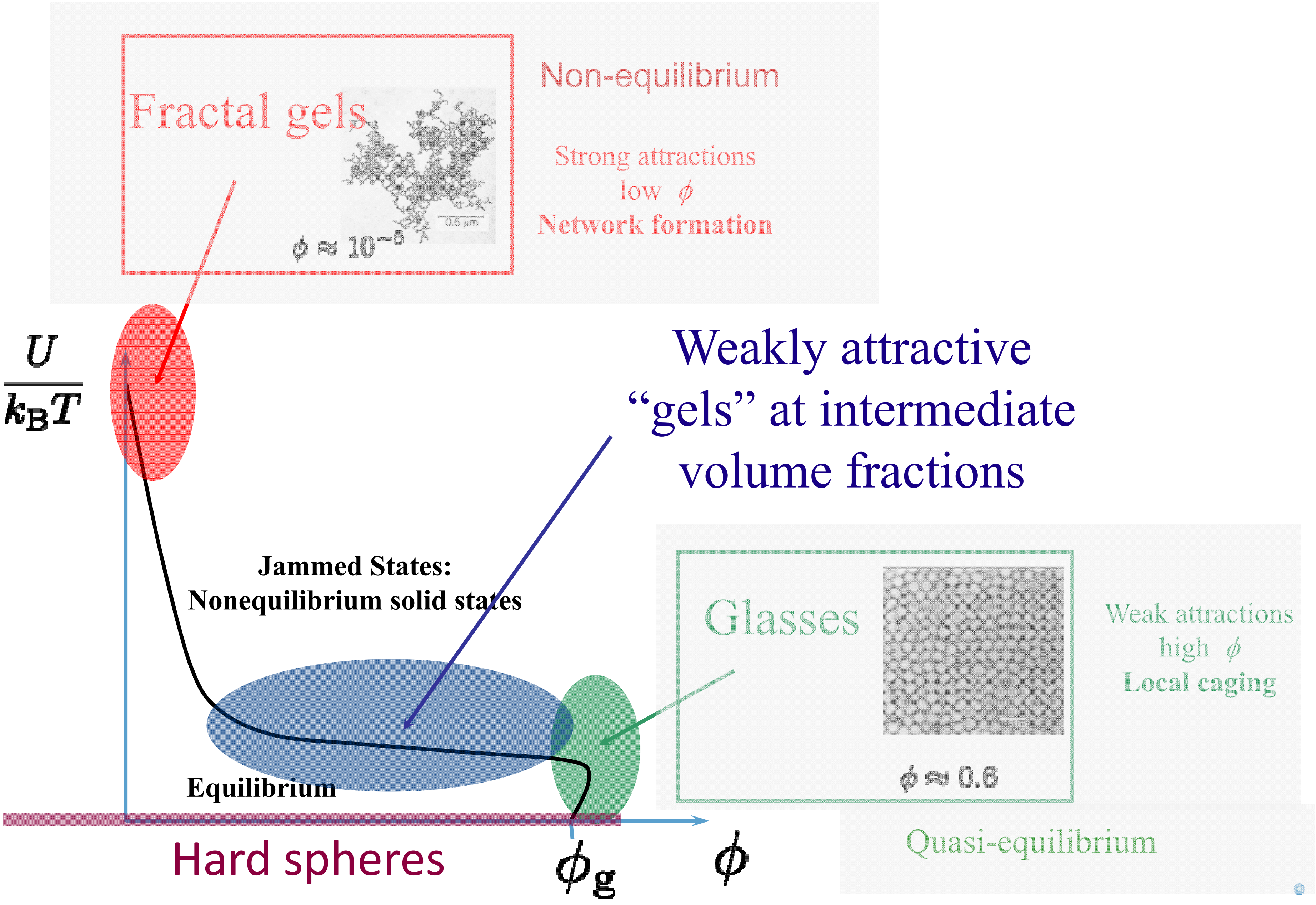
$$N_c = \left(\frac{R_c}{a}\right)^{d_f}$$

$$\phi = \frac{N_c}{\left(\frac{R_c}{a}\right)^3} = \left(\frac{R_c}{a}\right)^{d_f - 3}$$

$$R_c = a\,\phi^{\frac{1}{d_f - 3}}$$

$$R_c \sim a\phi^{-1}$$

State diagram for colloidal particles



Fractal gels

$\phi \approx 10^{-5}$

Non-equilibrium

Strong attractions
low ϕ
Network formation

Weakly attractive "gels" at intermediate volume fractions

Jammed States:
Nonequilibrium solid states

Equilibrium

Hard spheres

Glasses

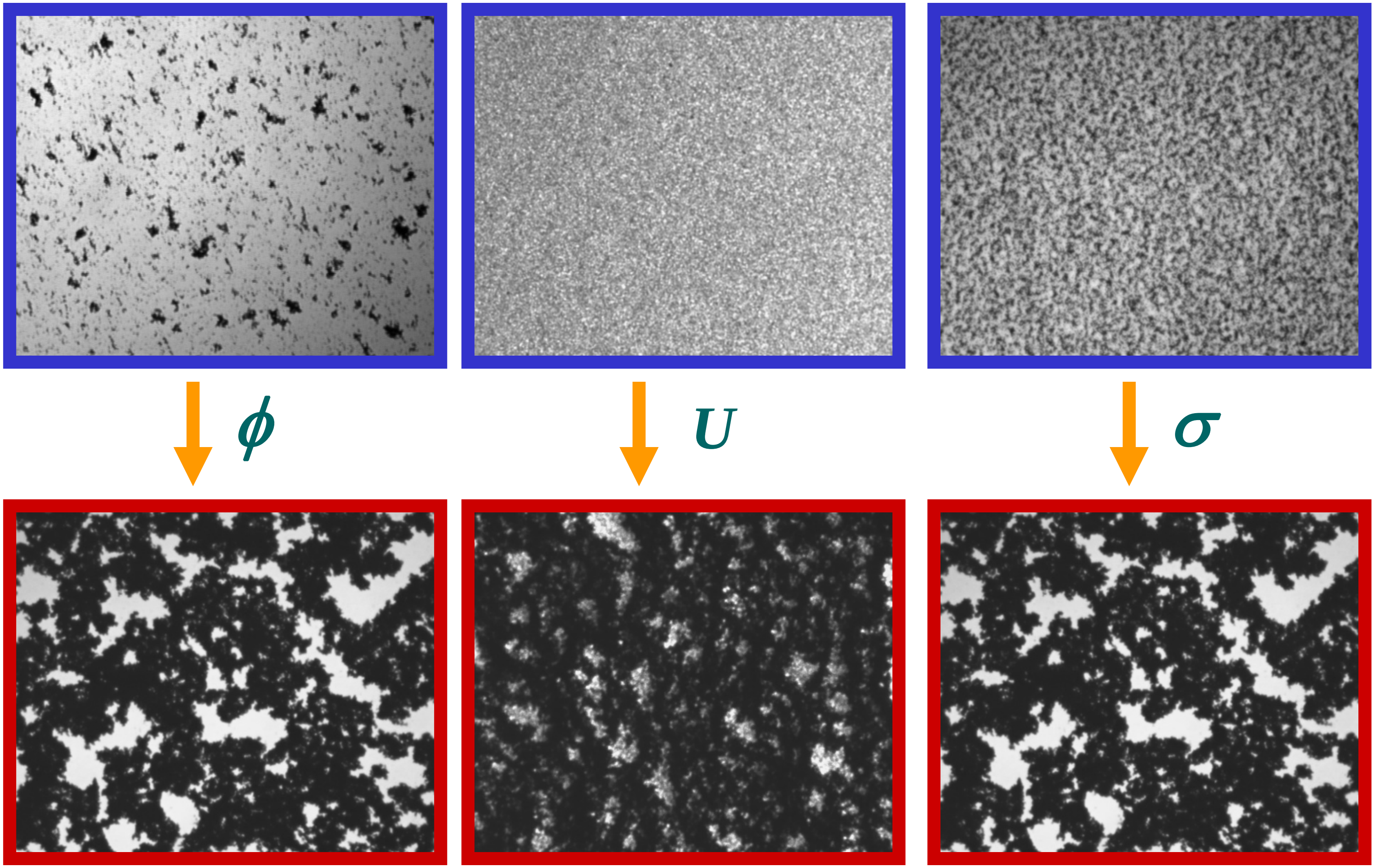
$\phi \approx 0.6$

Weak attractions
high ϕ
Local caging

Quasi-equilibrium

Gelation of Attractive Particles

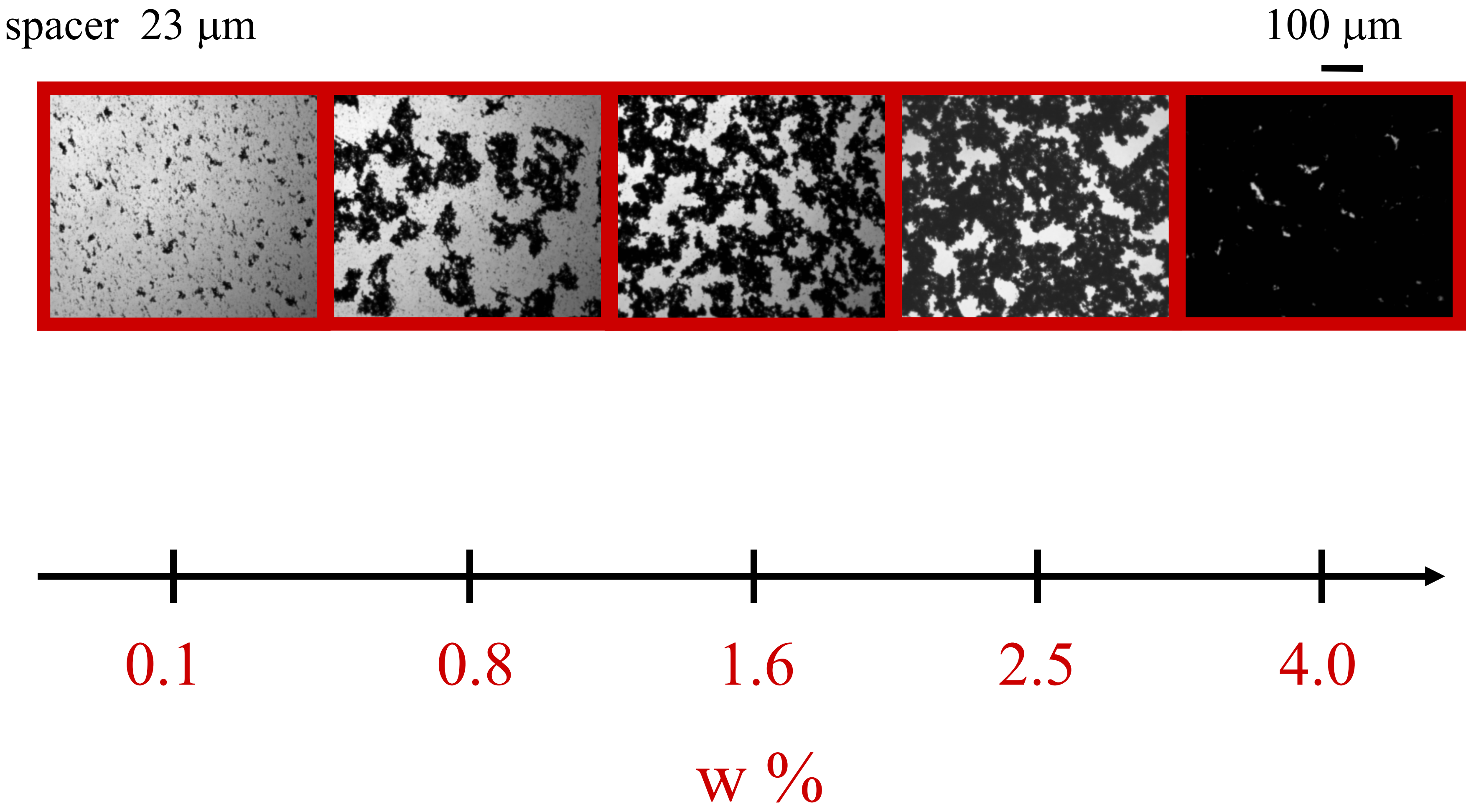
Carbon Black in Oil



Effect of Volume Fraction

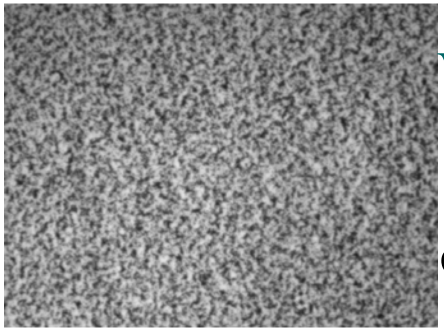
Carbon Black in S150N

$U \sim 10 \pm 2\ kT$ 25°C

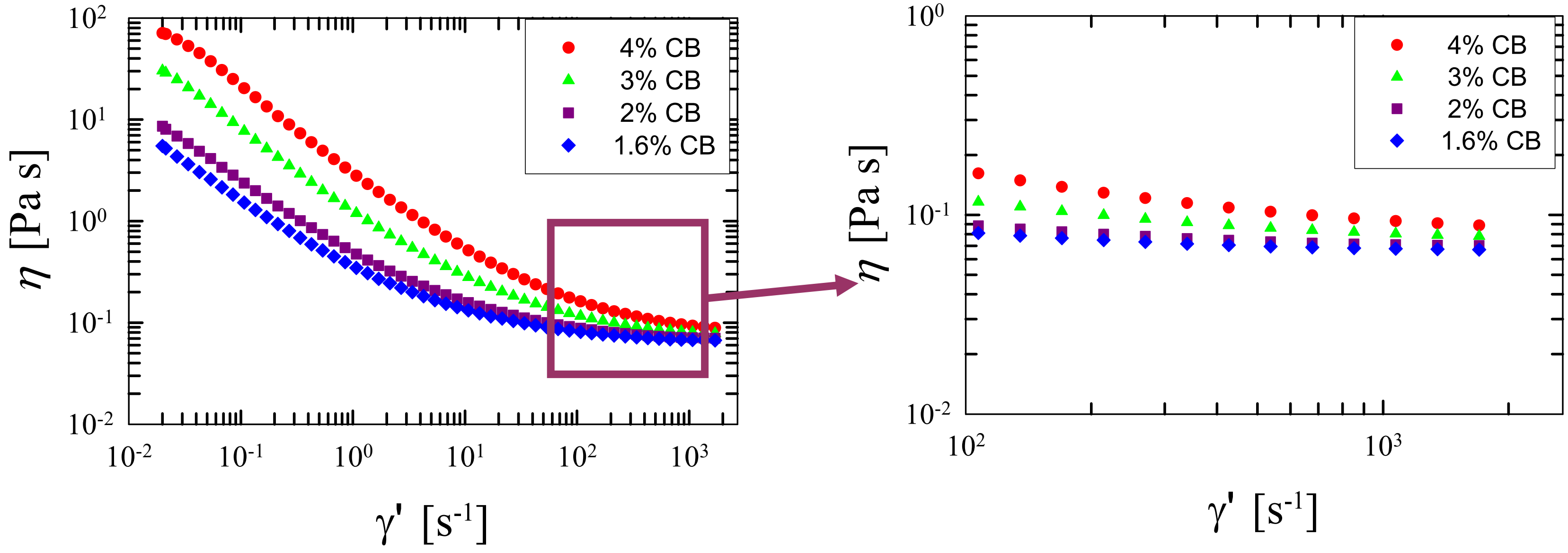


Determination of Volume Fraction

Shear breaks aggregates into 0.5 μm units



Volume fraction determined from ϕ-dependence of η



Concentration Series 25°C

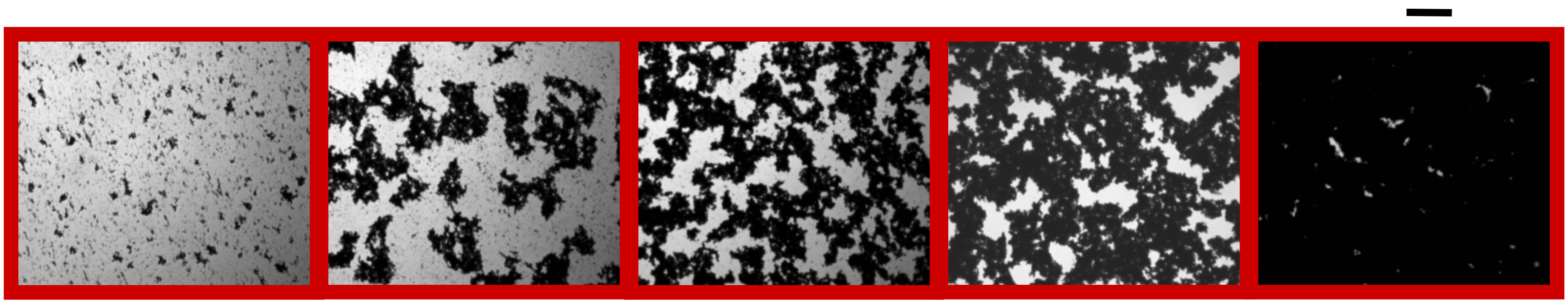
Concentration Series 25°C

Effect of Volume Fraction

Carbon Black in S150N

$U \sim 10 \pm 2$ kT 25°C

spacer 23 µm

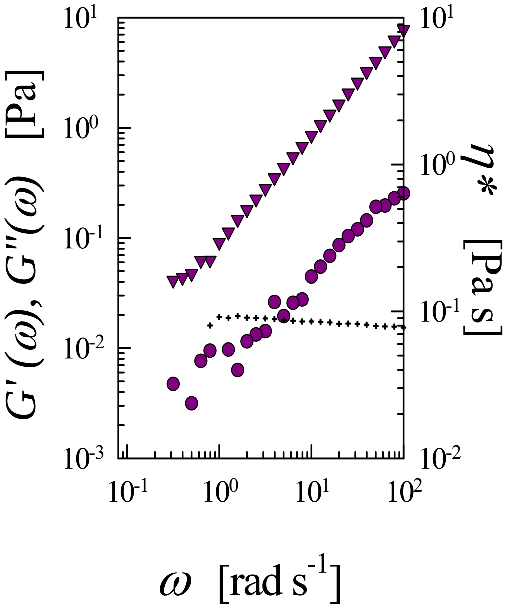


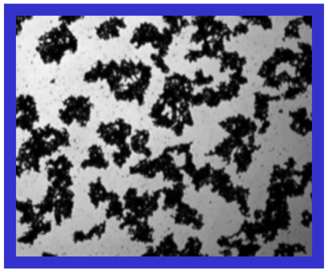
Φ %	0.3	3.3	6.4	9.7	14.9
w %	0.1	0.8	1.6	2.5	4.0

