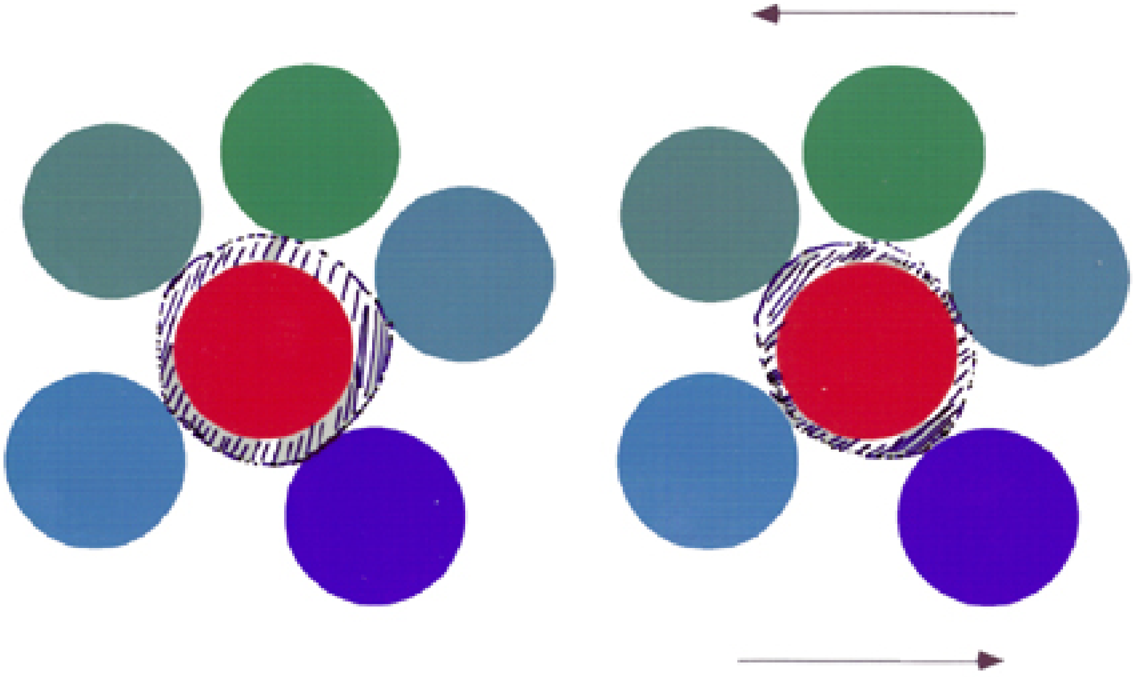
RHEOLOGY OF SOLID SPHERES



- ENTROPIC IN ORIGIN

FREQUENCY DEPENDENCE:

- High Frequency:
  - Cage plays no role

- Intermediate Frequency:
  - Strain distorts cage; energy storage

- Low Frequency:
  - Cage Breaks up
  - Mode coupling Theories for Glass Transition