Fluid-Like Behavior

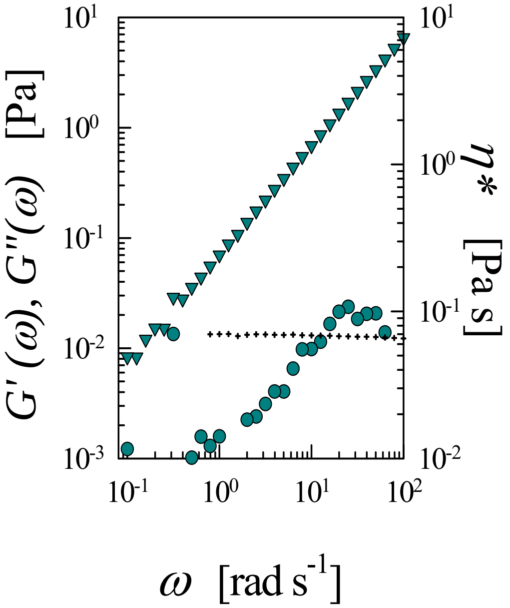
Carbon Black in S150N T=25°C

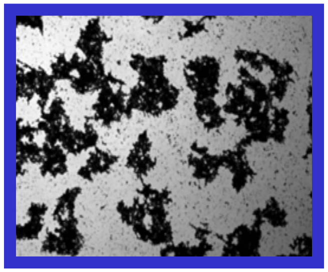
1.2% CB Φ = 0.048



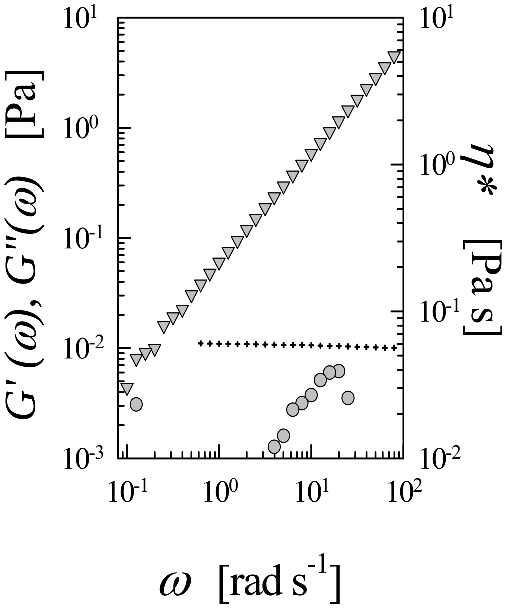


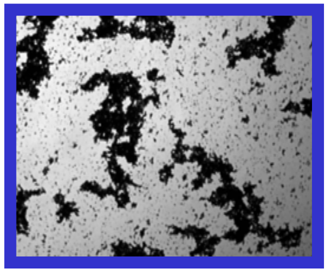
0.8% CB Φ = 0.033





0.4% CB Φ = 0.013

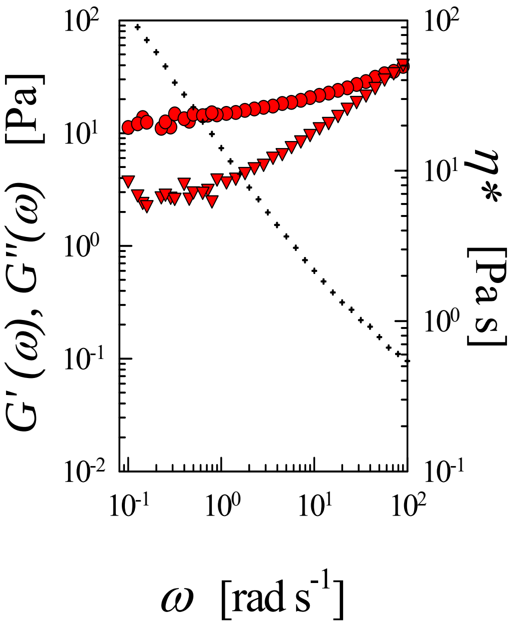


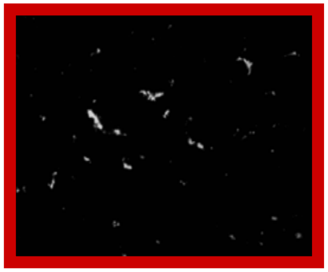


Solid-Like Behavior

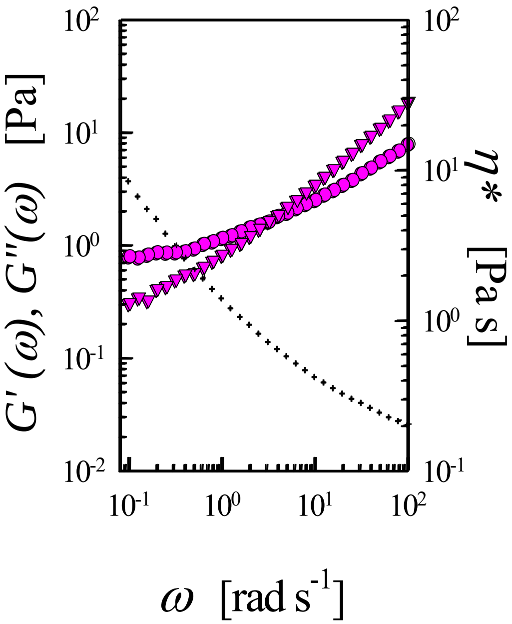
CB in S150N T=25^{o}C

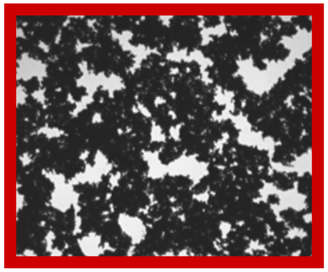
4% CB Φ = 0.149



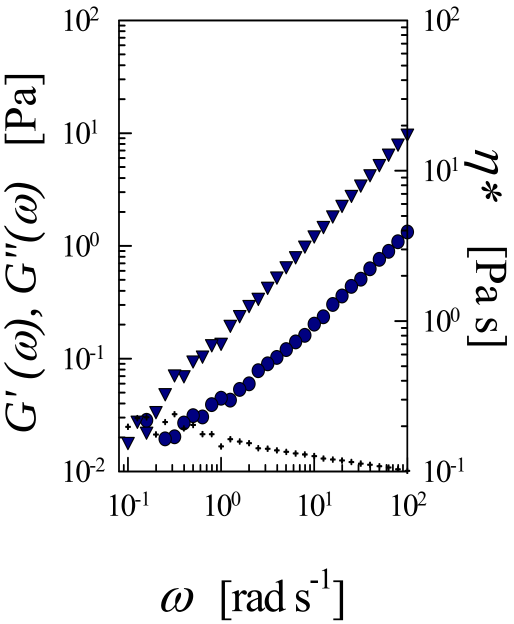


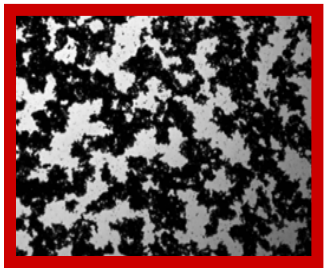
2.5% CB Φ = 0.097





1.6% CB Φ = 0.064

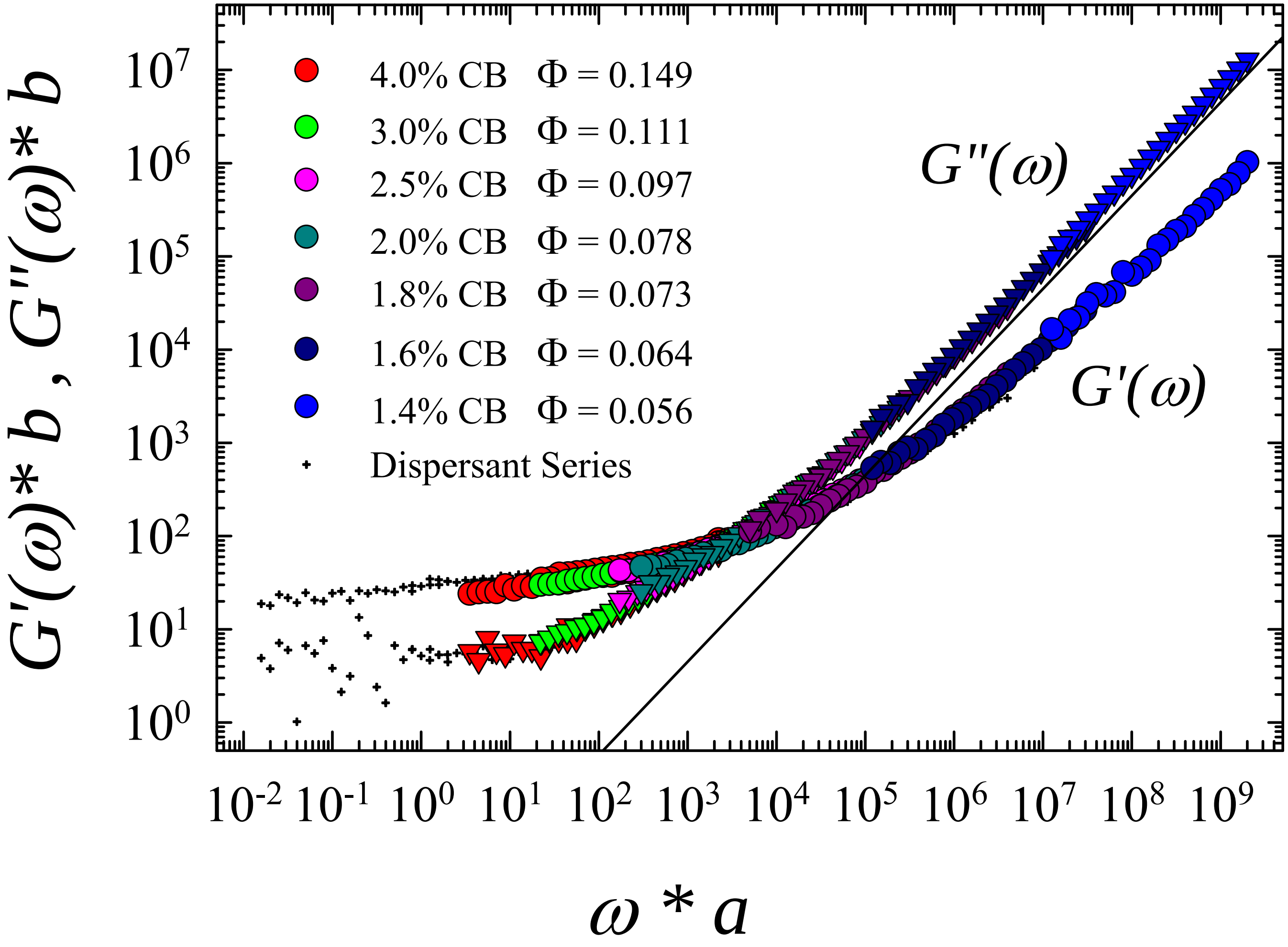




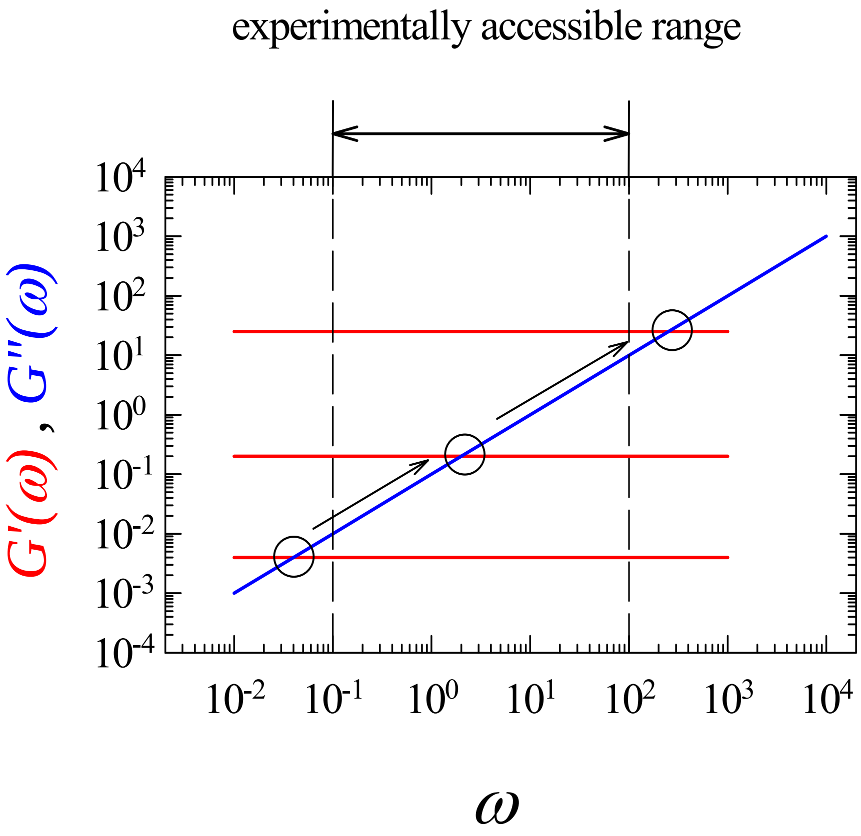
Scaling

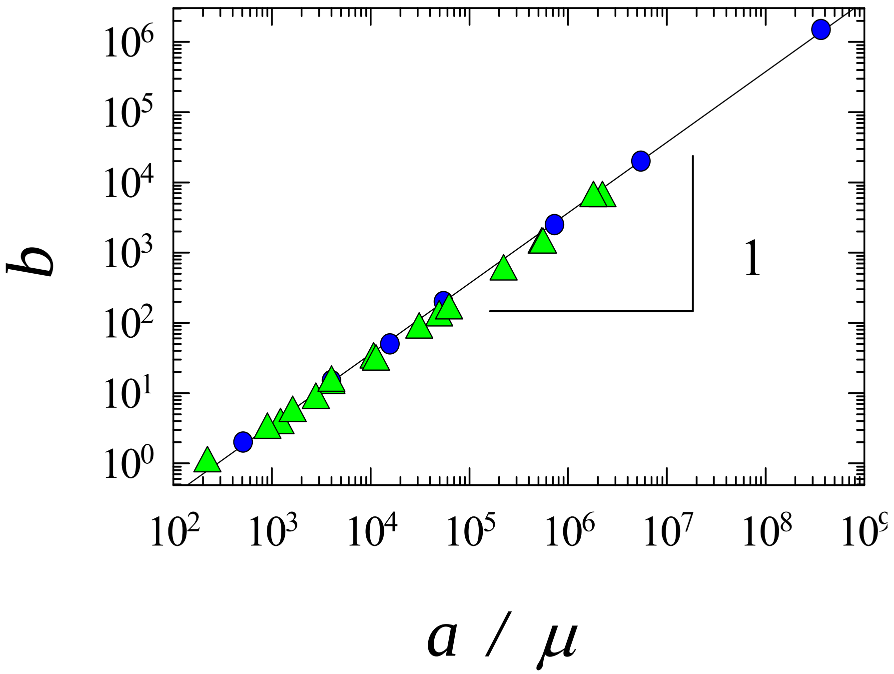
ϕ-Dependence

Carbon Black in S150N U ~ 10 ± 2 kT 25°C

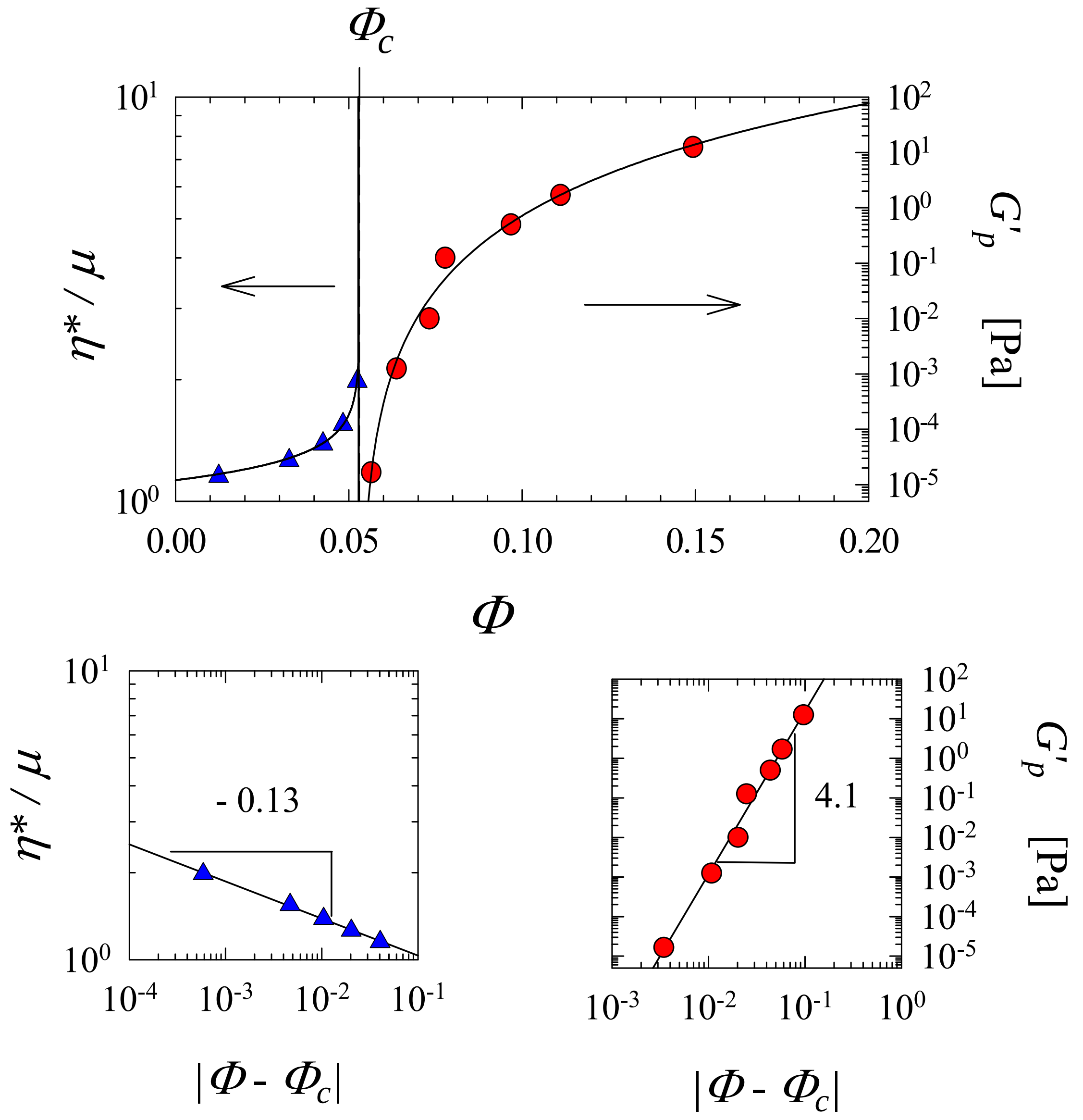


Scaling along the background-viscosity





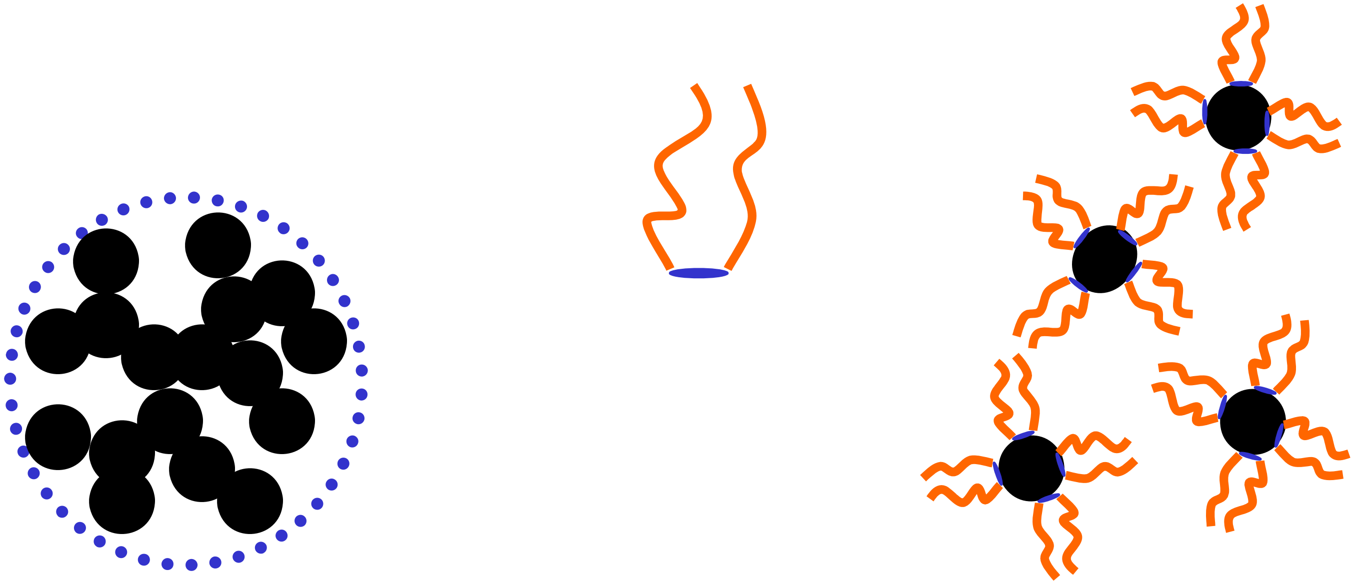
ϕ-Dependence of Fluid-Solid Transition



Effect of Dispersant

Decrease Interaction Energy

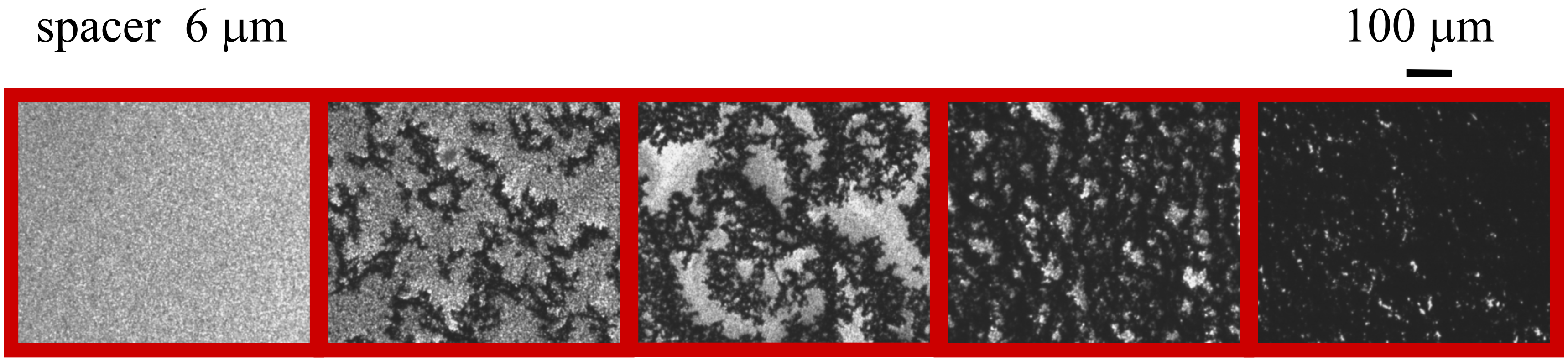
Decrease Aggregation

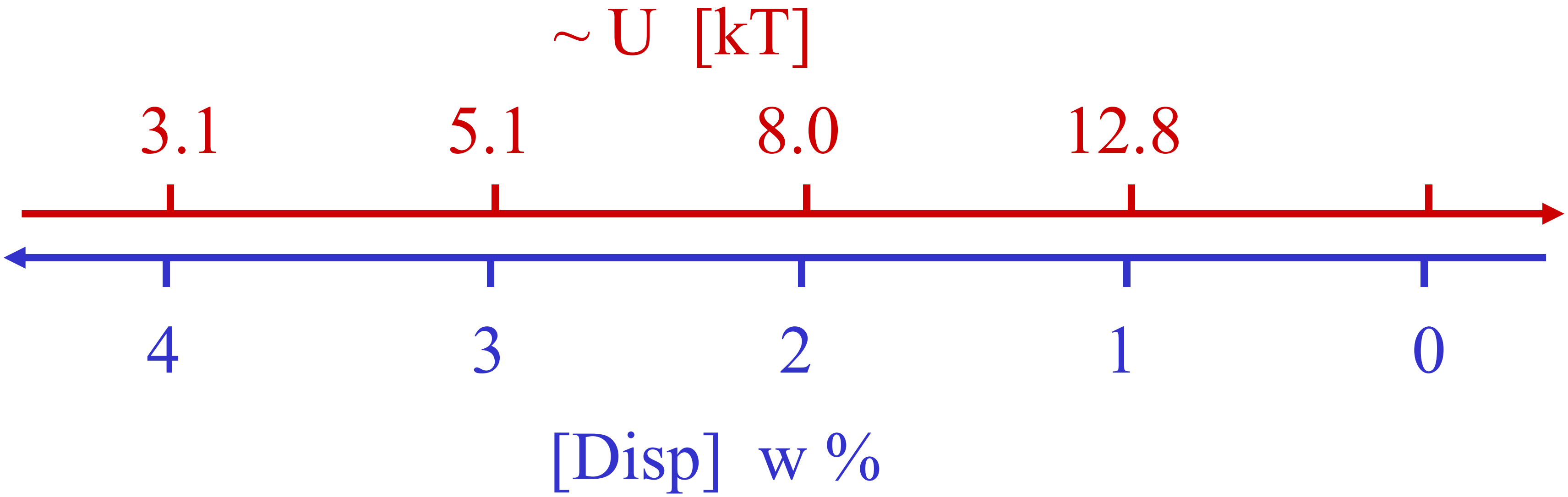


Amount of Dispersant controls Interaction Energy

Effect of Dispersant Concentration

Carbon Black in Oil $\phi = 0.14$ 100^{o}C





~ U [kT]

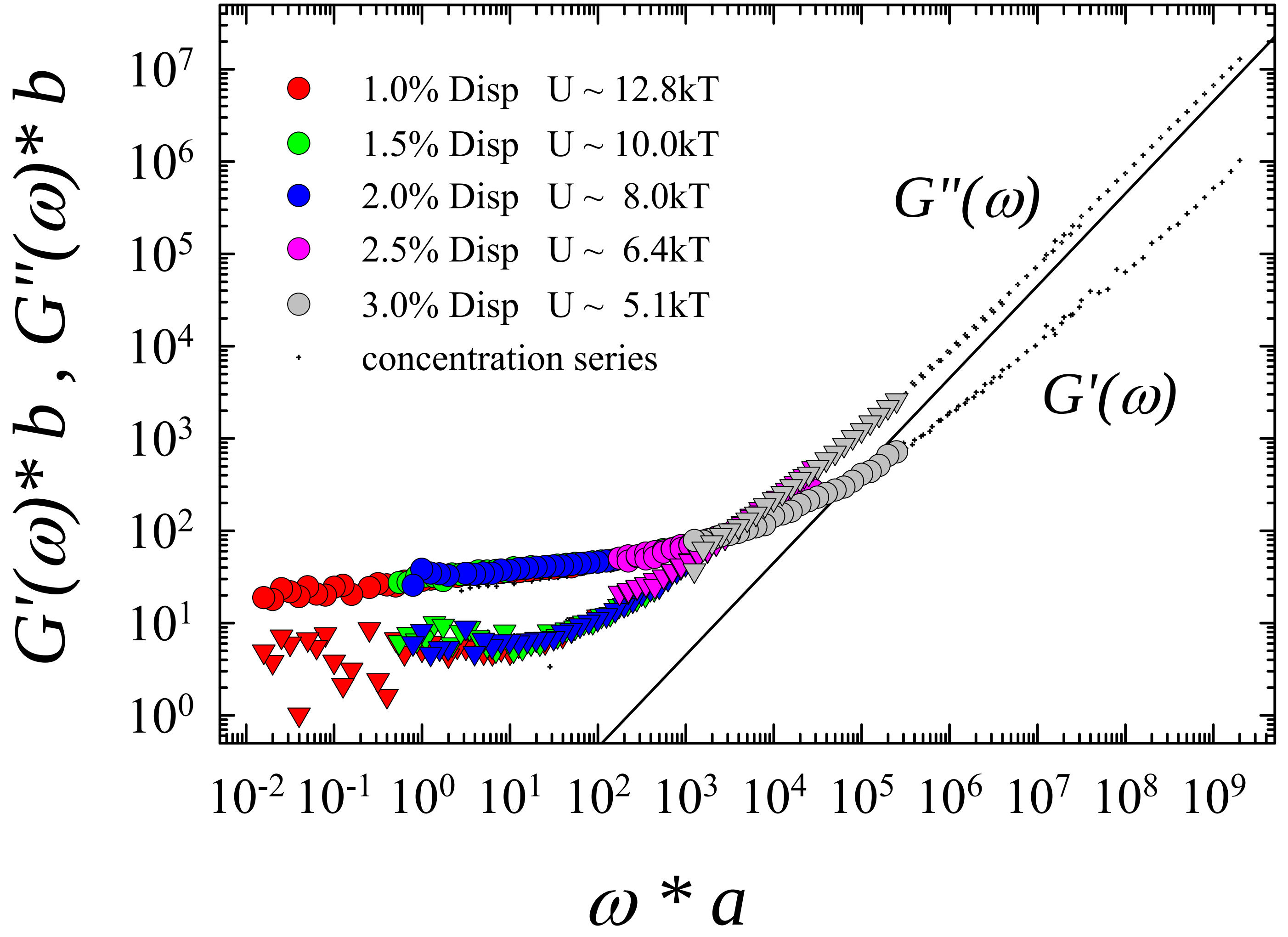
3.1 5.1 8.0 12.8

4 3 2 1 0

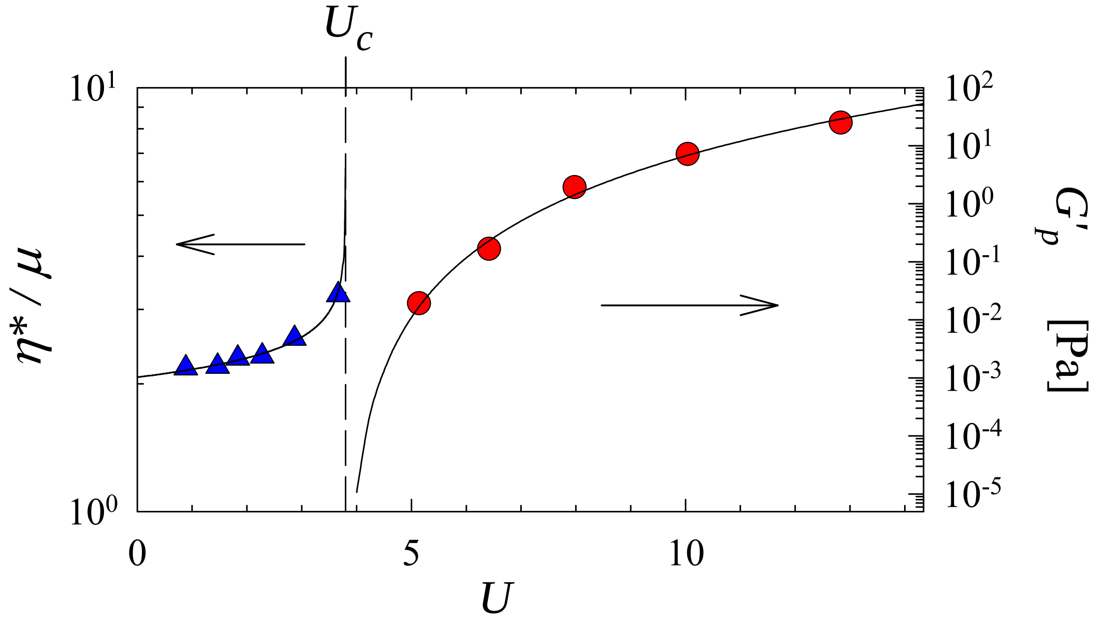
[Disp] w %

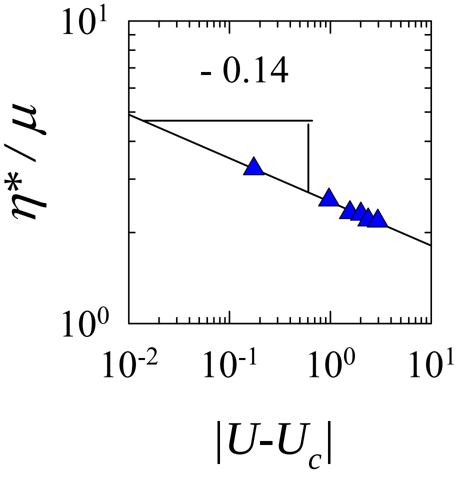
Scaling: *U-Dependence*

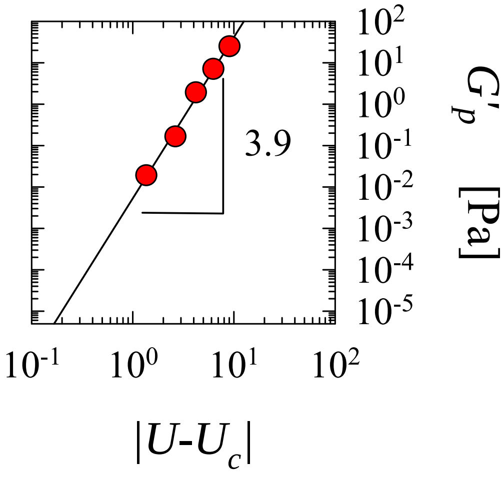
Carbon Black in S150N $\phi \sim 0.14$ T=25°C



Fluid-Solid Transition   *U*-Dependence

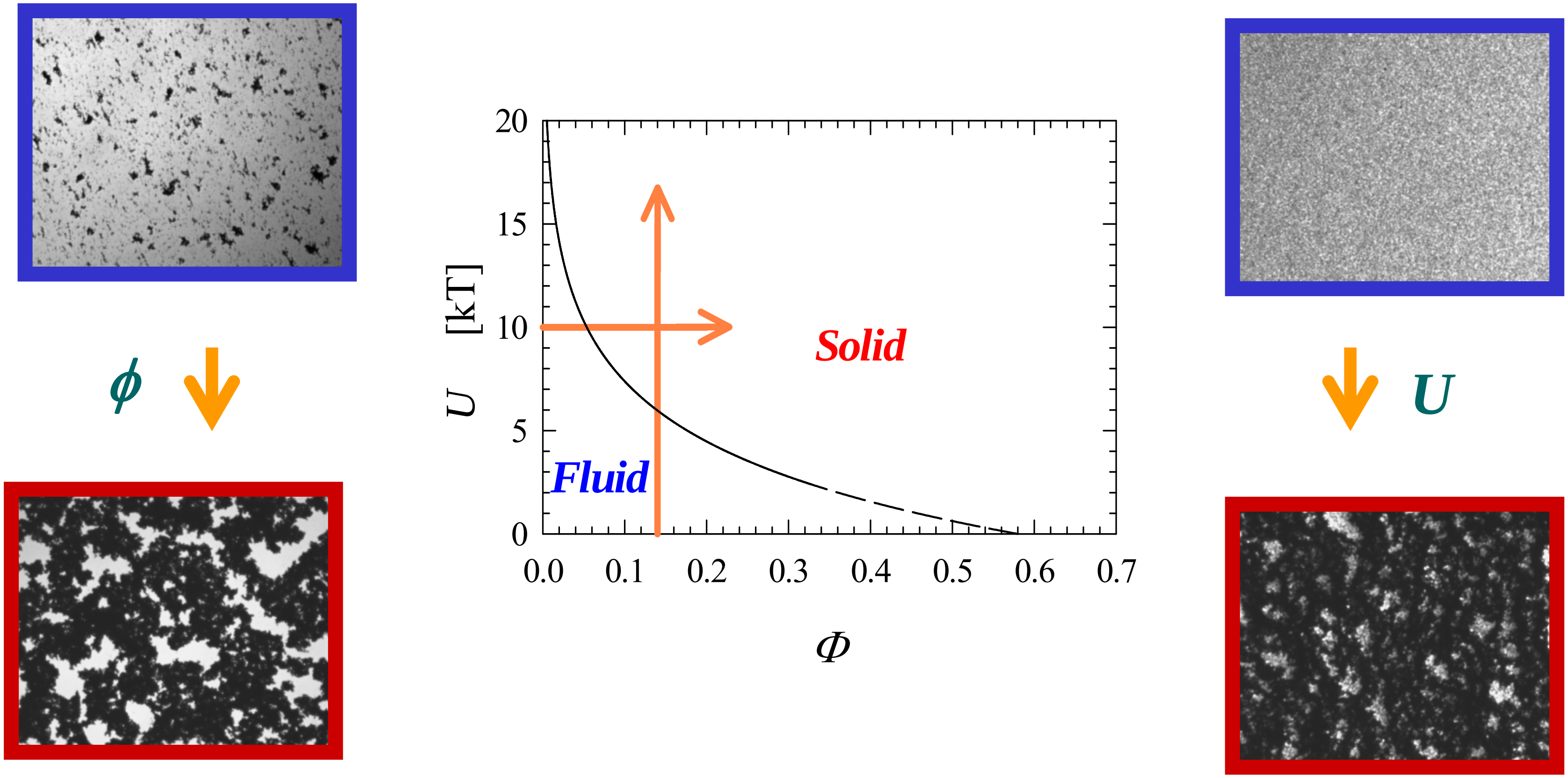






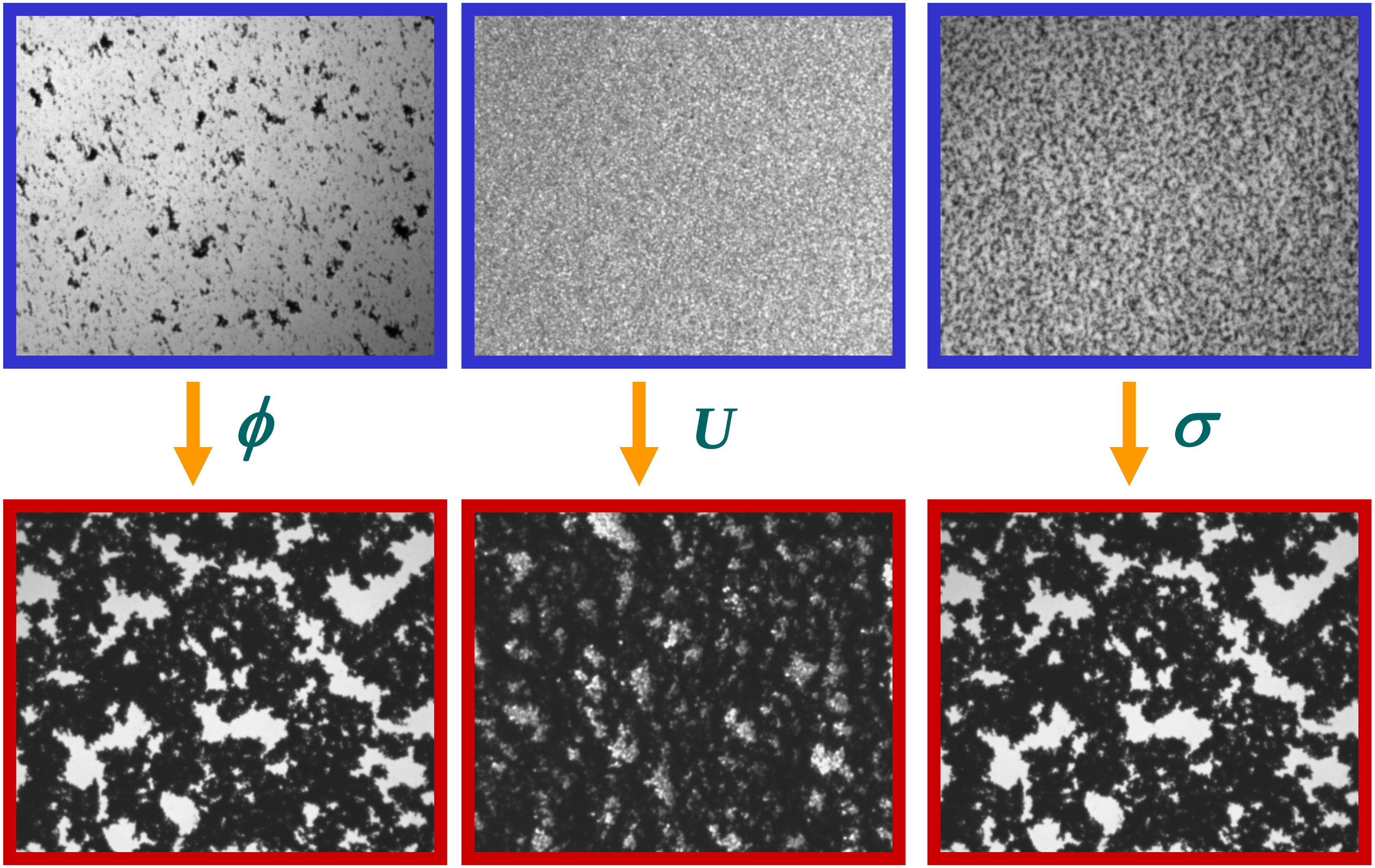
Fluid-Solid Transition

Weakly Attractive Systems

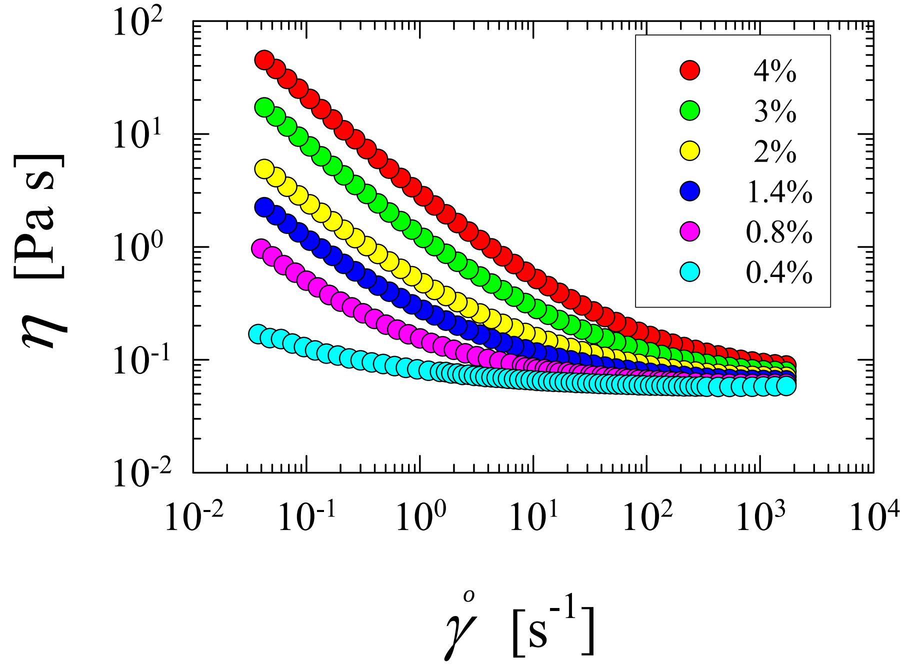


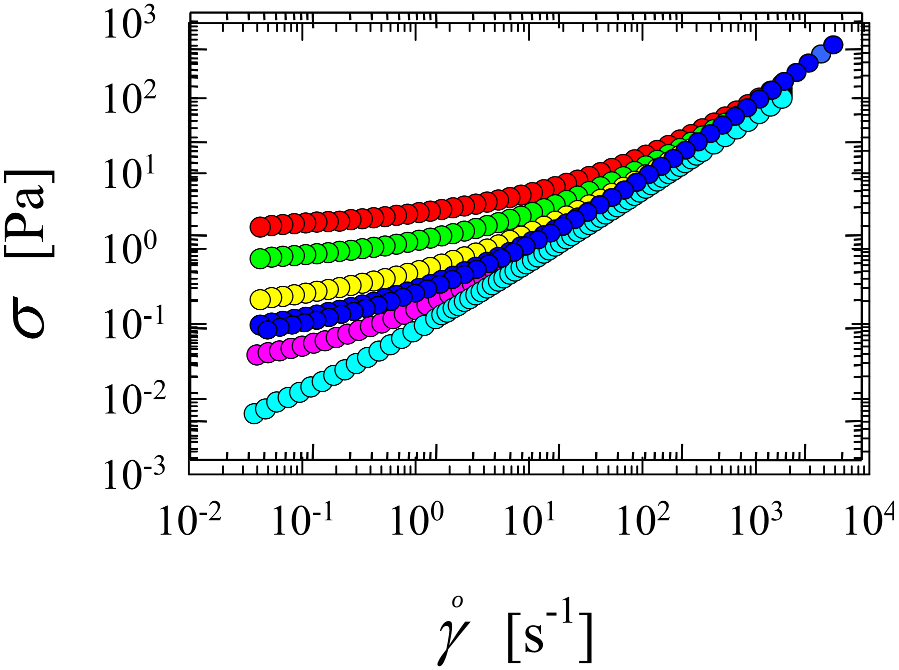
Fluid-Solid Transitions

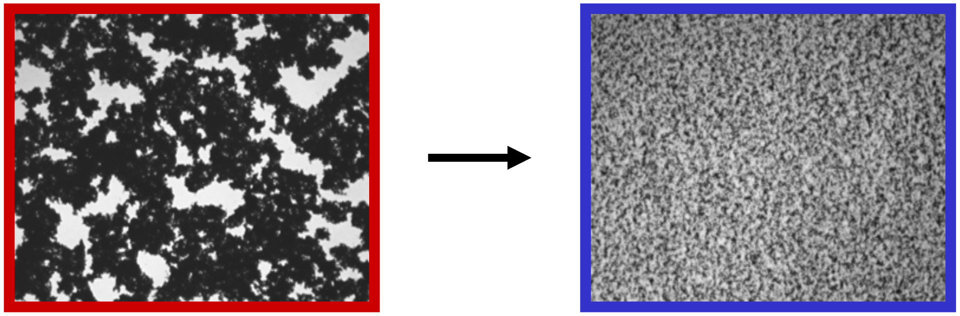
Carbon Black in Oil



Fluidization through Shear

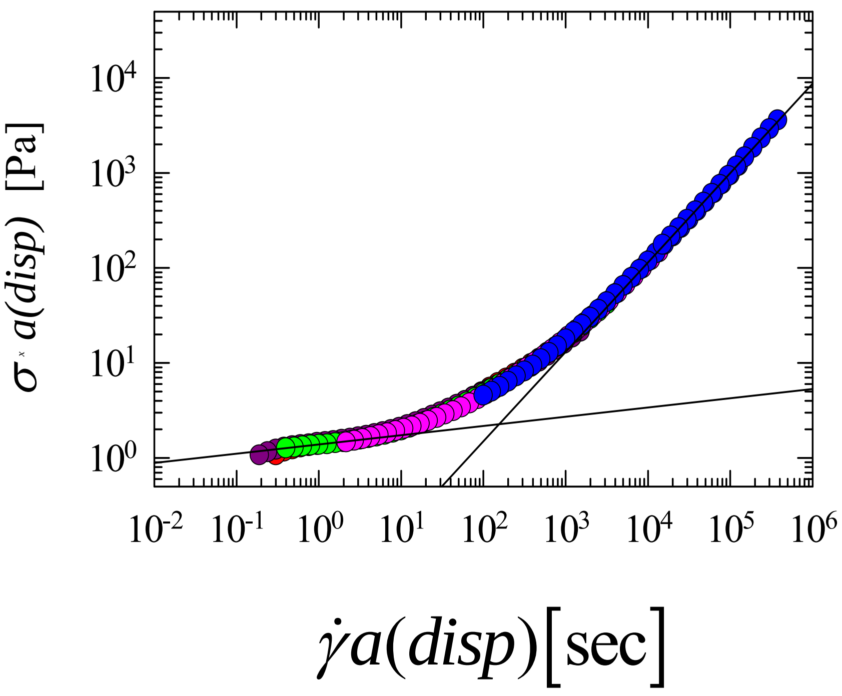


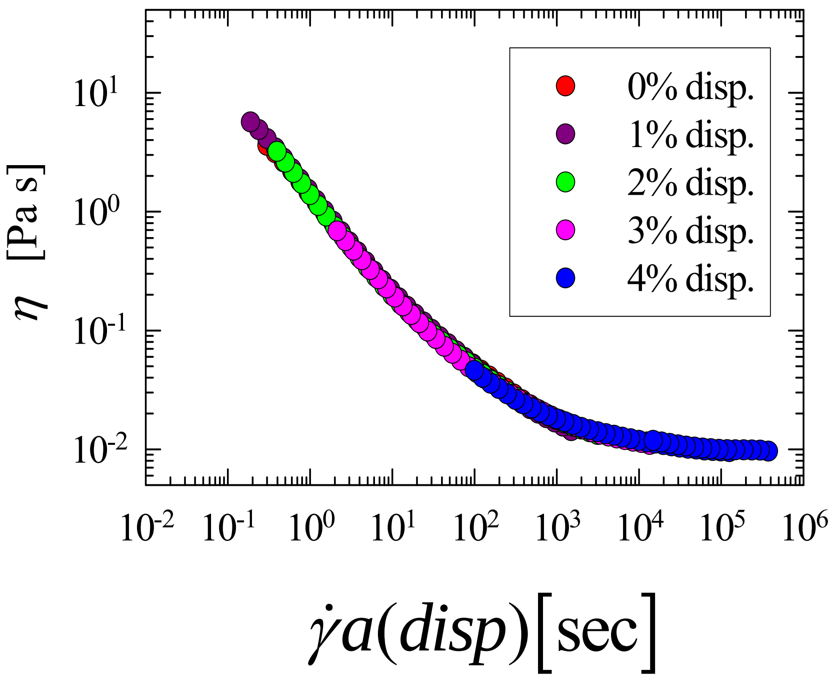




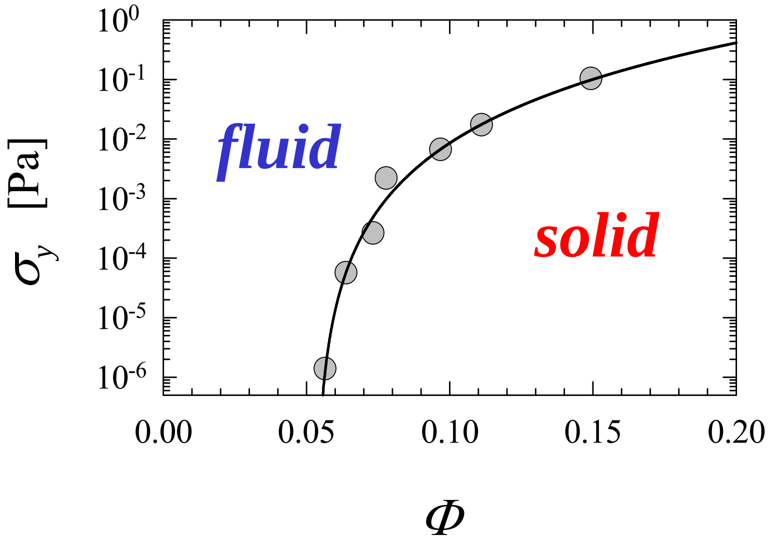
CB in S150N 25oC

Dispersant-Shear Equivalence

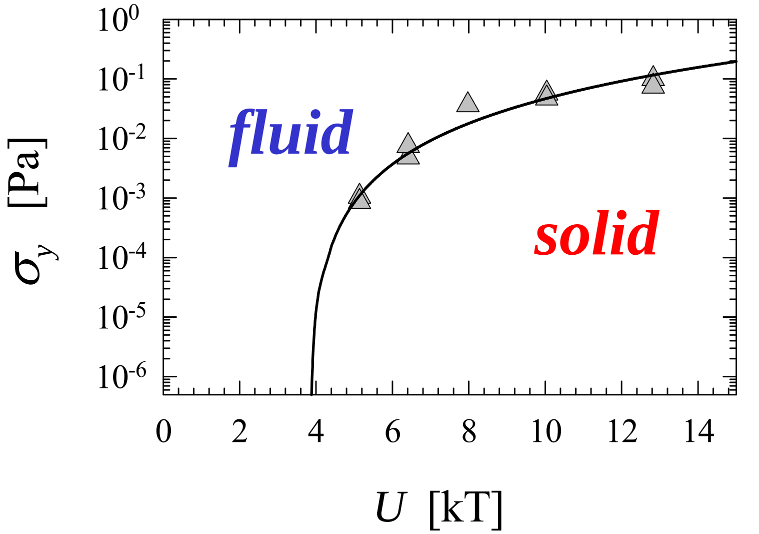




Shear Induced Fluid-Solid-Transition

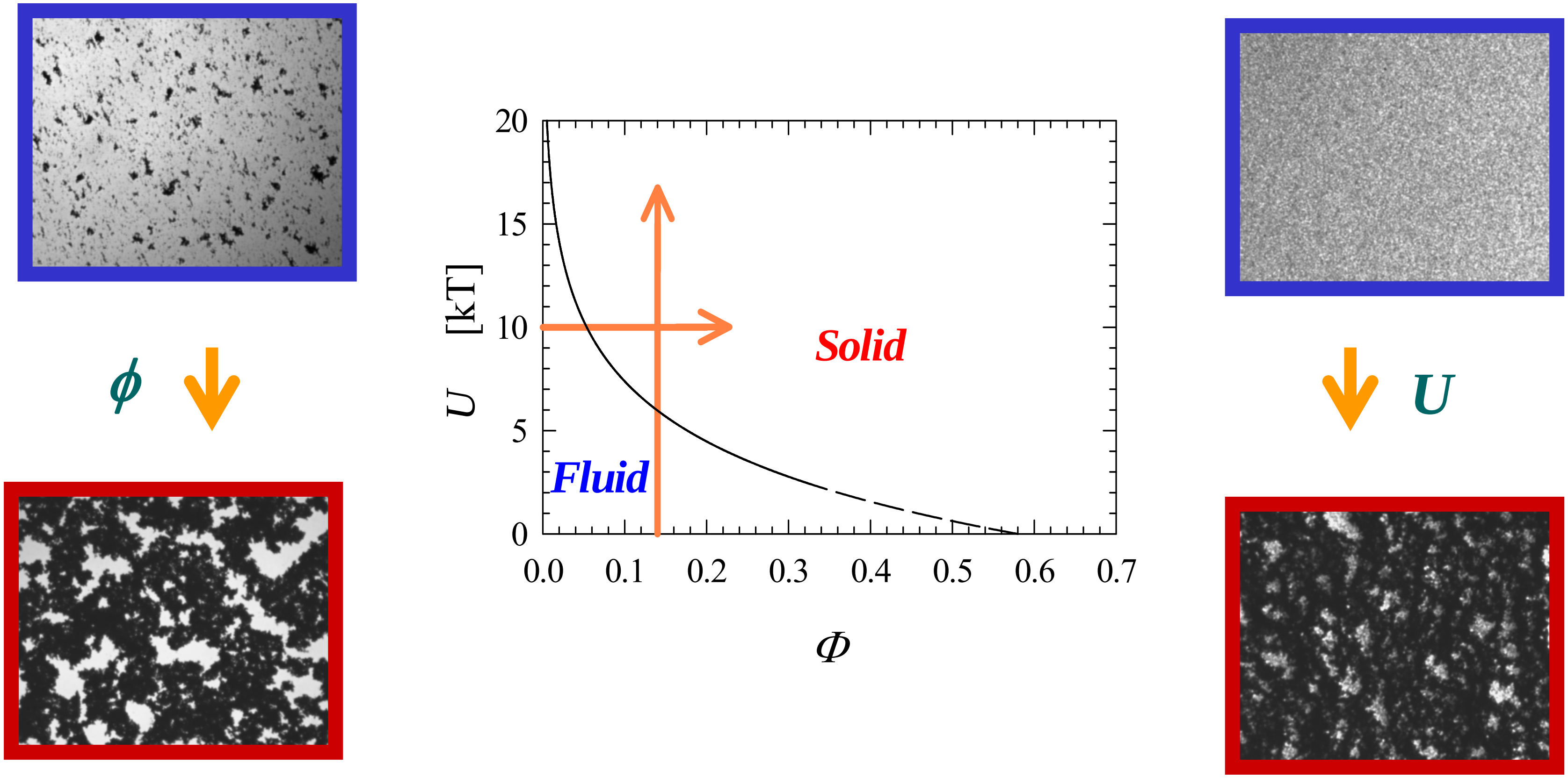


$$\sigma_y = \sigma_\Phi \, (\Phi\text{-}\Phi_c)^{3.4}$$



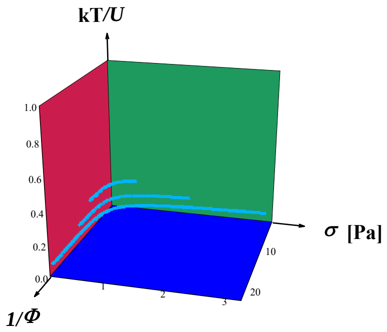
$$\sigma_y = \sigma_u \, (U\text{-}U_c)^{2.4}$$

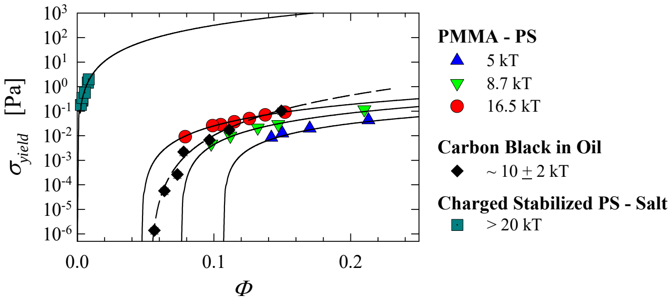
Phase Boundary in *U*-*ϕ* Plane



Yield Stress as Phase Boundary

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

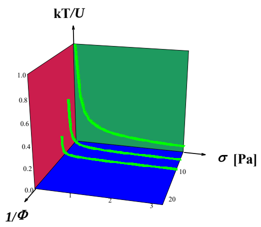


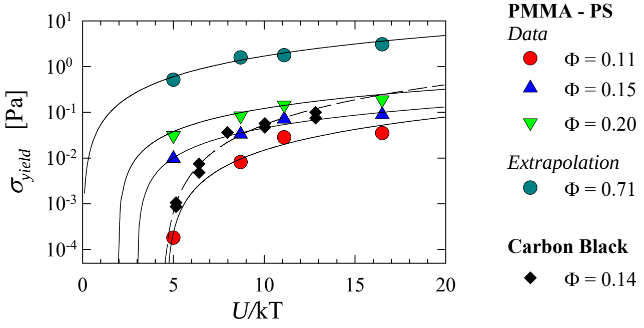


Phase Boundary in $U - \sigma$ Plane

ϕ = const.

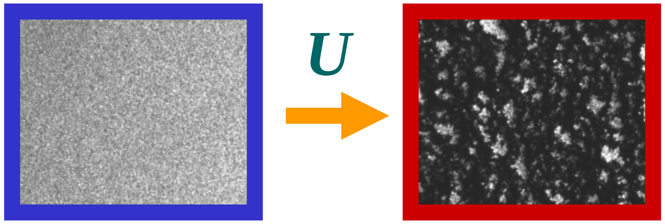
$$\sigma_y = \sigma_o \, (U - U_c)^{\nu}$$

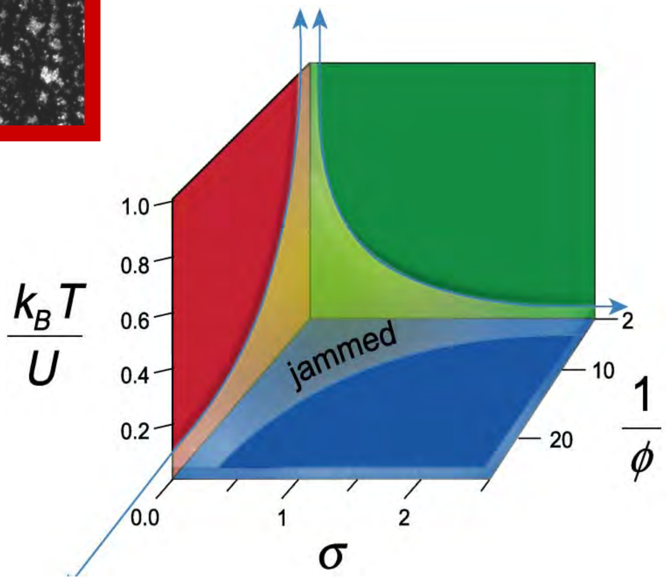


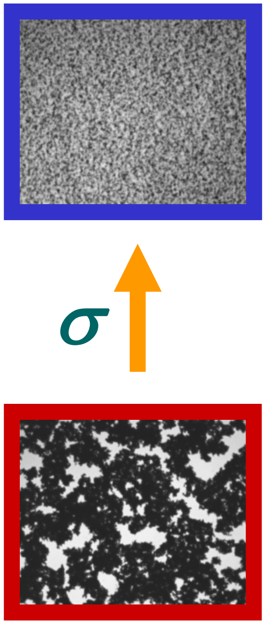


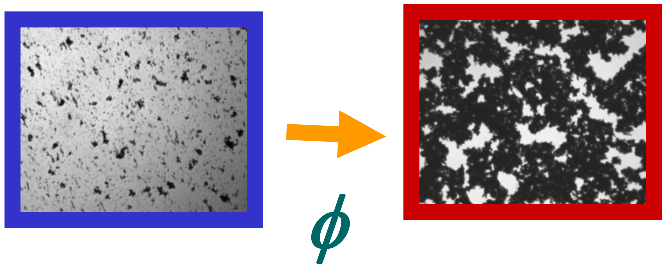
Jamming Phase Diagram for Attractive Systems

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





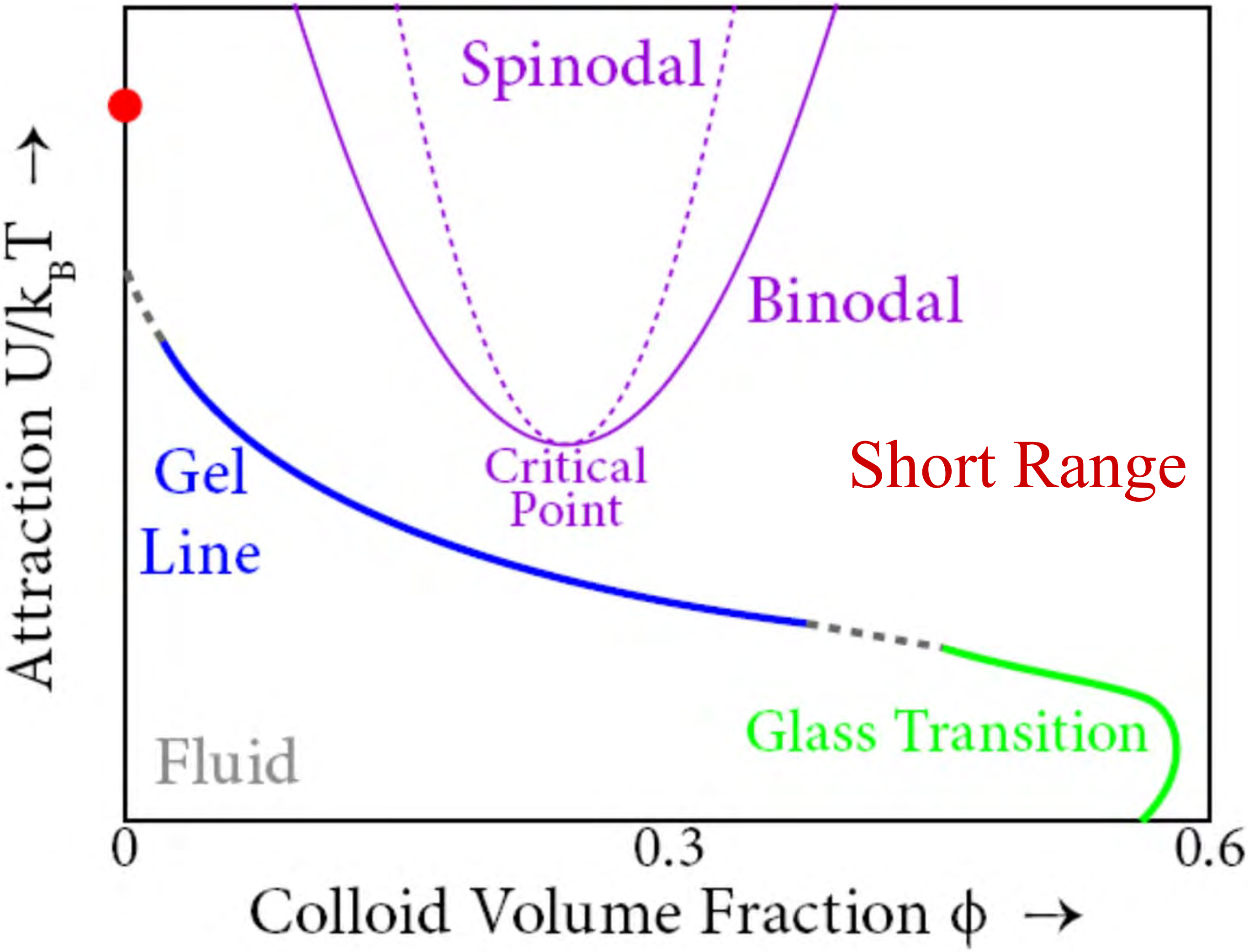




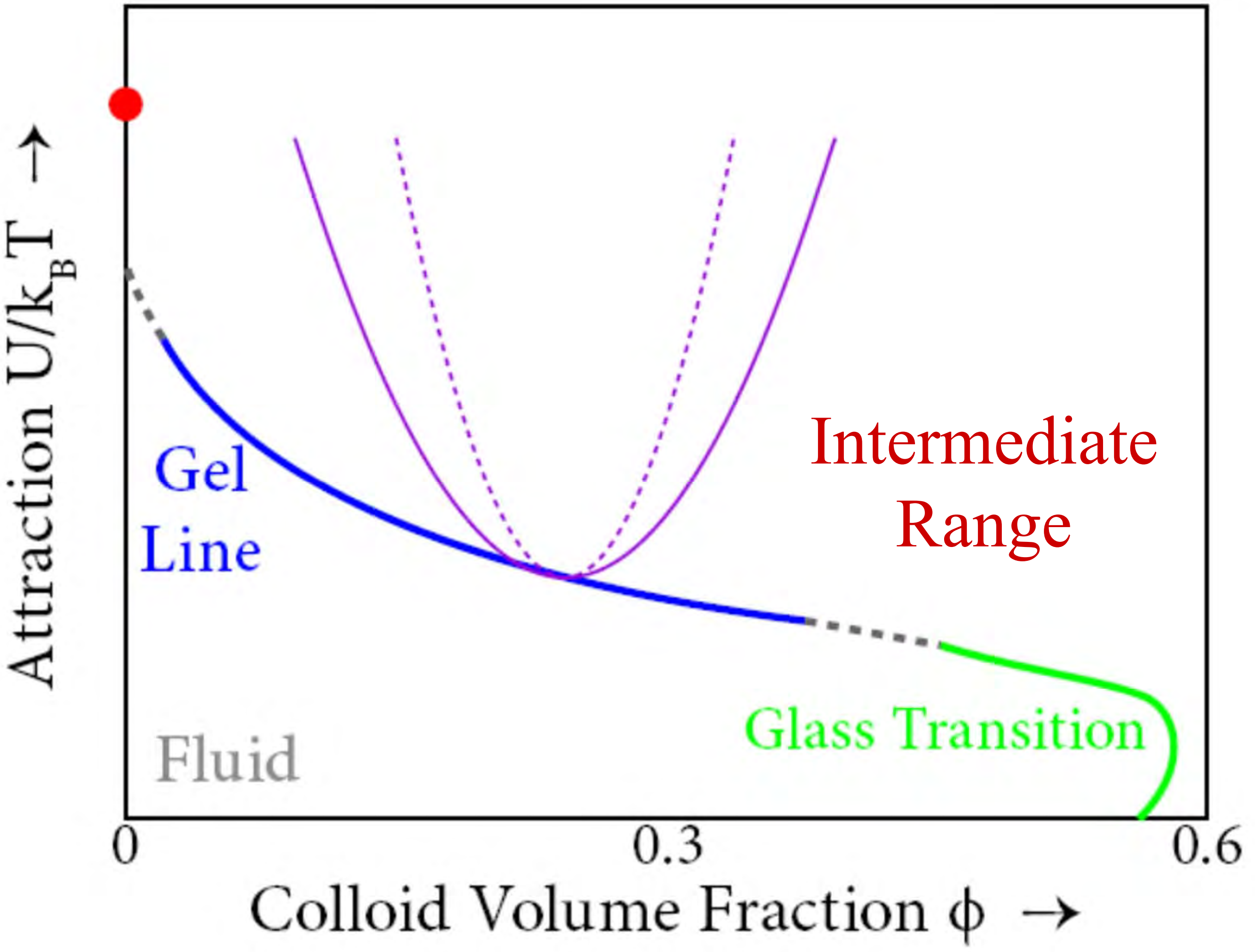
Completely new way to look at viscosity of soot in oil

Dependence on range of interaction

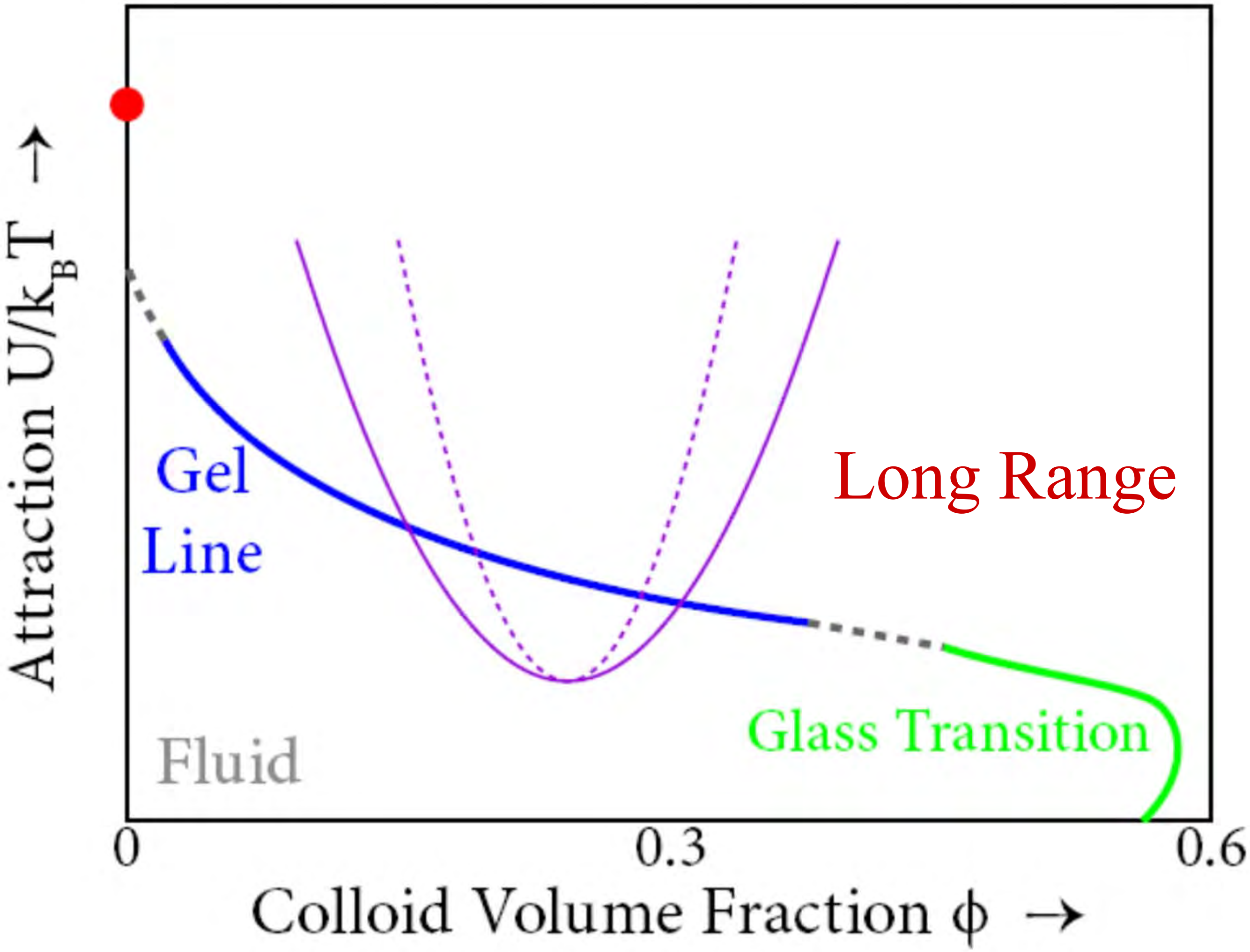
Attractive colloidal particles



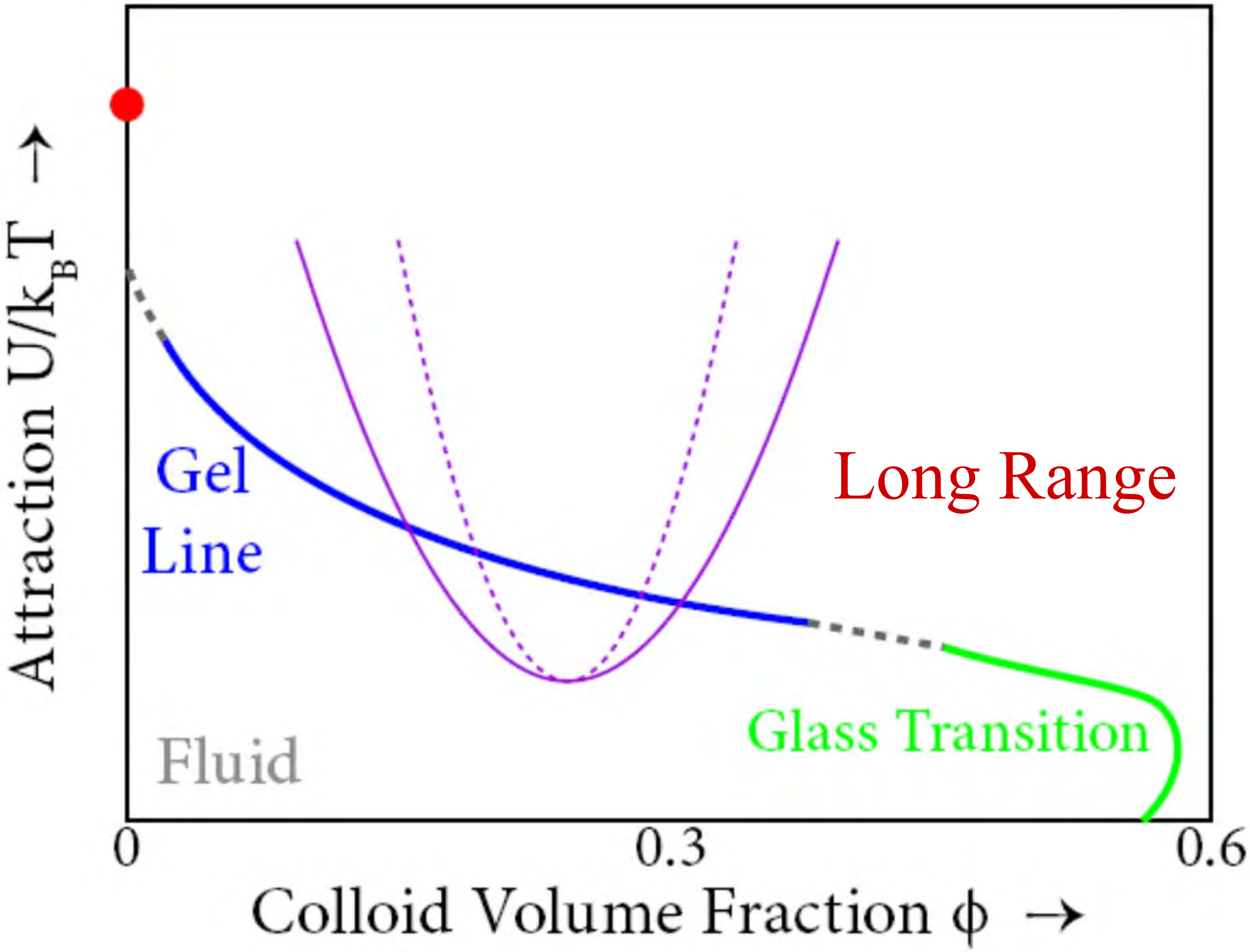
Attractive colloidal particles



Attractive colloidal particles

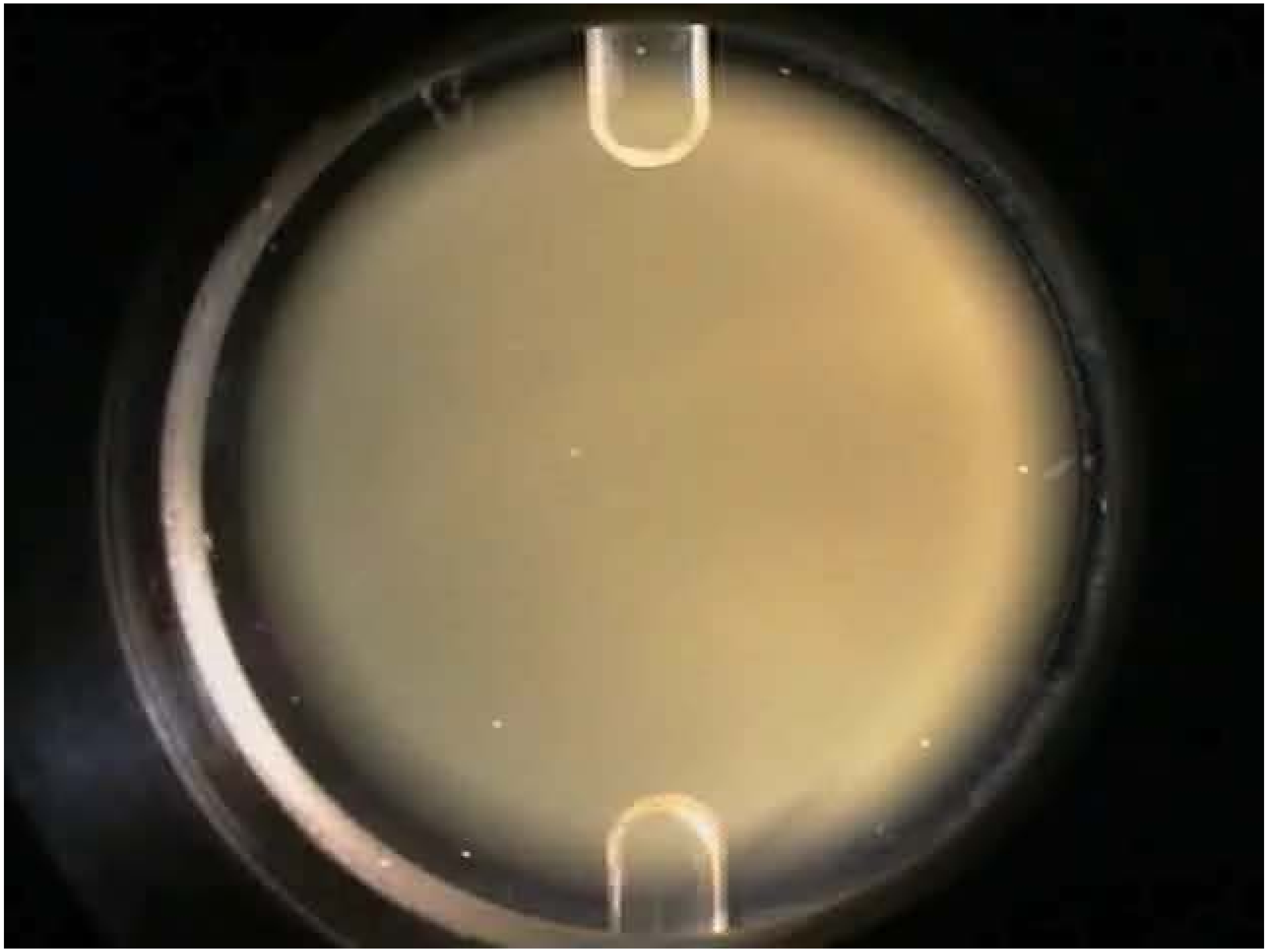


Long-range attraction



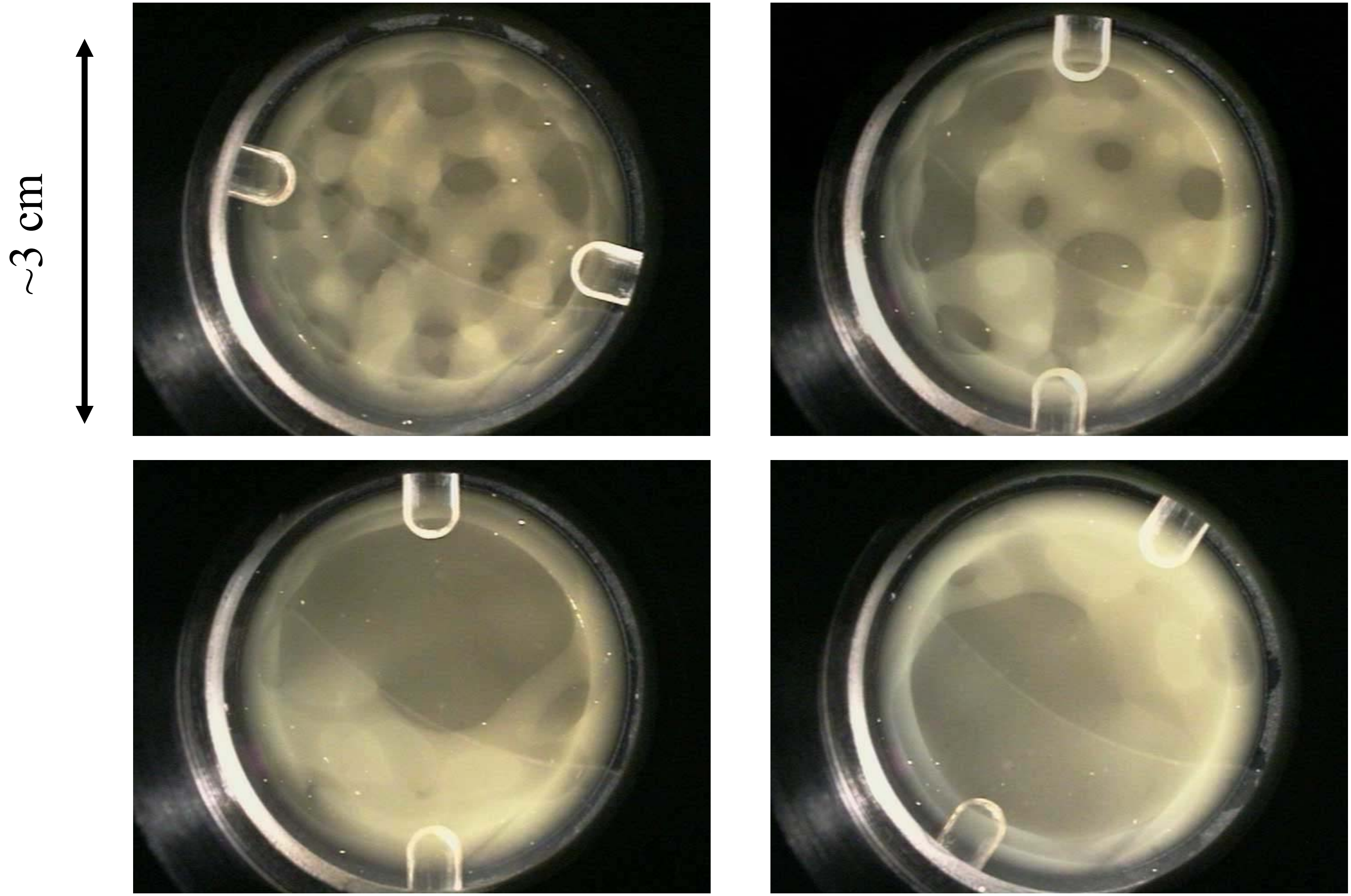
Reduce gravity

Spinodal Decomposition of Colloid Polymer

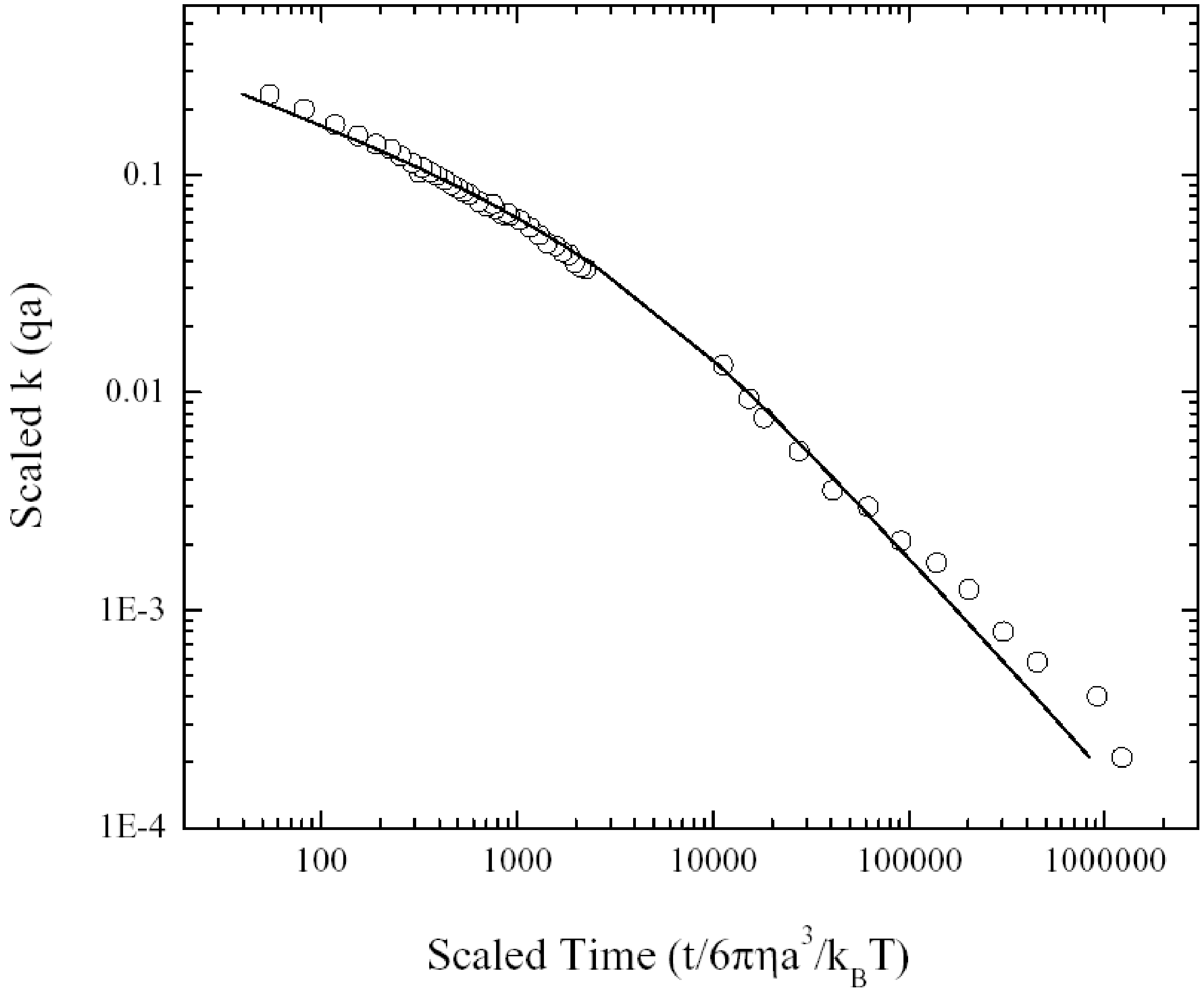


35 hours

Time Evolution of Phase Separation

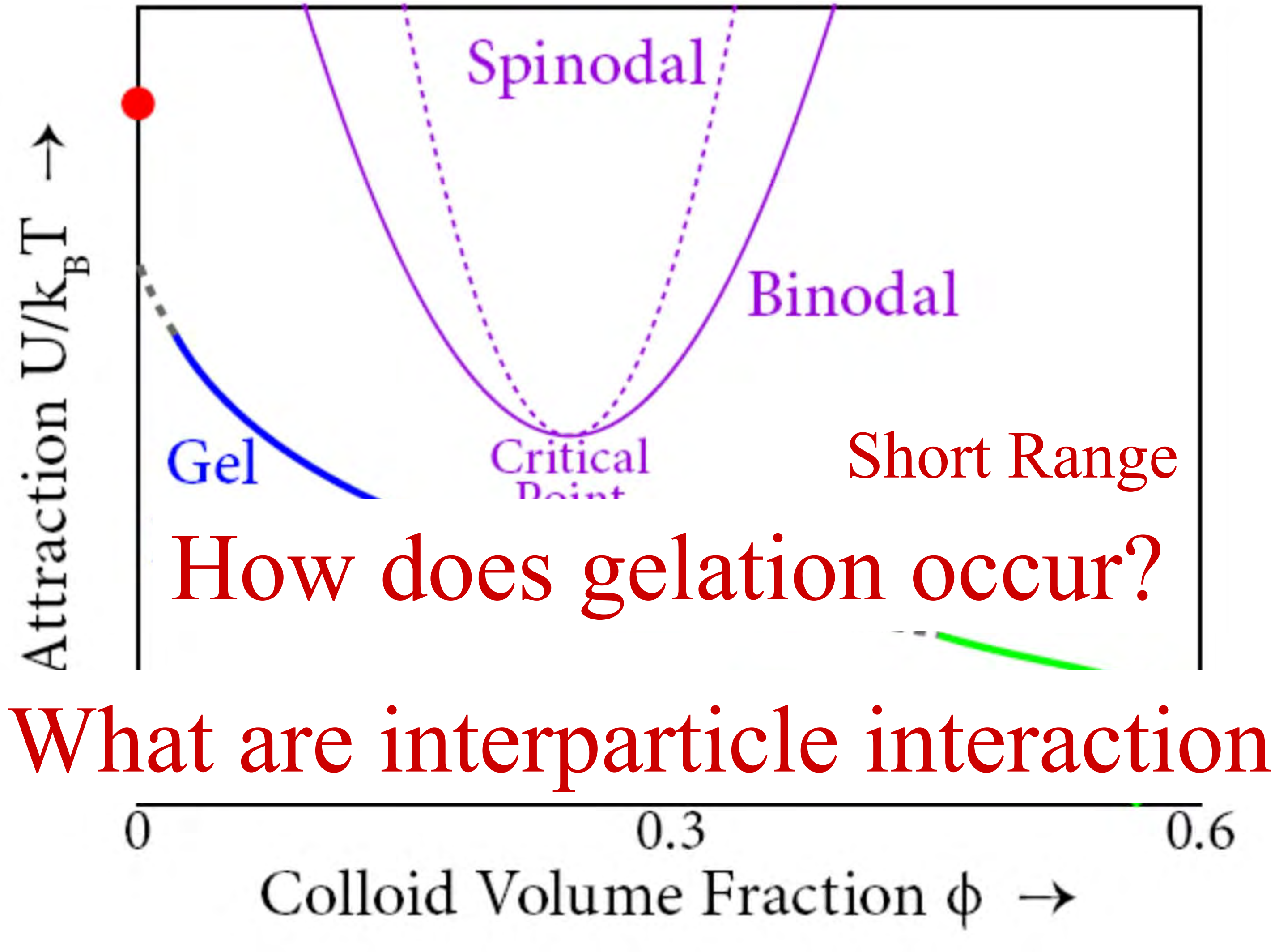


Comparison with Furukawa Theory



Long-time evolution of spinodal decomposition

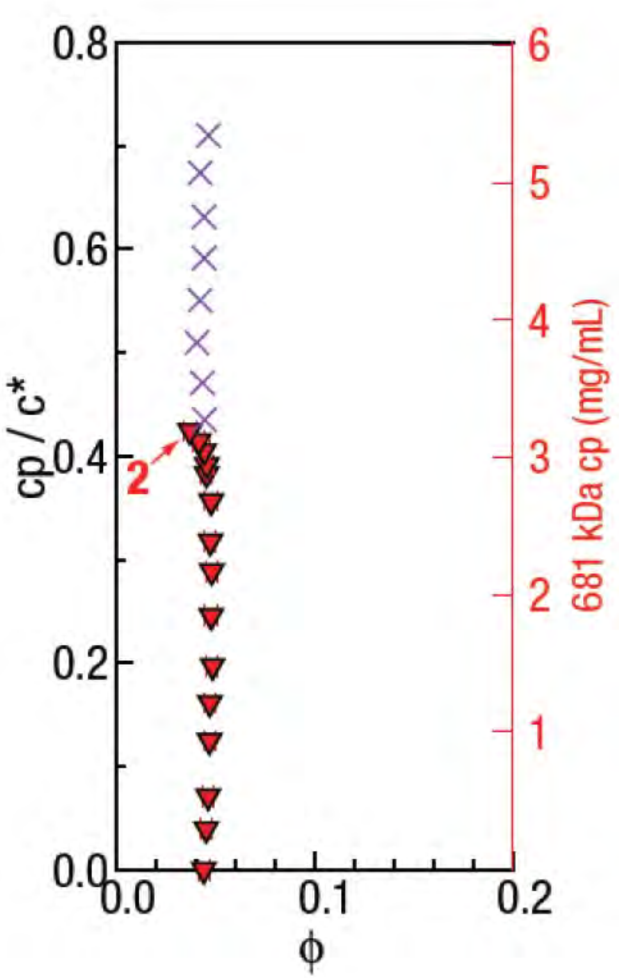
Short-range attraction

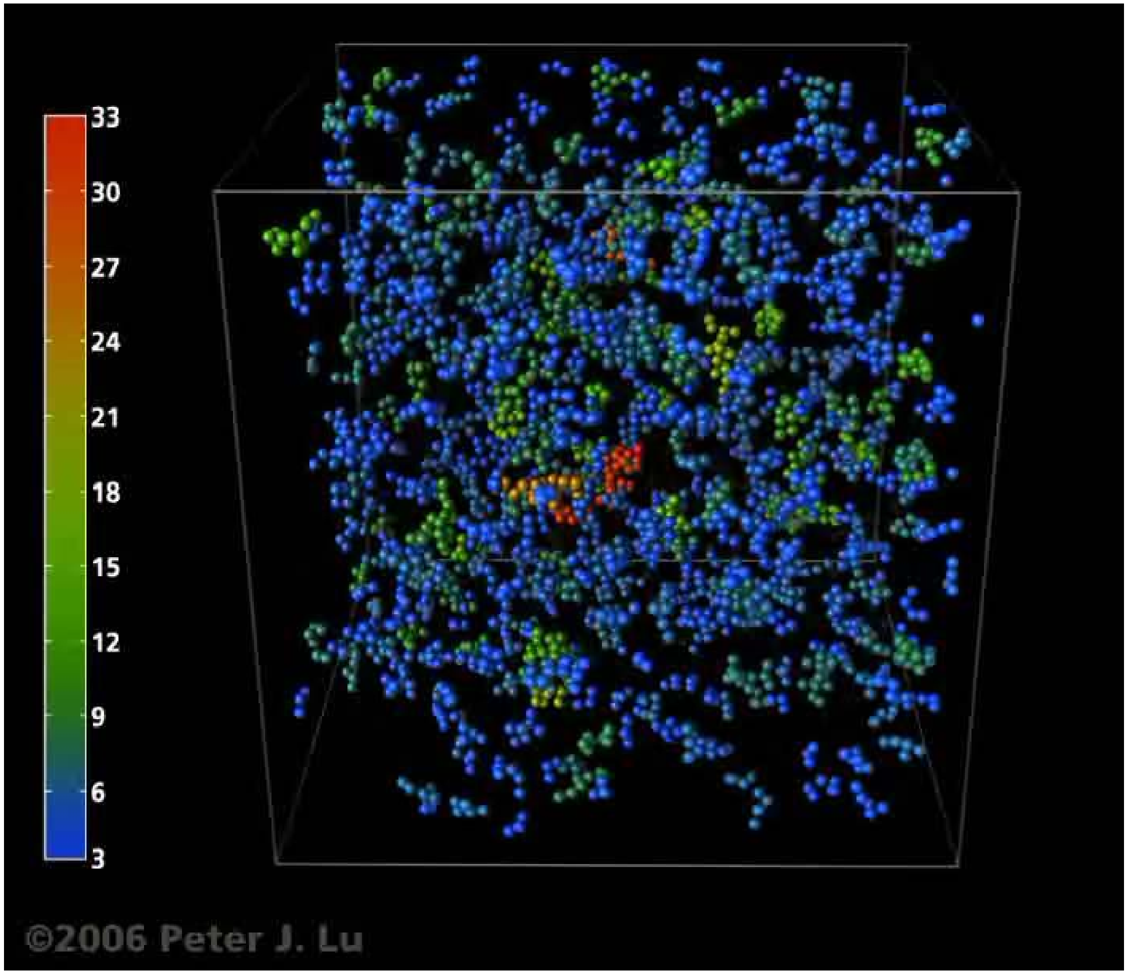


How does gelation occur?

What are interparticle interactions?

Structure at gelation → Fluid





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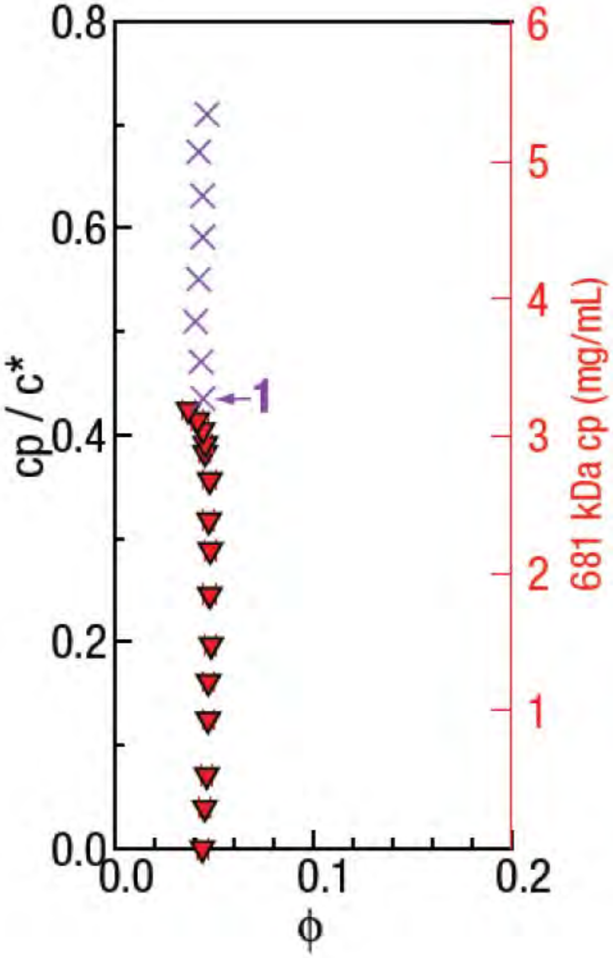
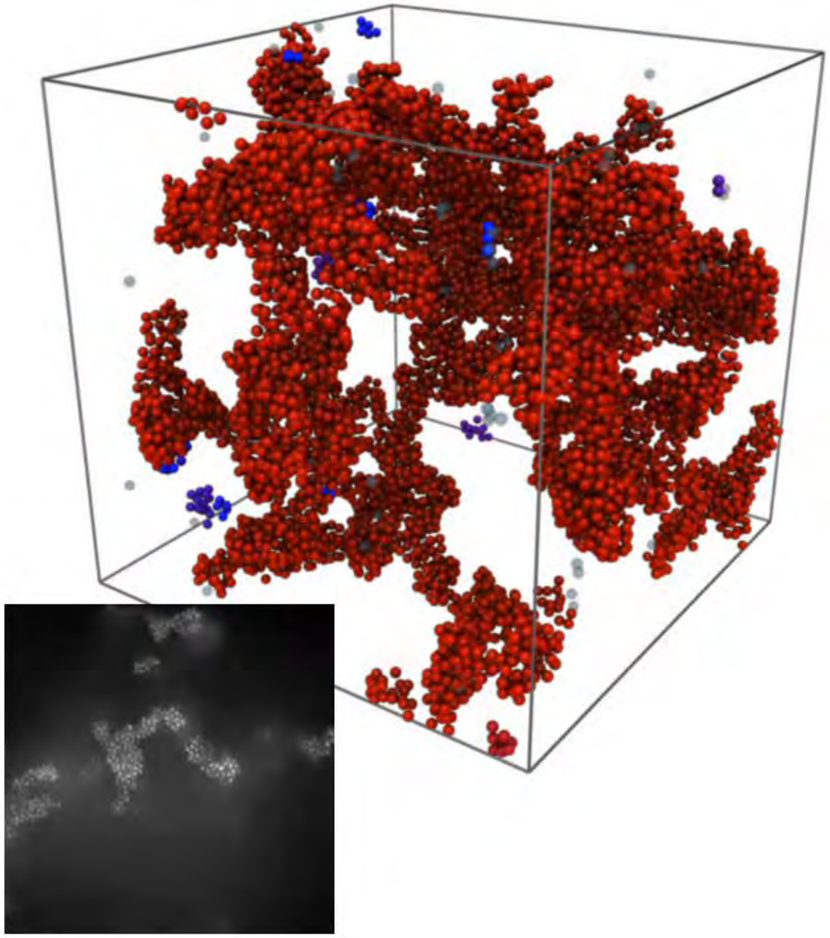
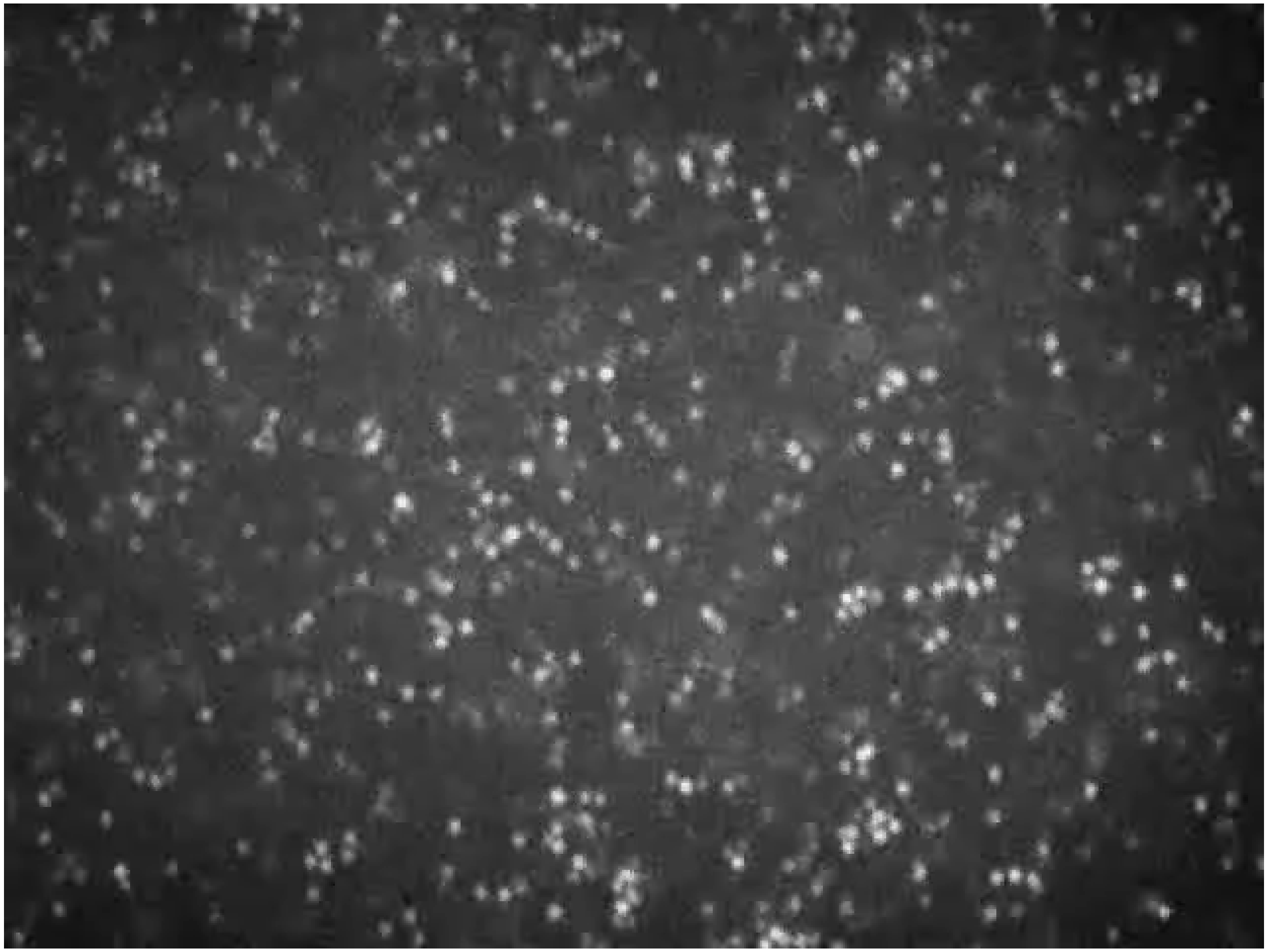
Structure at gelation → Gel

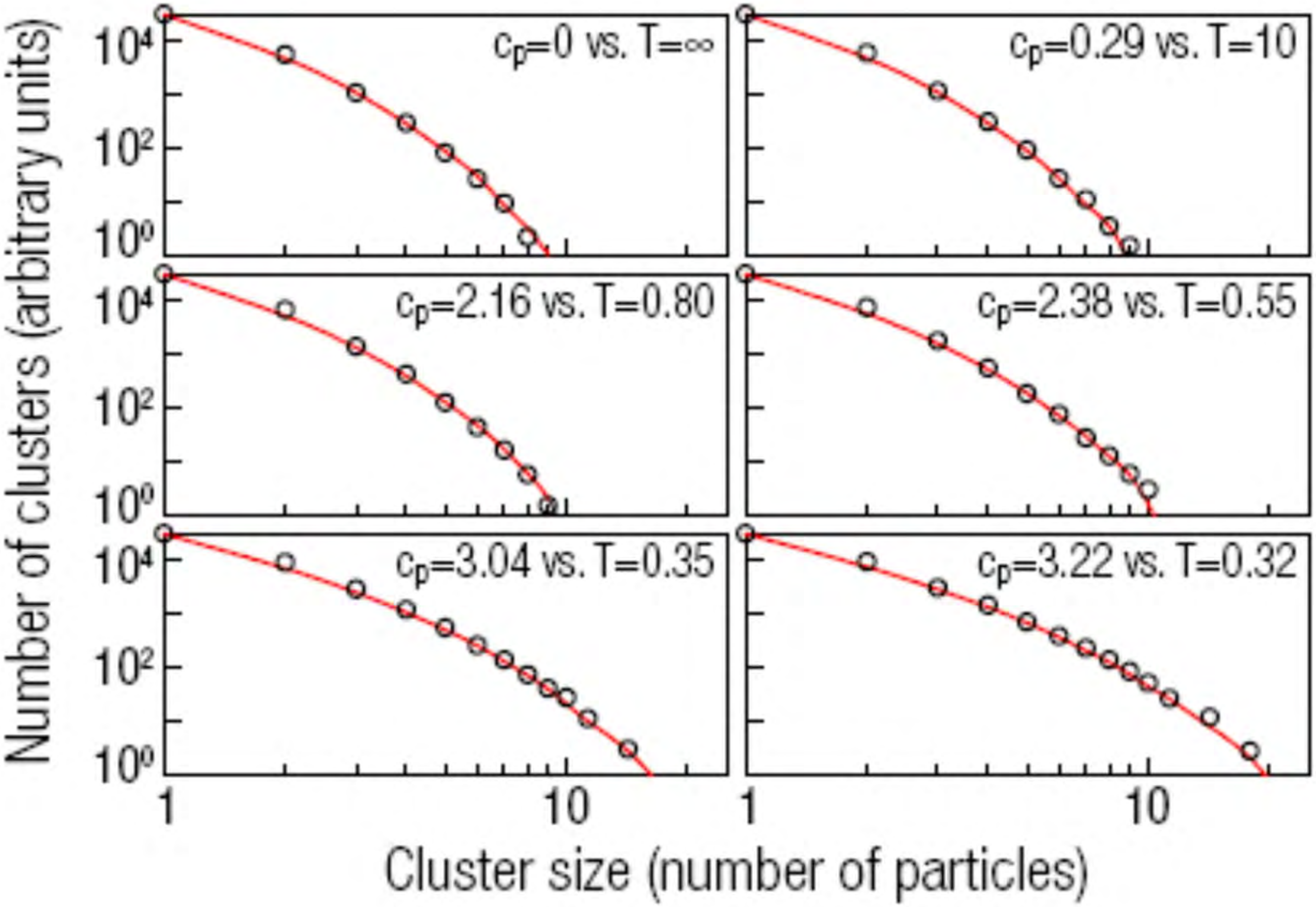




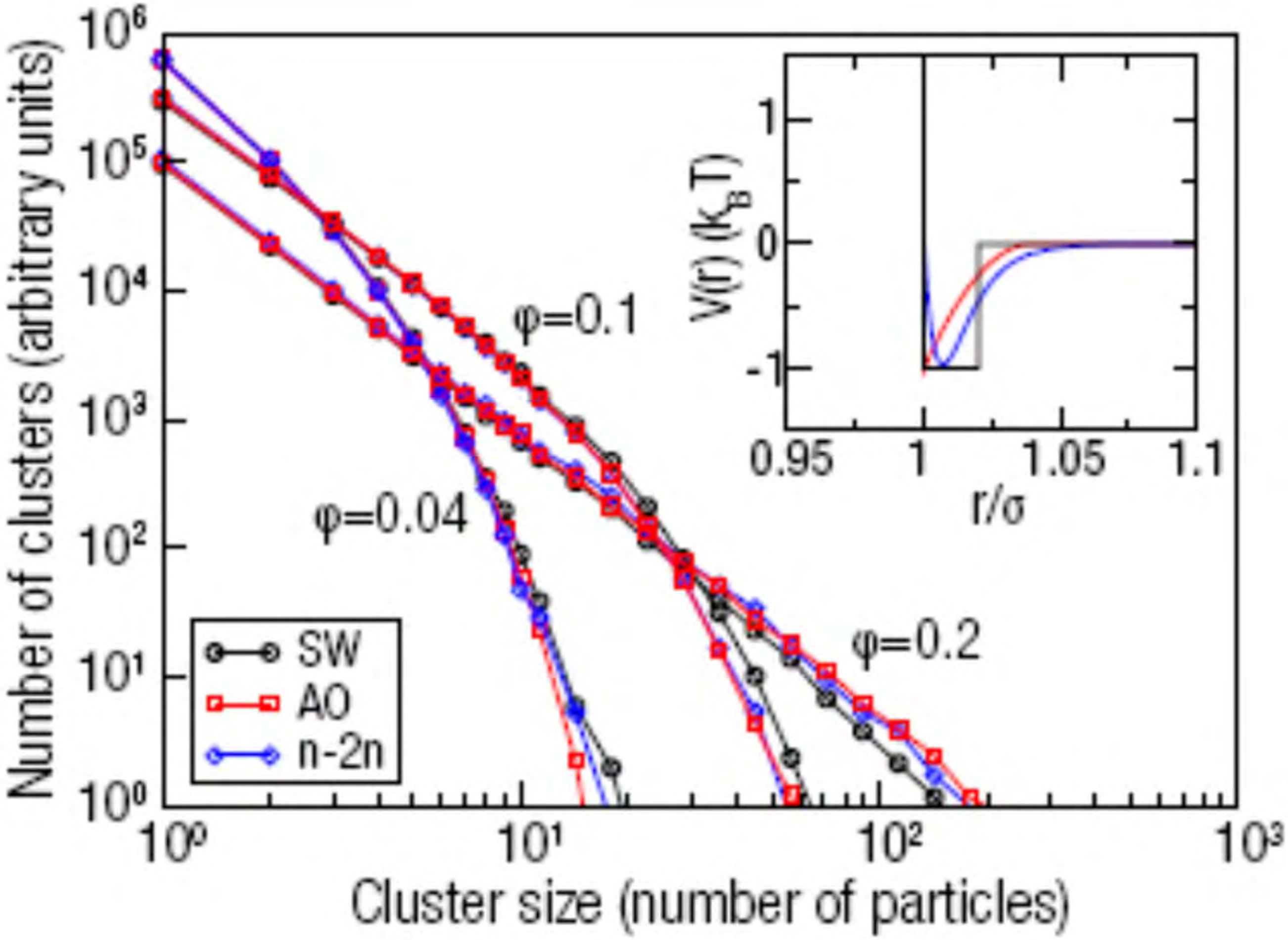
Weak attractive interaction



Cluster distribution: Determine interaction

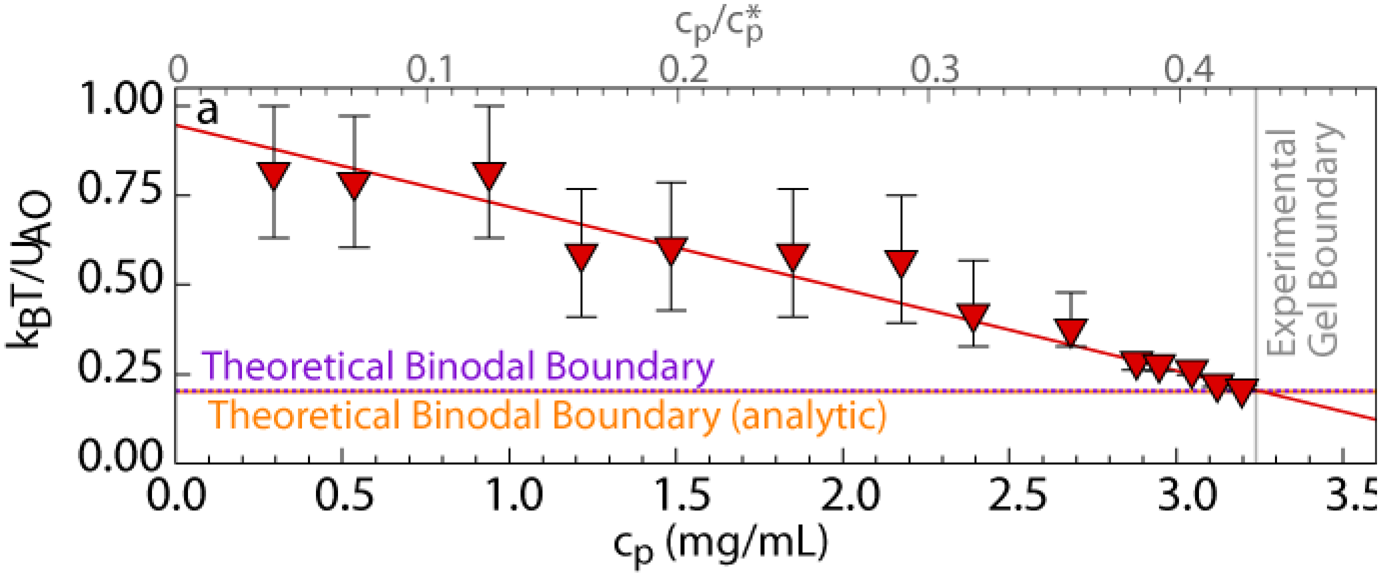


Cluster distribution: Independent of potential

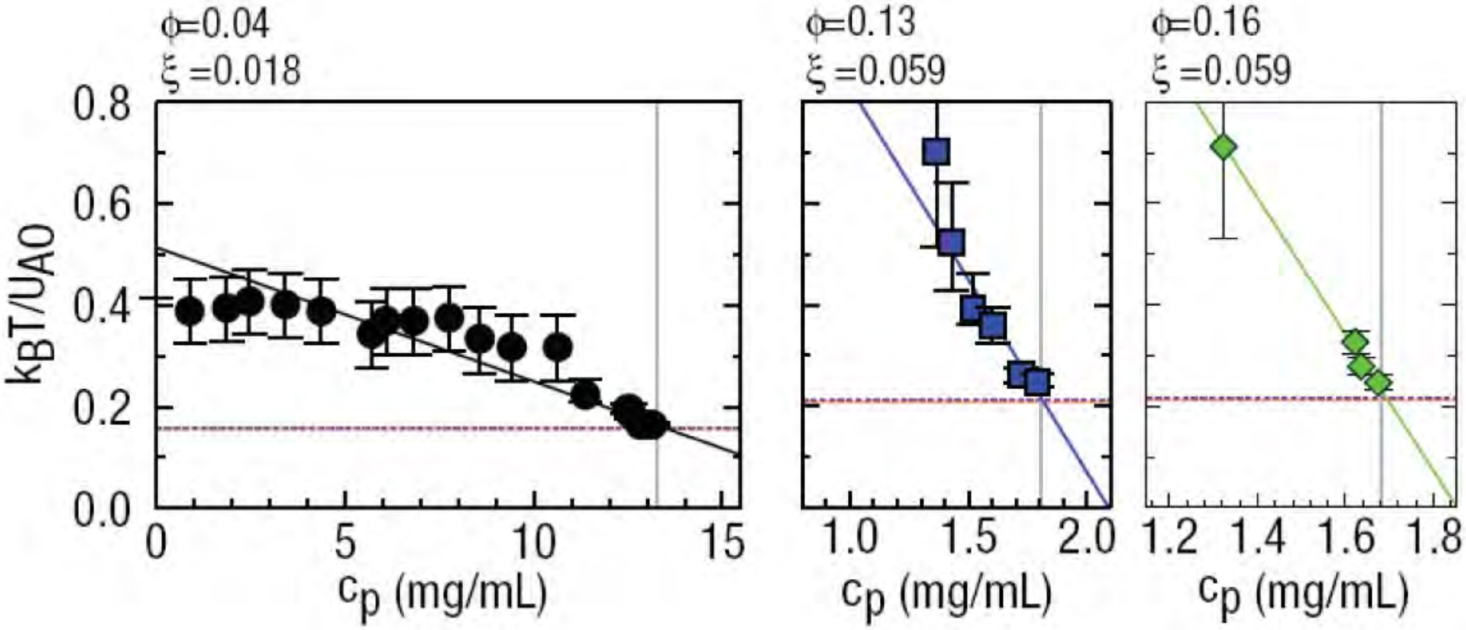


M. G. Noro and D. Frenkel, J. Chem. Phys. **113**, 2941 (2000).

Interaction energy at gelation



Interaction energy at gelation



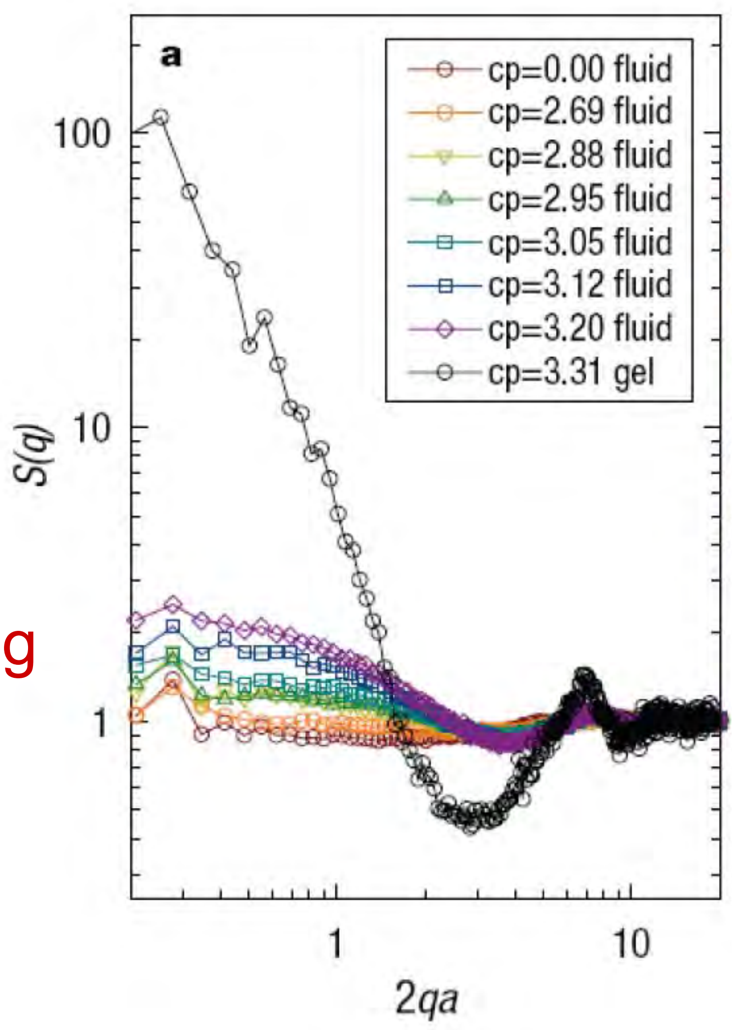
Same behavior for all ϕ, all ξ

Gelation is proceeded by spinodal decomposition

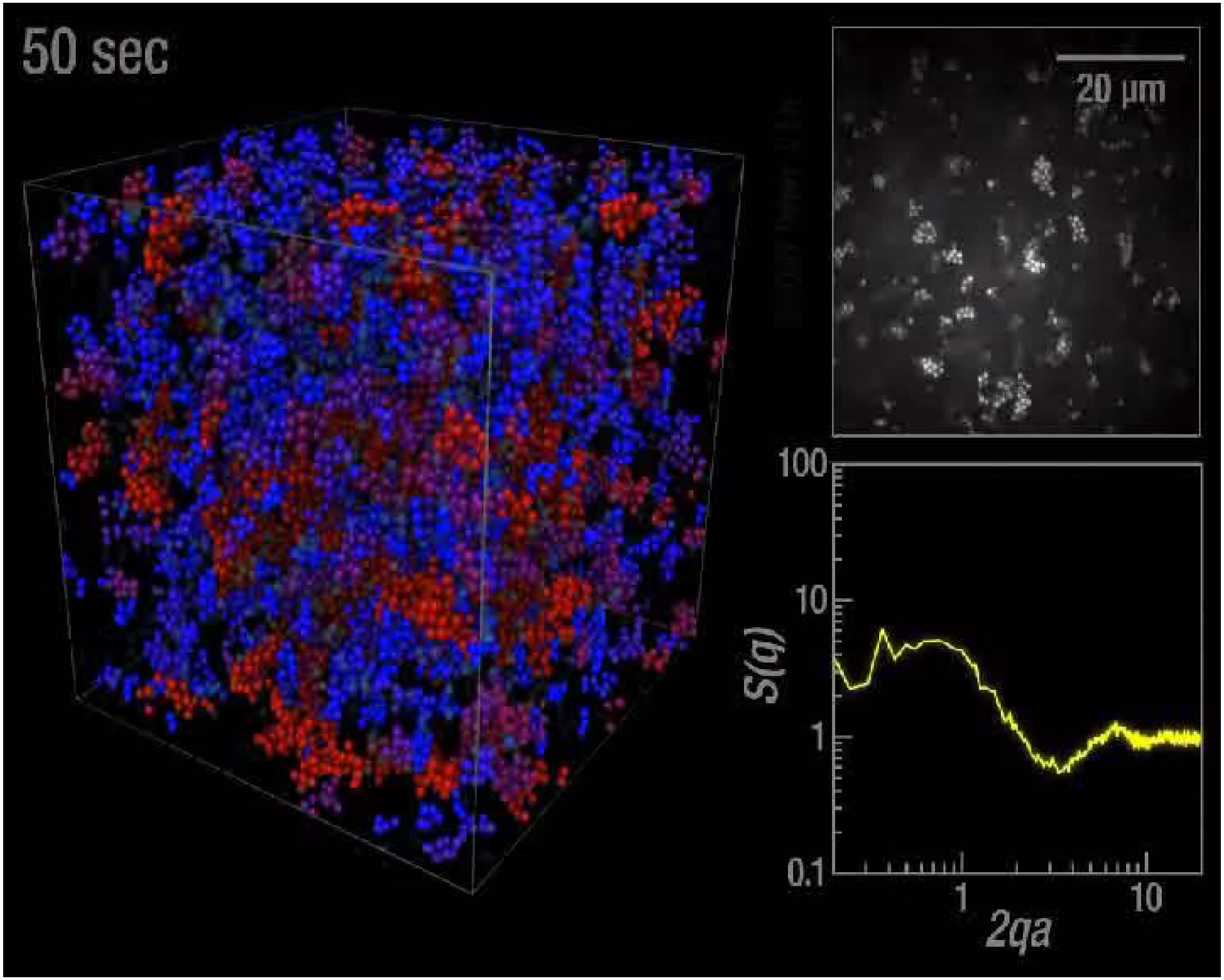
Implications?

$S(q)$ → spinodal decomposition

Increasing *U*

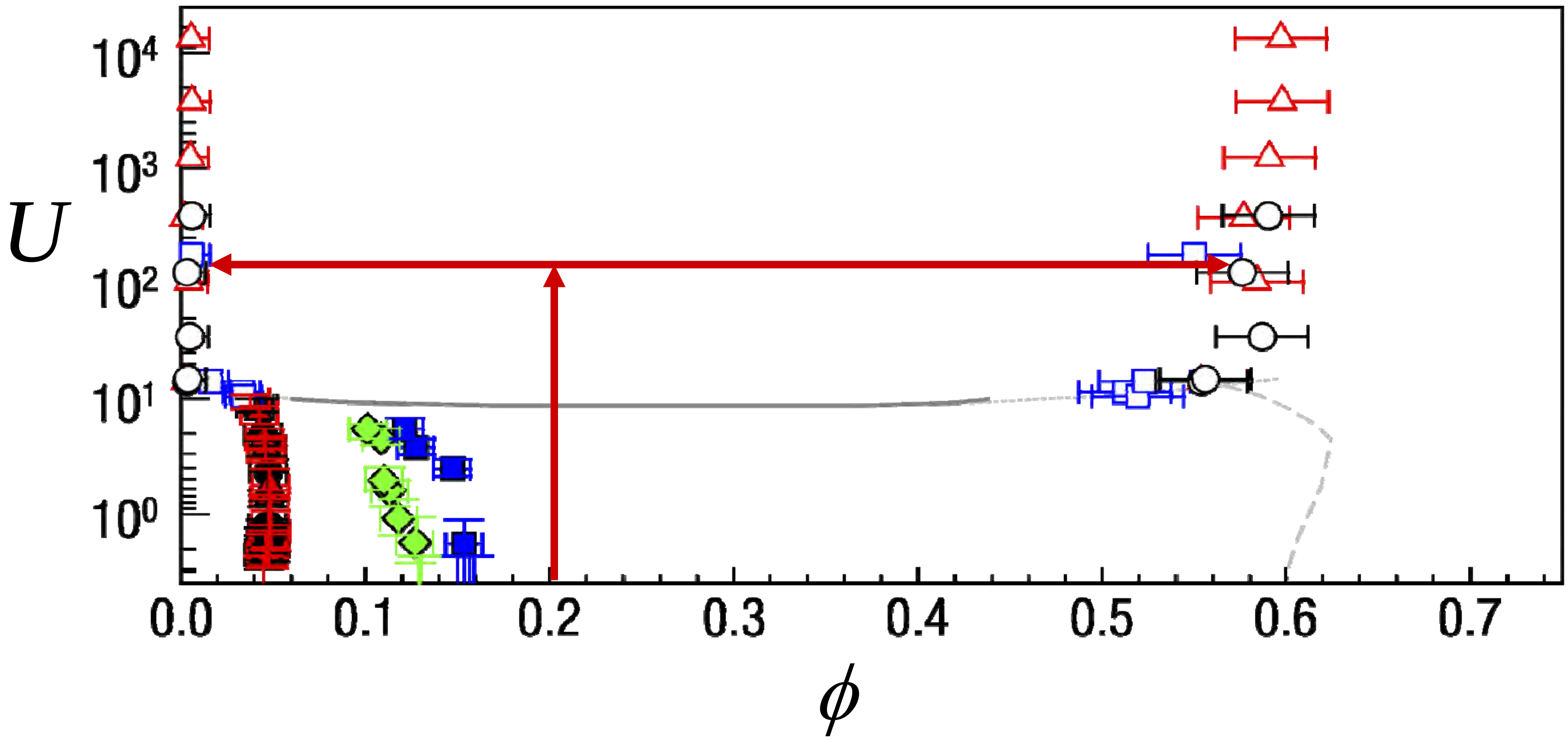


Gelation – spinodal decomposition

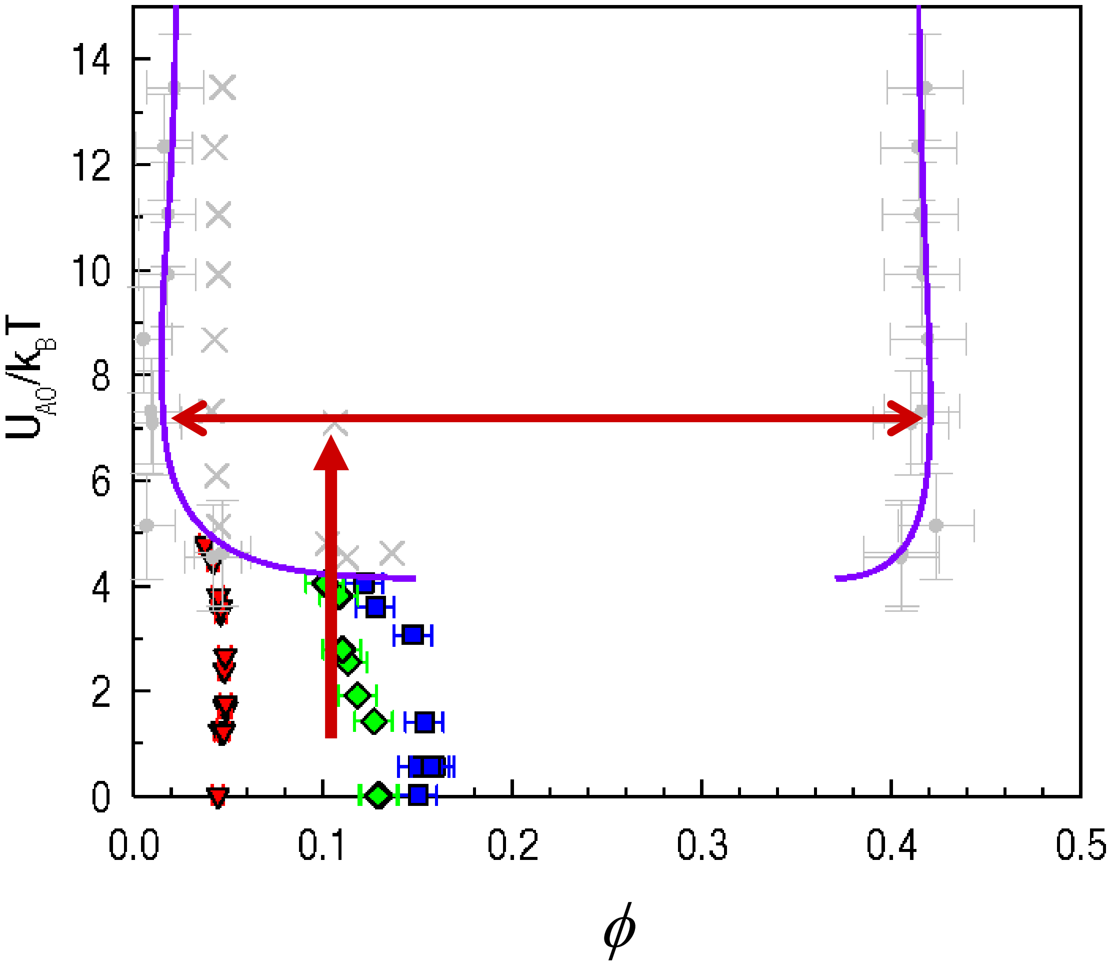


Schematic Phase Behavior for Colloidal Gels

Attractive glass



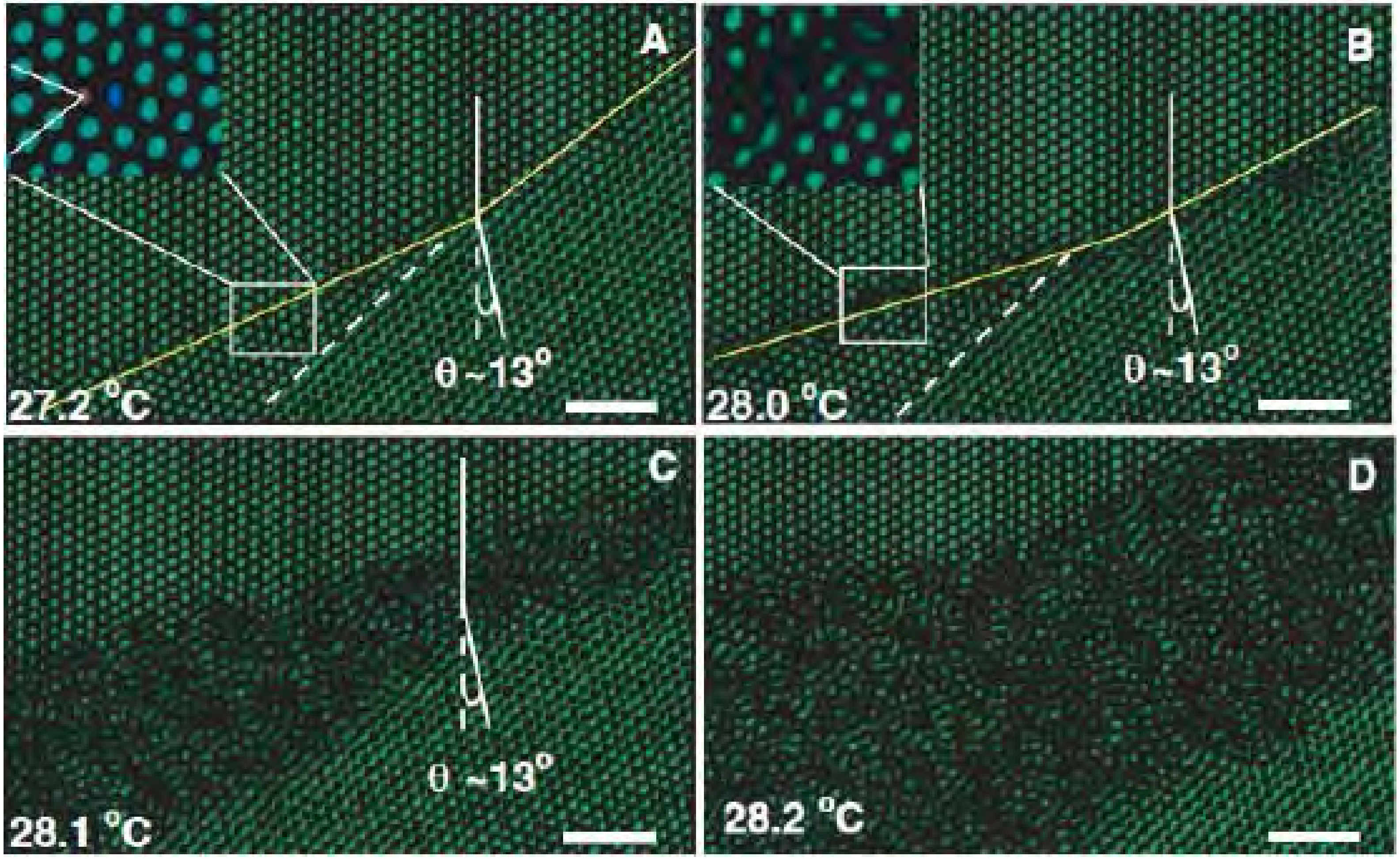
Gelation phase diagram



Dynamic arrest of phase separating system

How do crystals melt?

Colloidal crystals melt at grain boundaries



Yodh, Science

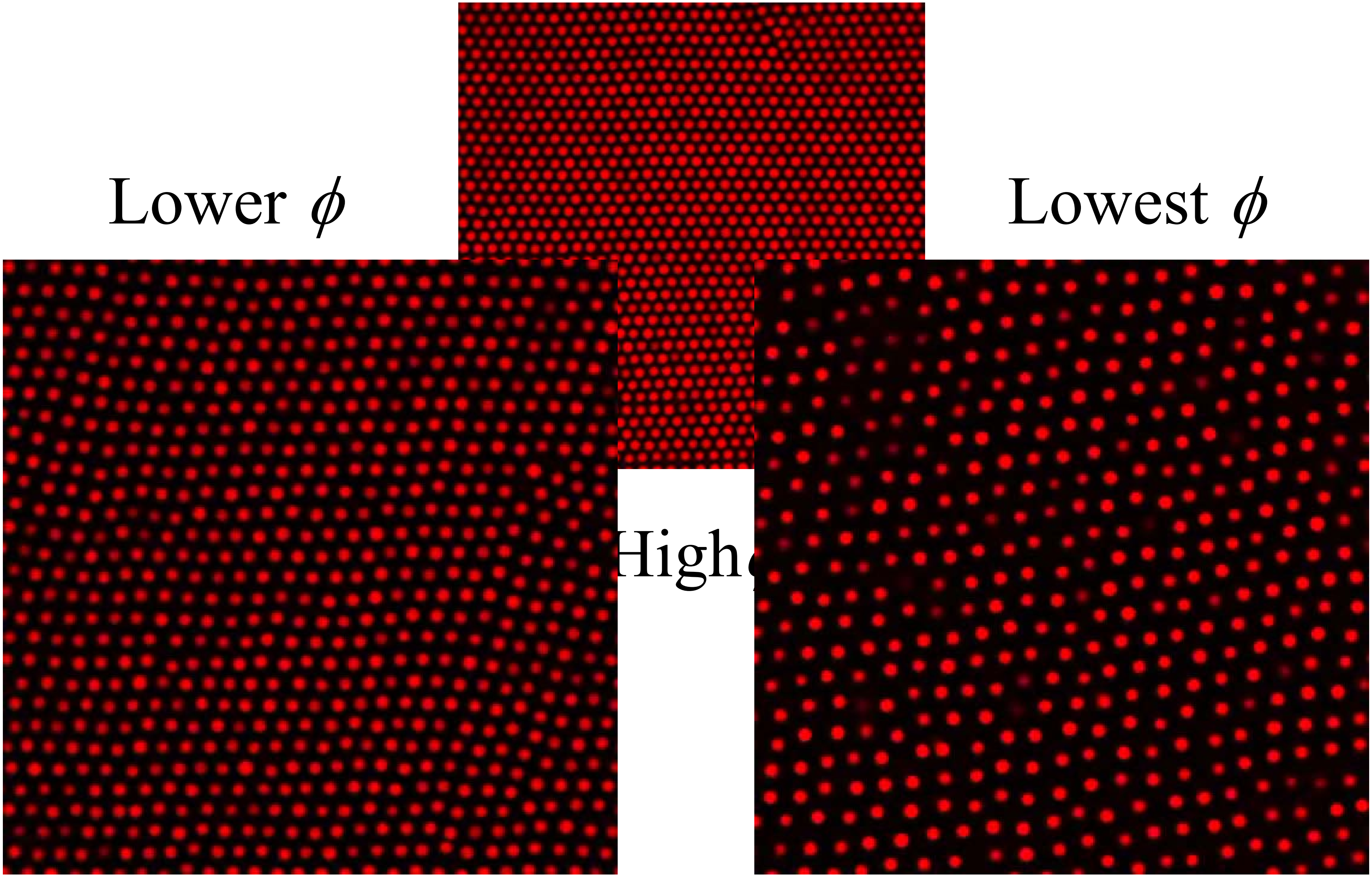
What if there are no interfaces?

Born melting:

- Elastic catastophe
- Elastic modulus goes to zero, and crystal melts

But how does this actually occur??

Volume fraction controls melting

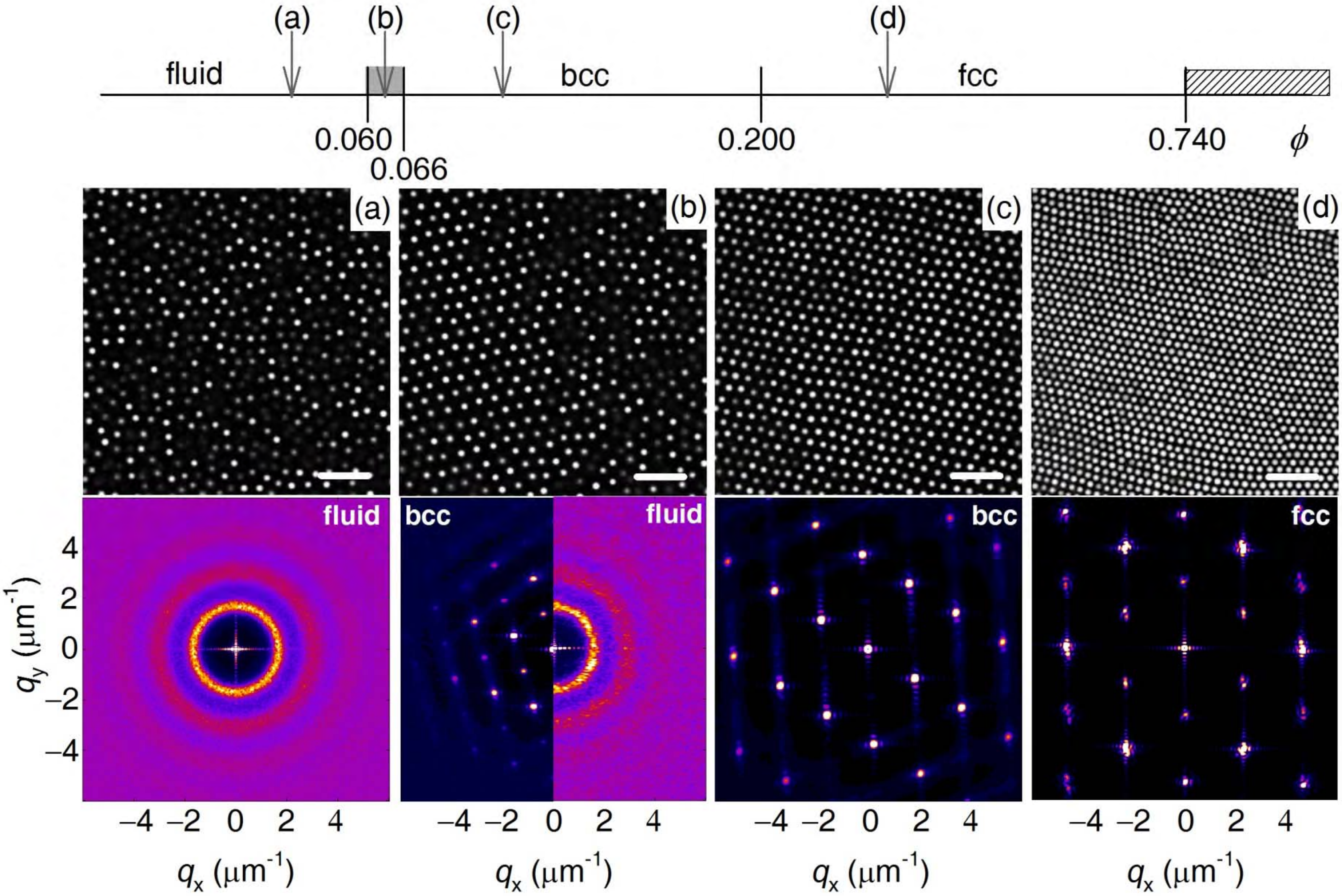


Lower ϕ

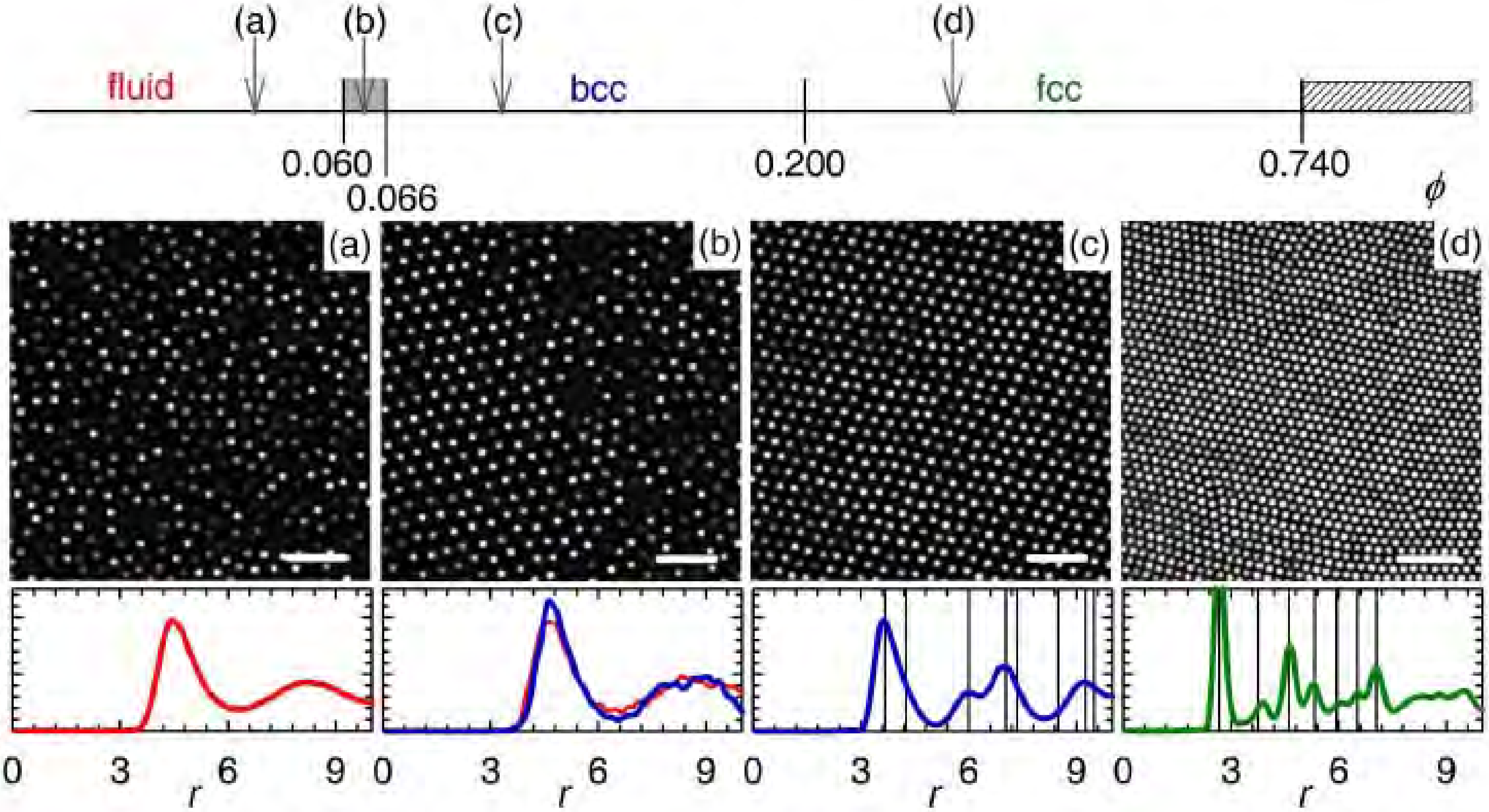
High

Lowest ϕ

Phase diagram of Wigner Crystals

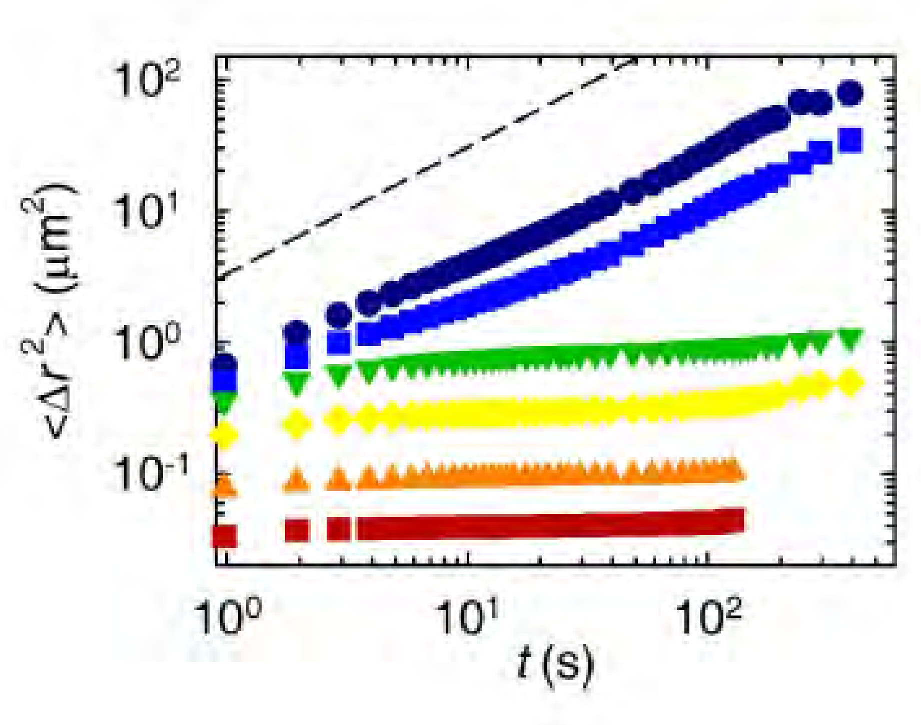


Phase diagram Wigner colloids

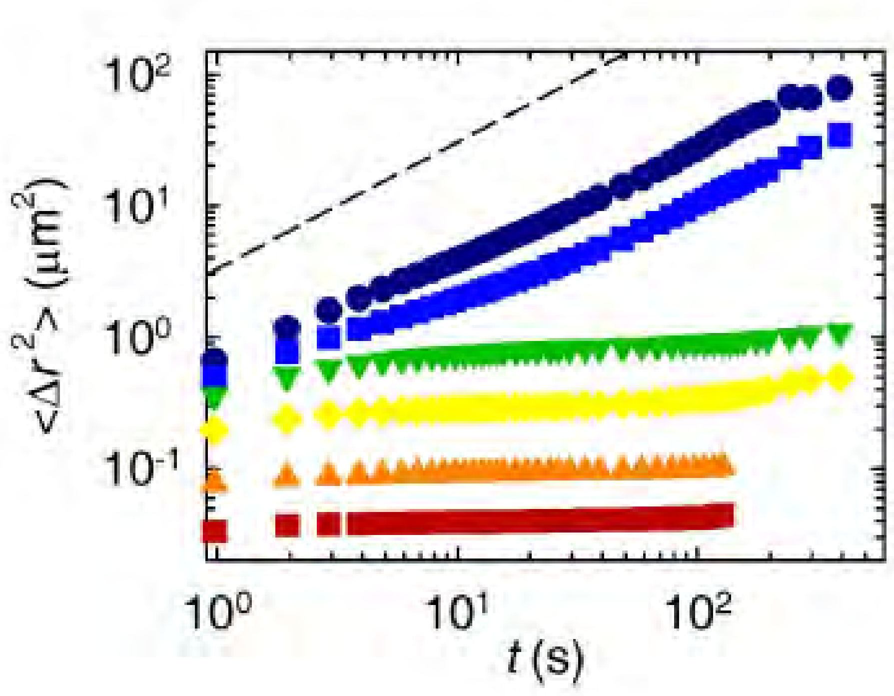


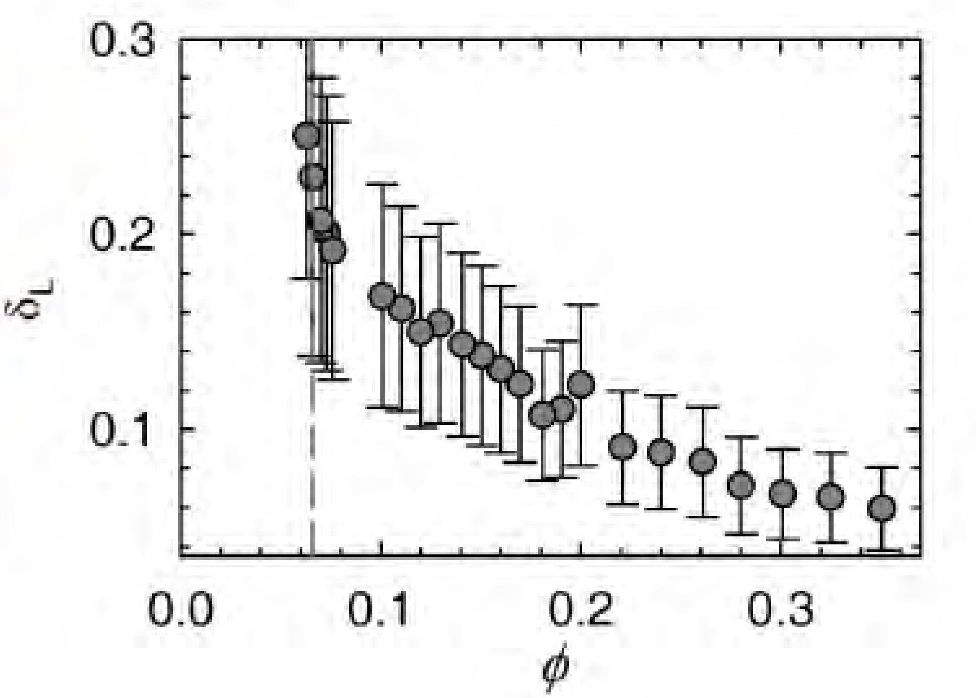
2.1 um charged PMMA suspended in decalin/tce/10 mM AOT (charging agent)
Good density match ($\Delta\rho < 0.01$ kg/m^3)

Mean squared displacement



Mean squared displacement

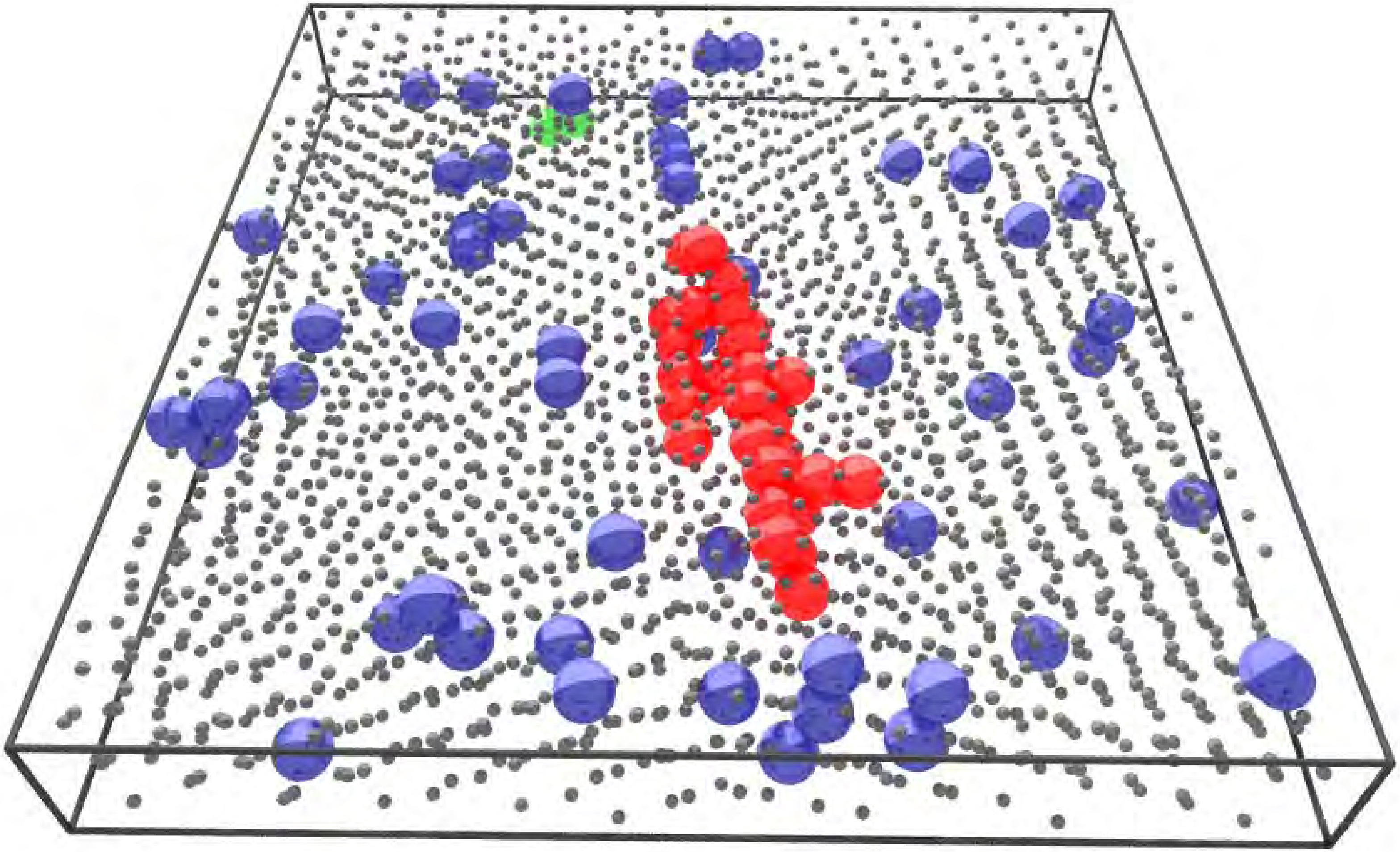




Lindemann parameter
Fraction of lattice parameter

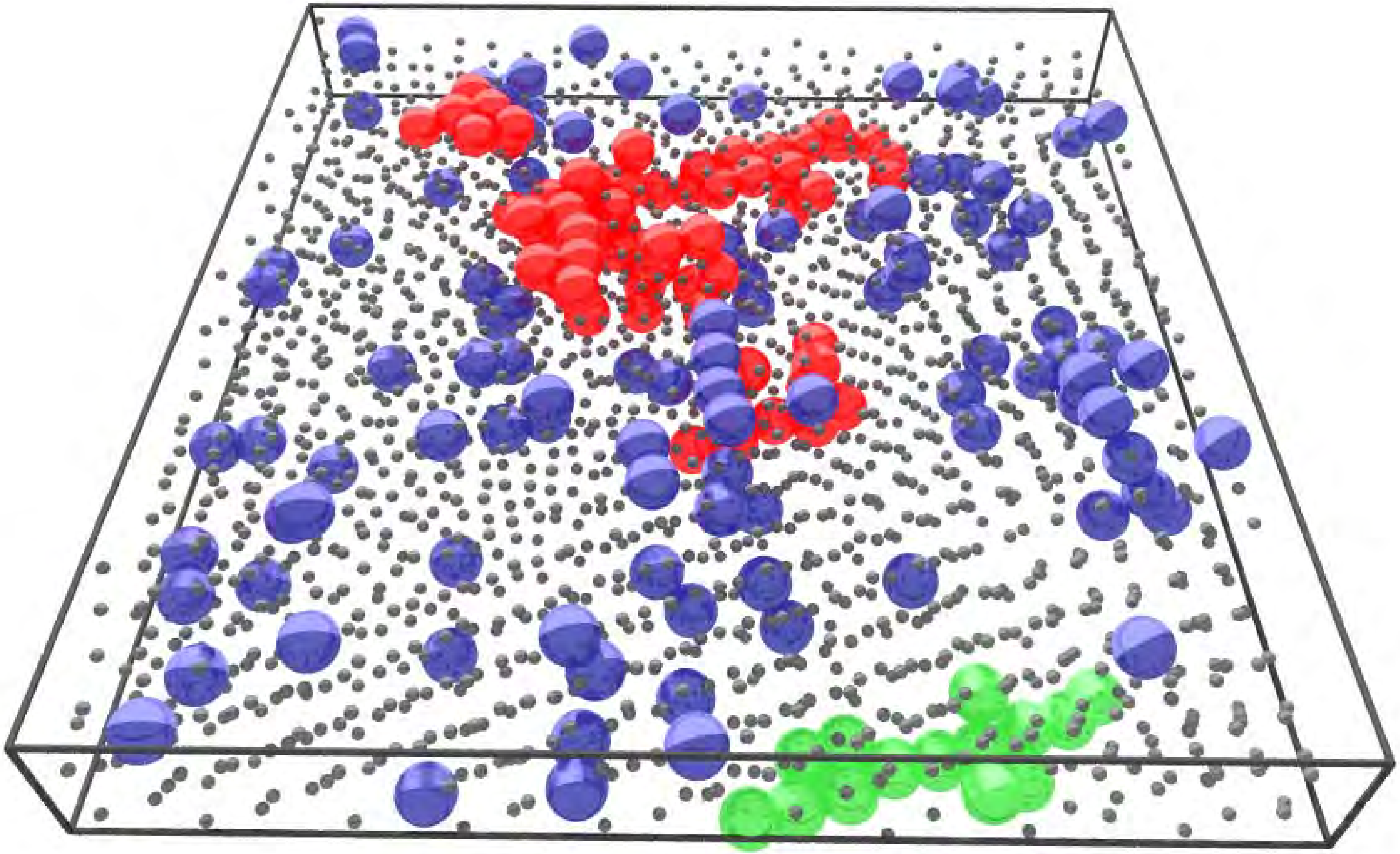
‘Hot’ particles are highly spatially correlated

$\phi = 0.120$



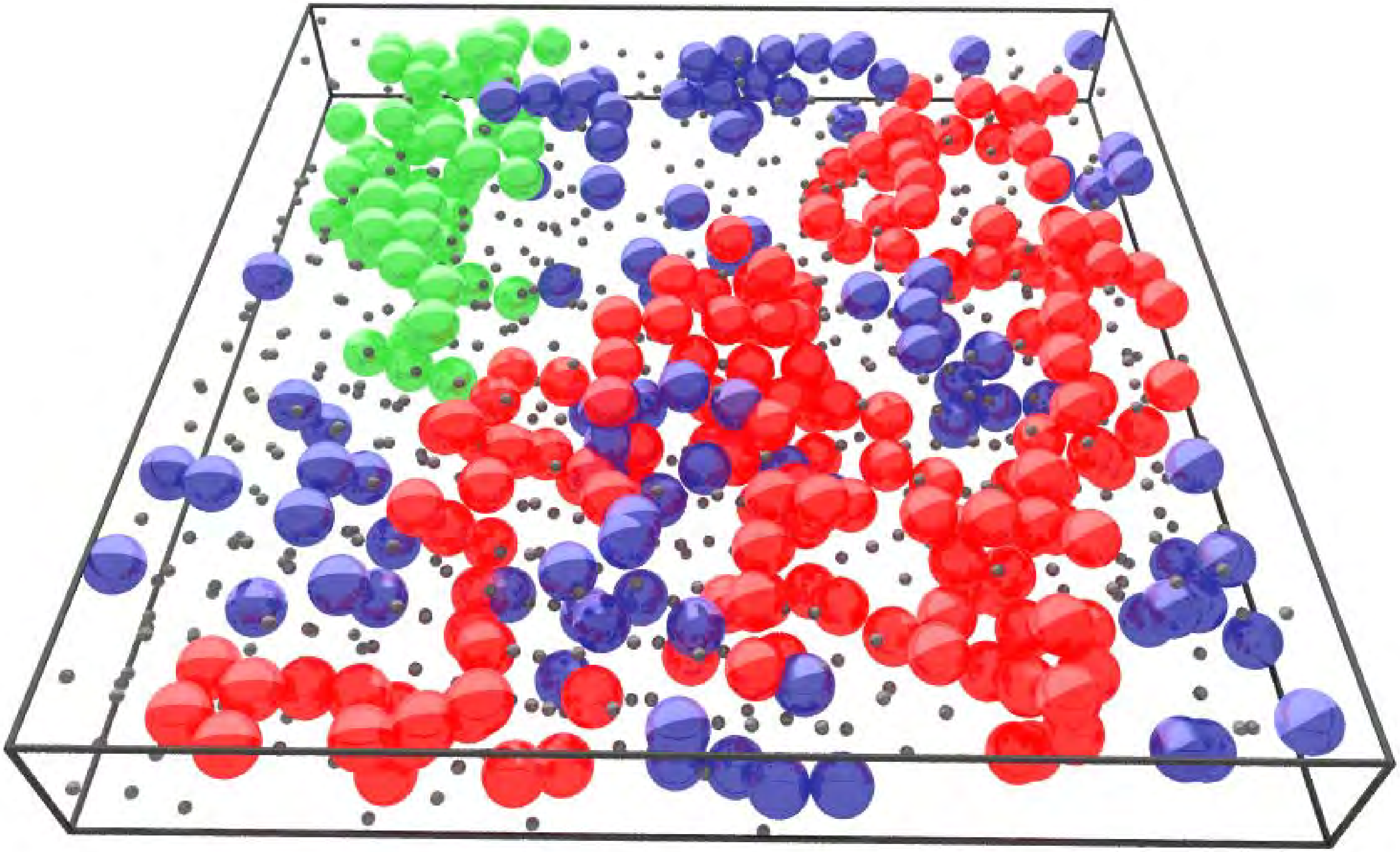
‘Hot’ particles are highly spatially correlated

$\phi = 0.101$



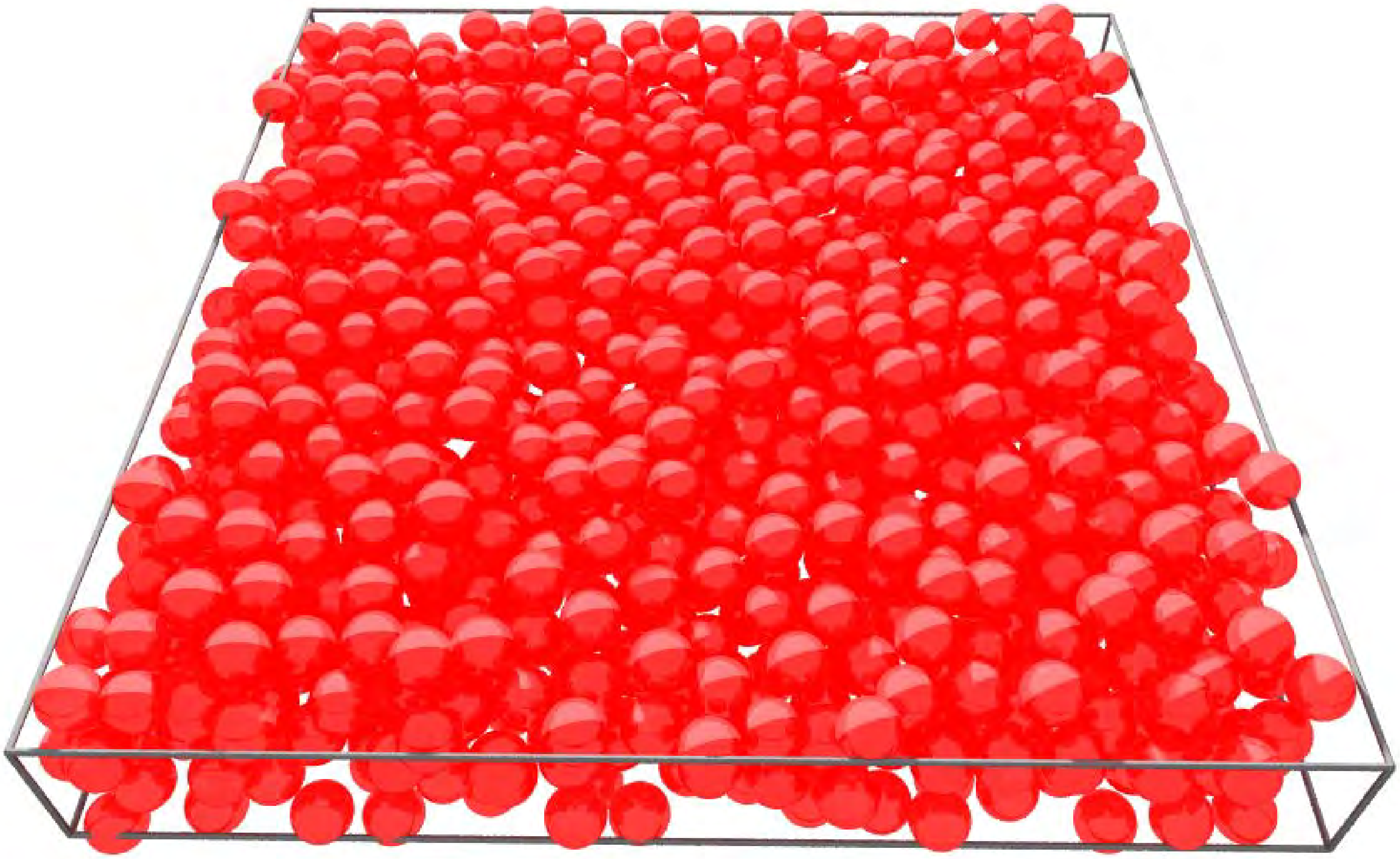
‘Hot’ particles are highly spatially correlated

$\phi = 0.066$



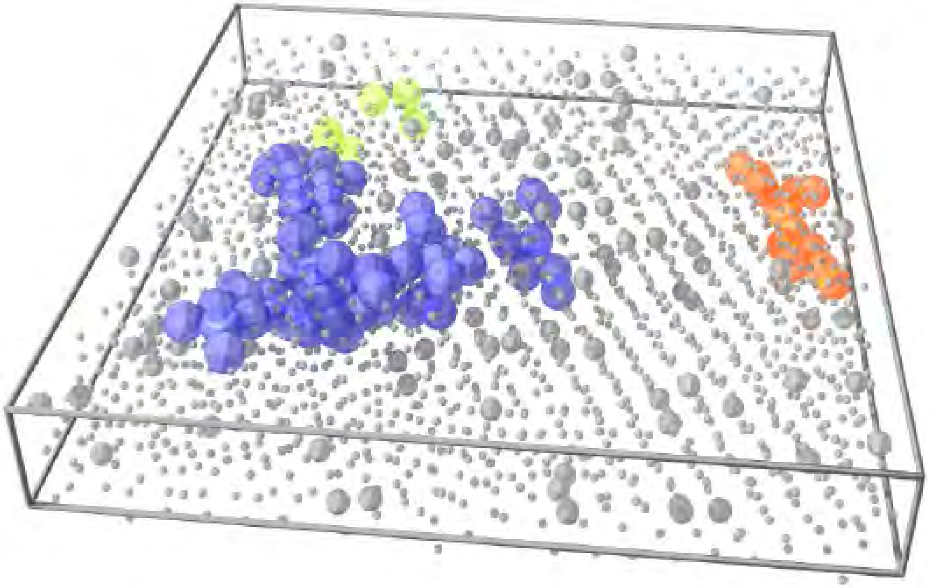
‘Hot’ particles are highly spatially correlated

$\phi = 0.050$

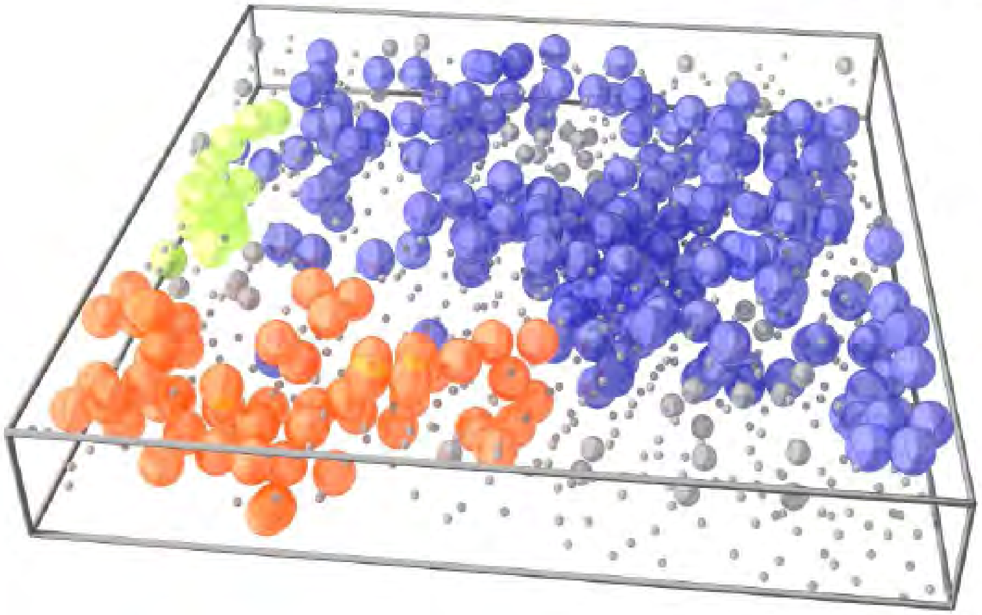


Melted

‘Hot’ particles are strongly correlated in space

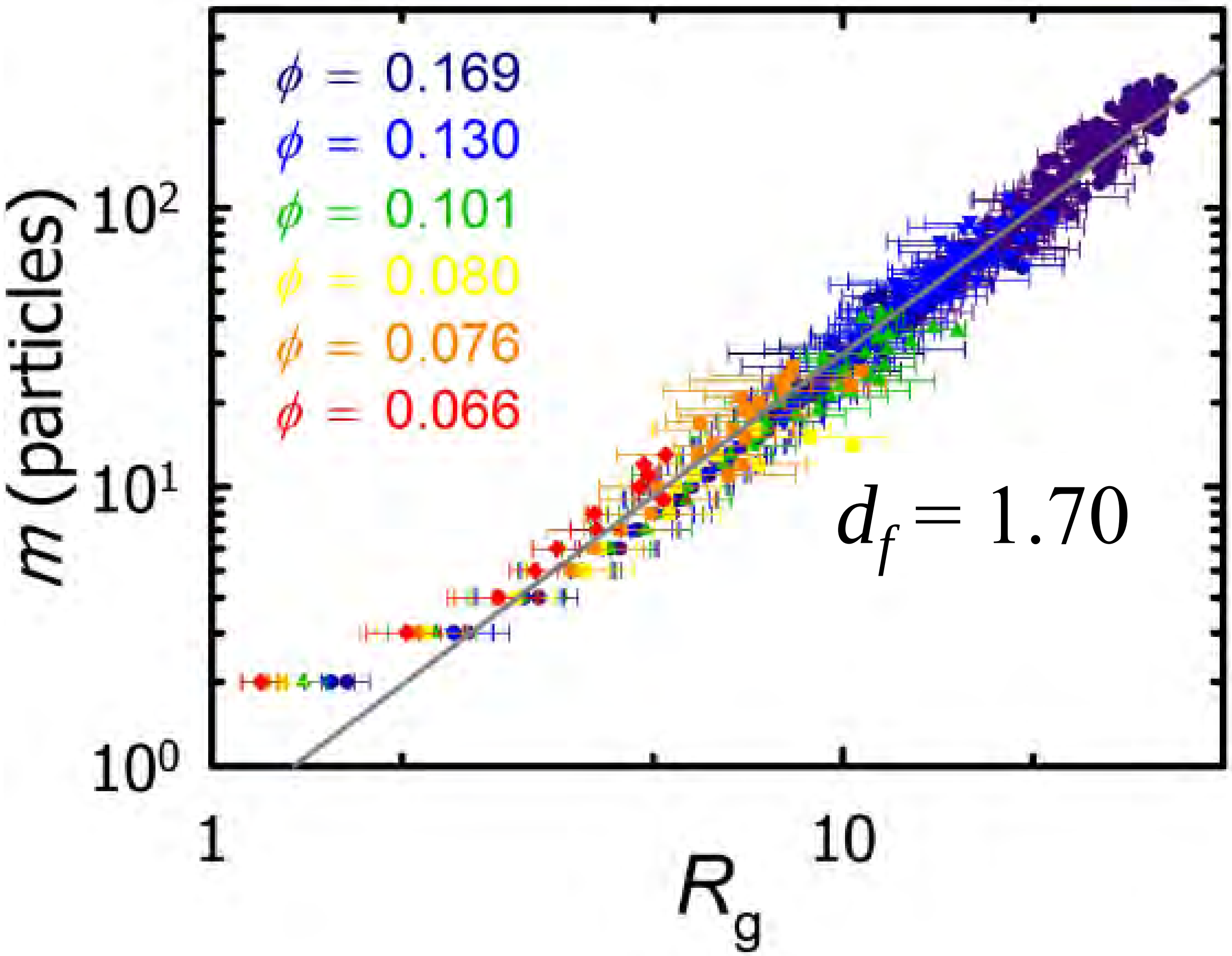


$\phi = 0.101$
$\phi - \phi_m = 0.037$

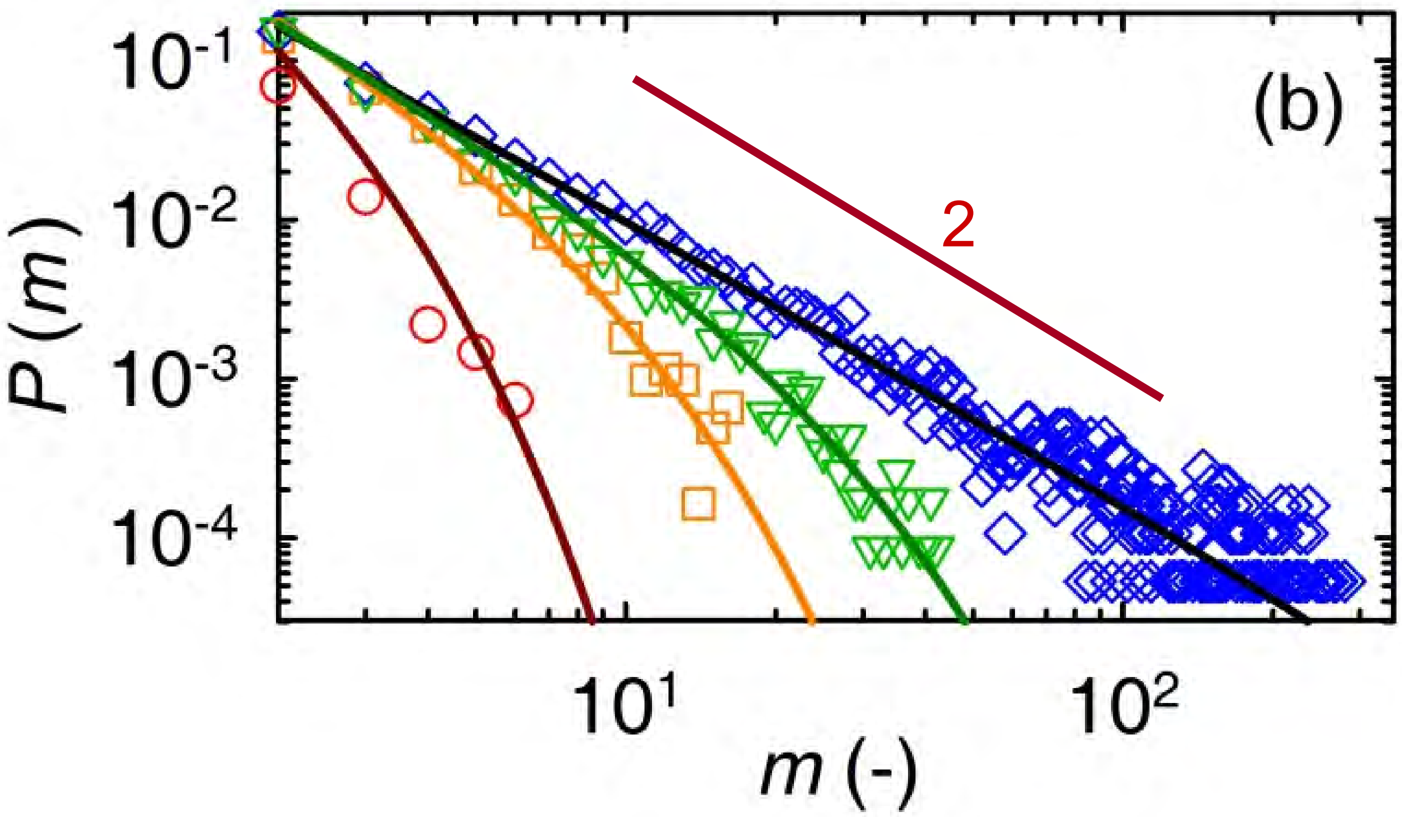


$\phi = 0.066$
$\phi - \phi_m = 0.002$

‘Hot’ clusters are fractal

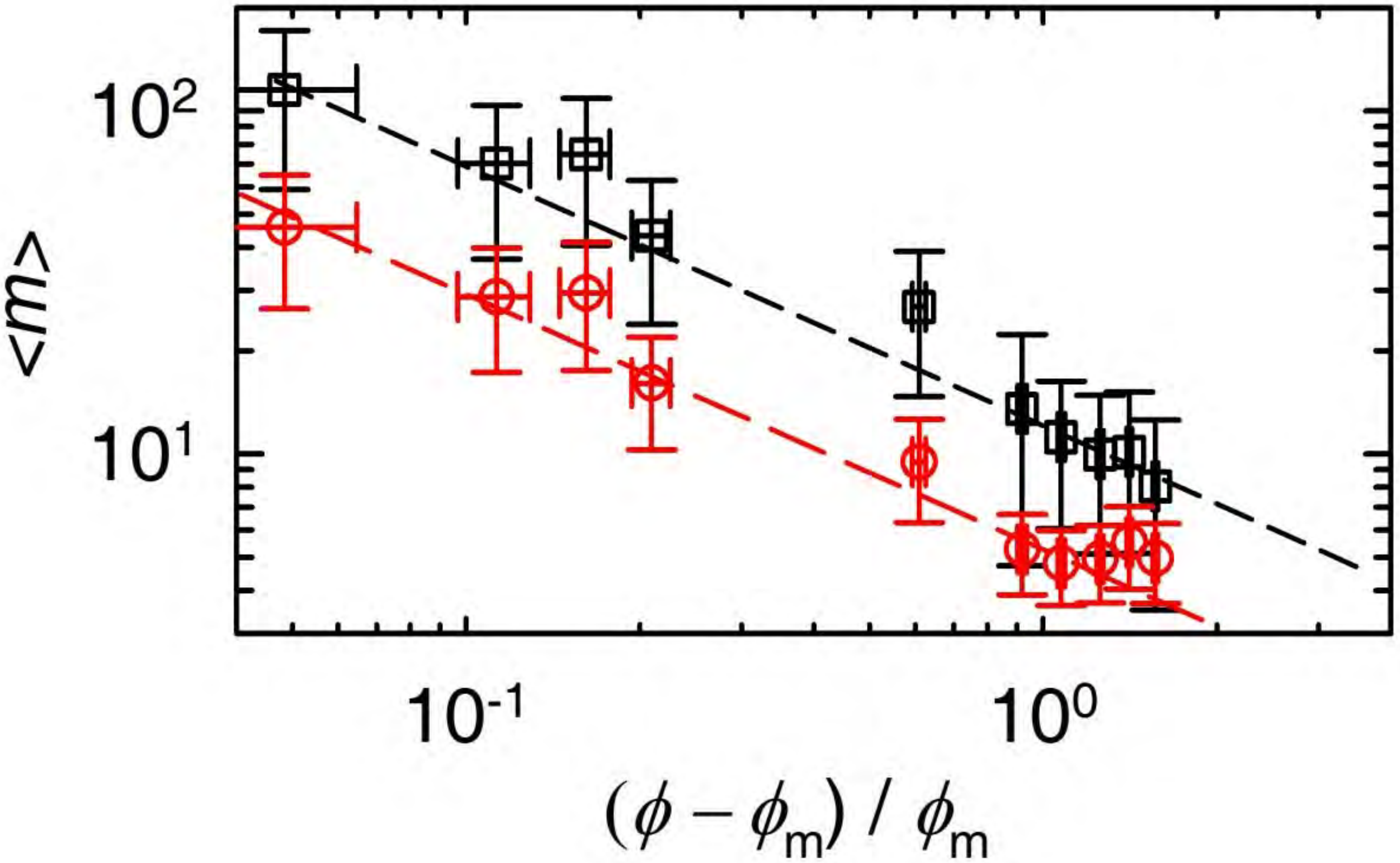


Cluster-mass distribution

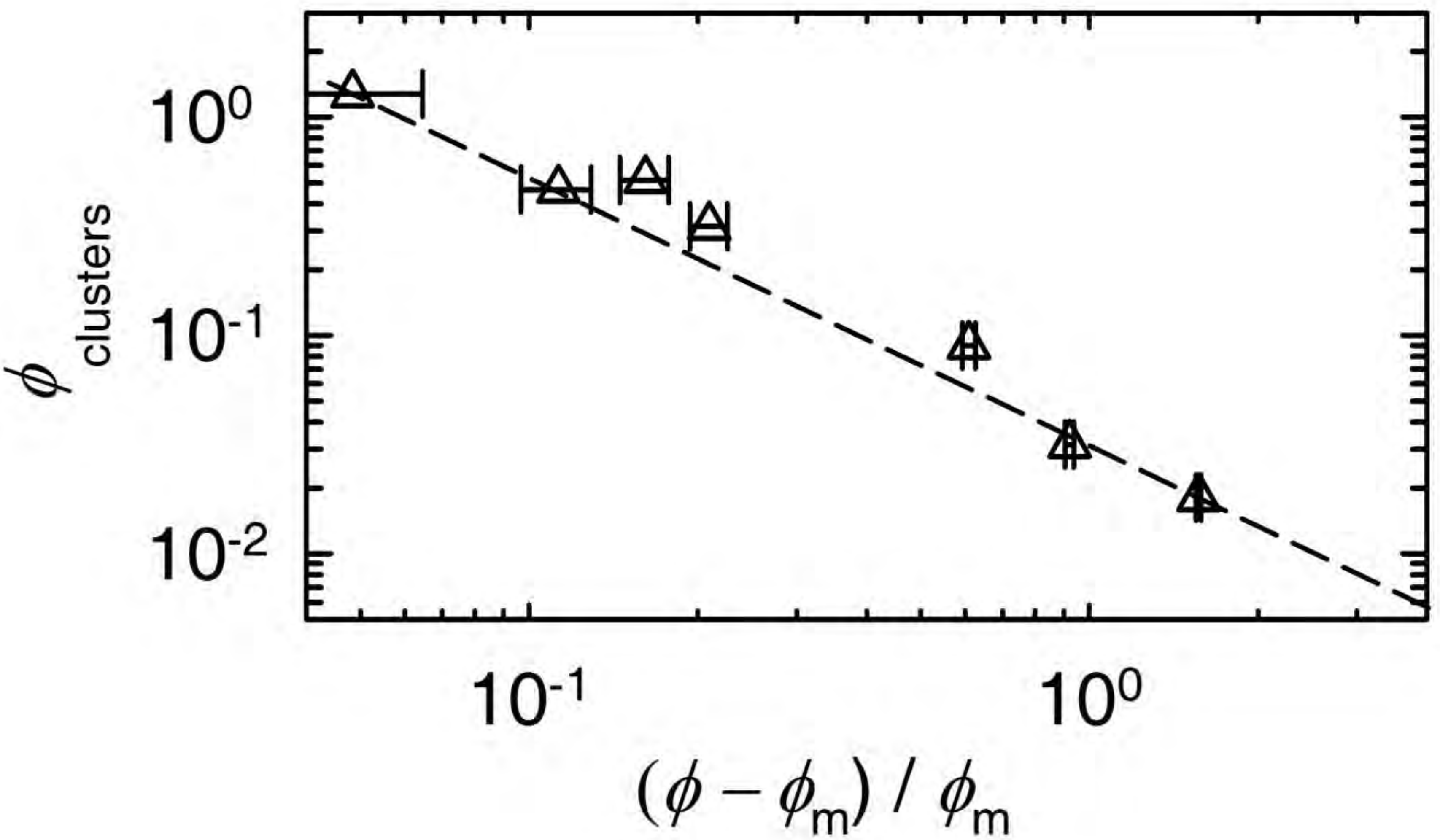


Power-law with exponential cut off

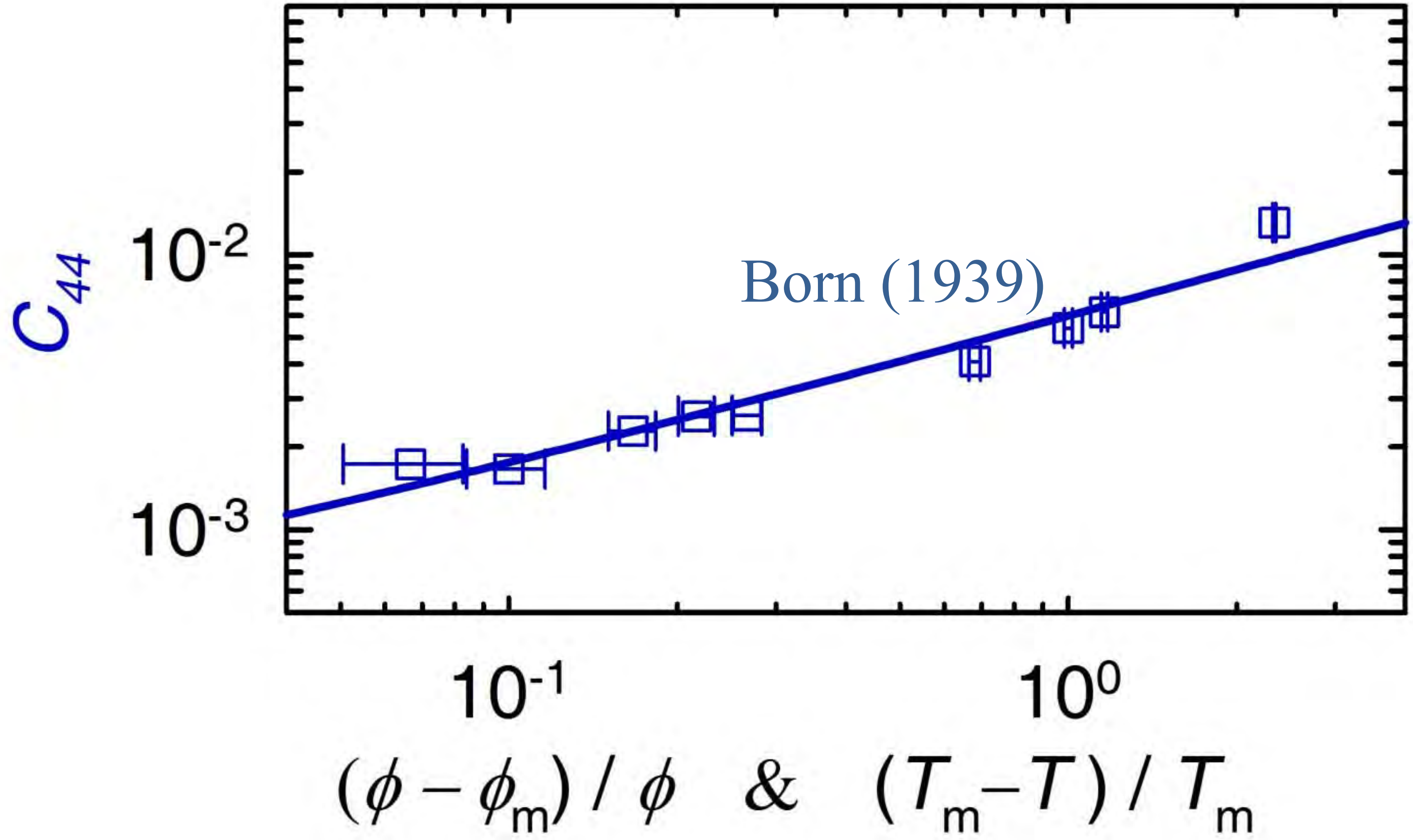
Scaling behavior of cluster size



Scaling behavior of cluster volume fraction



Scaling behavior of elasticity

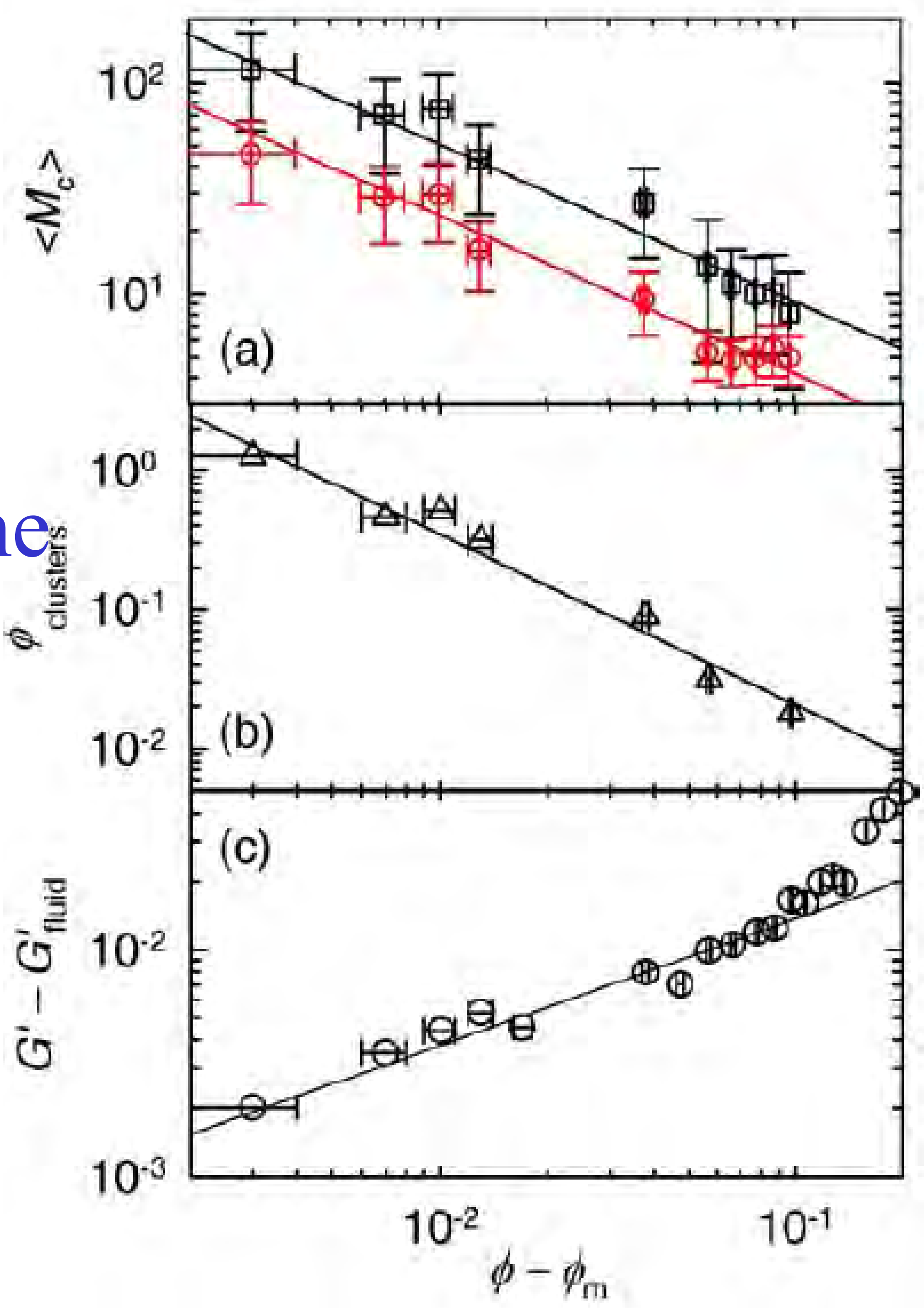


Scaling behavior

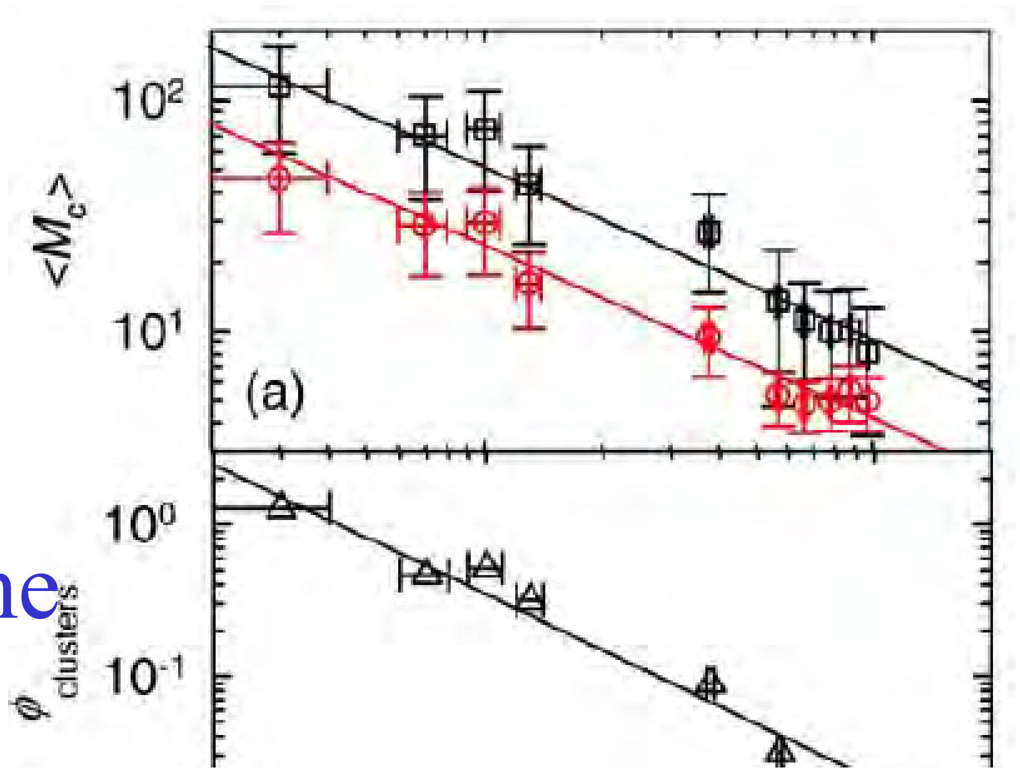
1. Cluster size

2. Cluster volume fraction

3. Elasticity

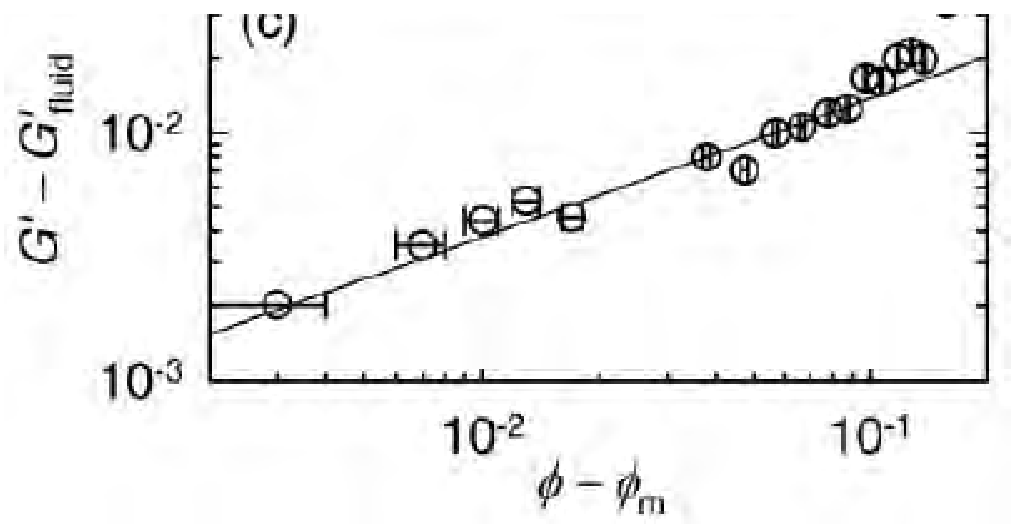


Scaling behavior



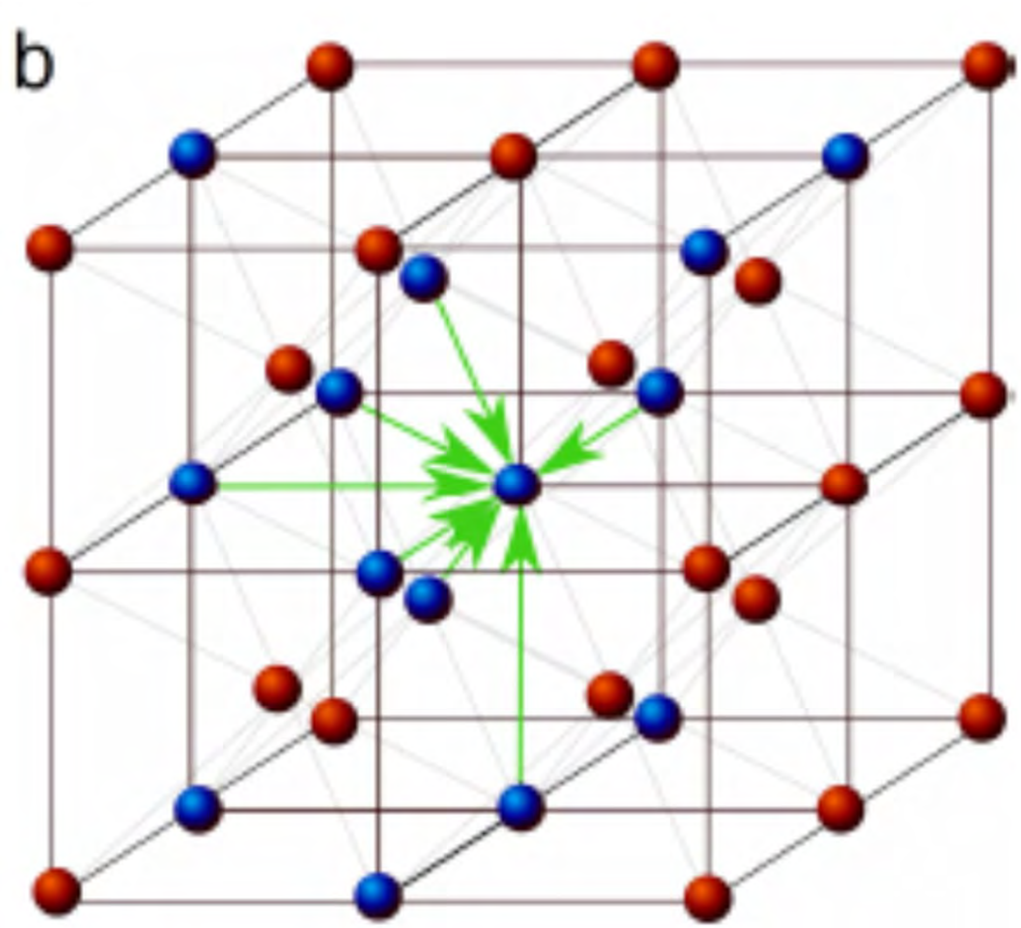
1. Cluster size
2. Cluster volume fraction

Second-order character of 3D melting



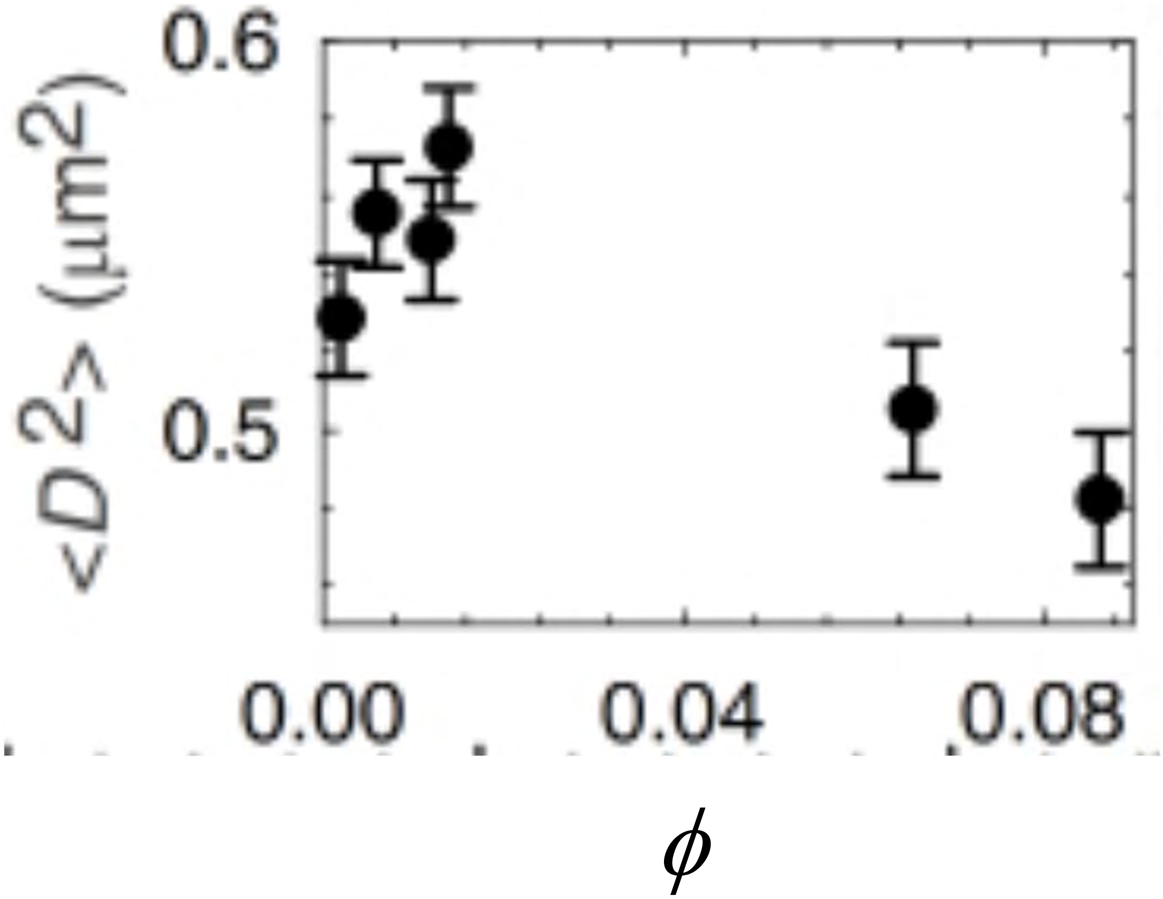
3. Elasticity

Hot particles lead to non-affine motion



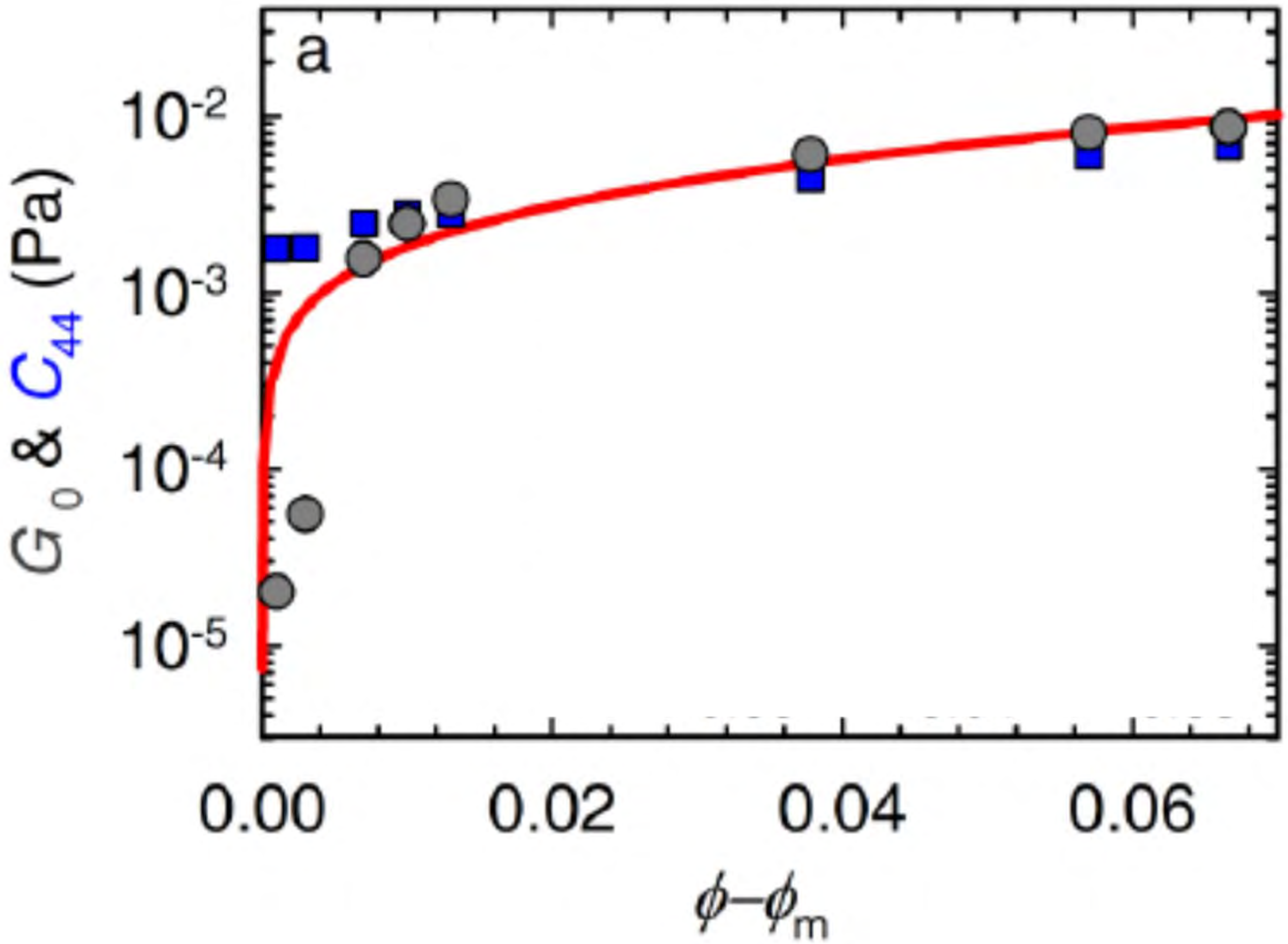
Breaks force balance → weakens lattice

Non-affine motion increases as ϕ decreases



Calculate elastic modulus *including* non-affine motion

Behavior of elasticity



- C_{44} remains approximately constant with ϕ
- Non-affine modulus does vanish

2^{nd} order behavior for melting

- 1D melting is always 2^{nd} order
- 2D melting is through hexatic → 2^{nd} order
- 3D melting has 2^{nd} order character if the lattice is perfect
- Non-affine shear modulus:
  - Provides weakened regions
  - Mechanical stability is lost
  - Generalizes Born melting
- 3D melting of Wigner lattice is weakly 1^{st} order

The End