VISCOELASTICITY

SOLID $\tau = G\gamma$

FLUID $\tau = \eta\dot{\gamma}$

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

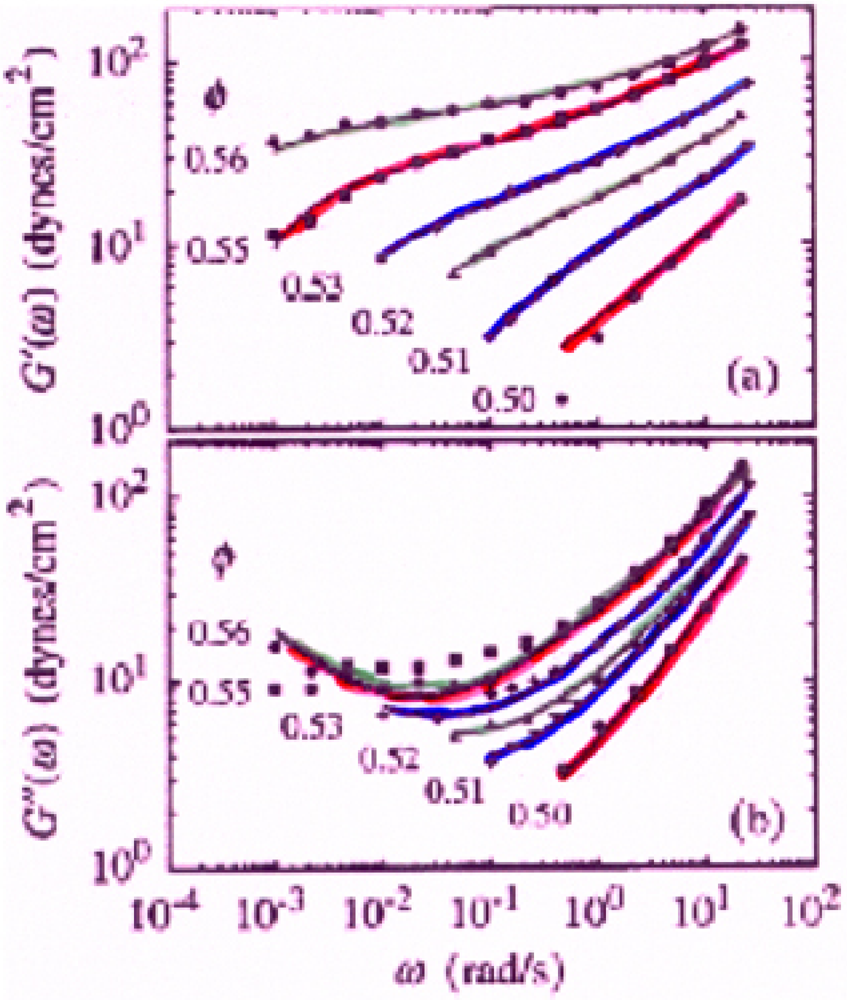
$$\tau = \left[G'(\omega) + i\,G''(\omega)\right]\gamma$$

MODULUS : $G'(\omega)$ ELASTIC

$G''(\omega)$ VISCOUS

RELATED BY KRAMERS - KRONIG

CHARACTERIZES SOFT MATERIALS



THEORETICAL FITS TO DATA.

RHEOLOGY OF HARD SPHERES.

$$G^*(\omega) = \underbrace{G^*_{glass}(\omega)}_{\text{GLASS STRUCTURE}} + \underbrace{G^*_{diff.}(\omega)}_{\text{ENTROPY}} + \underbrace{i\eta_\infty \omega}_{\text{SUSPENSION VISCOSITY.}}$$

$G^*_{glass}(\omega)$

- NOT KNOWN
- USE MODE COUPLING THEORY:

↳ ALL MODES COUPLED TO ONE DOMINAN MODE

↳ ALL CORRELATION FUNCTIONS HAVE SAME FORM.

$$C_{\tau\tau}(t) = f^c_{\tau\tau} + h_{\tau\tau} C_\sigma \left[\left(\frac{t}{t_\sigma}\right)^{-a'} - B\left(\frac{t}{t_\sigma}\right)^{b'} \right.$$

FUNCTIONAL FORM FOR DENSITY FLUCTUATIONS.

THEORY PUTS MANY CONSTRAINS ON PARAMETE

$f^c_{\tau\tau} \sim 1$

$h_{\tau\tau} \sim 1$

$C_\sigma \sim \sigma^{1/2}$

$t_\sigma \sim \sigma^{1/2a'}$

$\sigma = \frac{\phi_g - \phi}{\phi_g}$

$a' = 0.30$

$b' = 0.55$

$B = 0.96$

$G^*_{glass}(\omega)$:

$$G^*_{glass}(\omega) = G_0 \, i\omega \int_0^\infty C_{zz}(\tau)\, e^{i\omega t}\, d\tau .$$

→ f^c_{zz} → ENERGY STORAGE

h_{zz} .... → STORAGE & DISSIPATION.

$G^*_{diff}(\omega)$

→ ENTROPIC → DUE TO DIFFUSION:

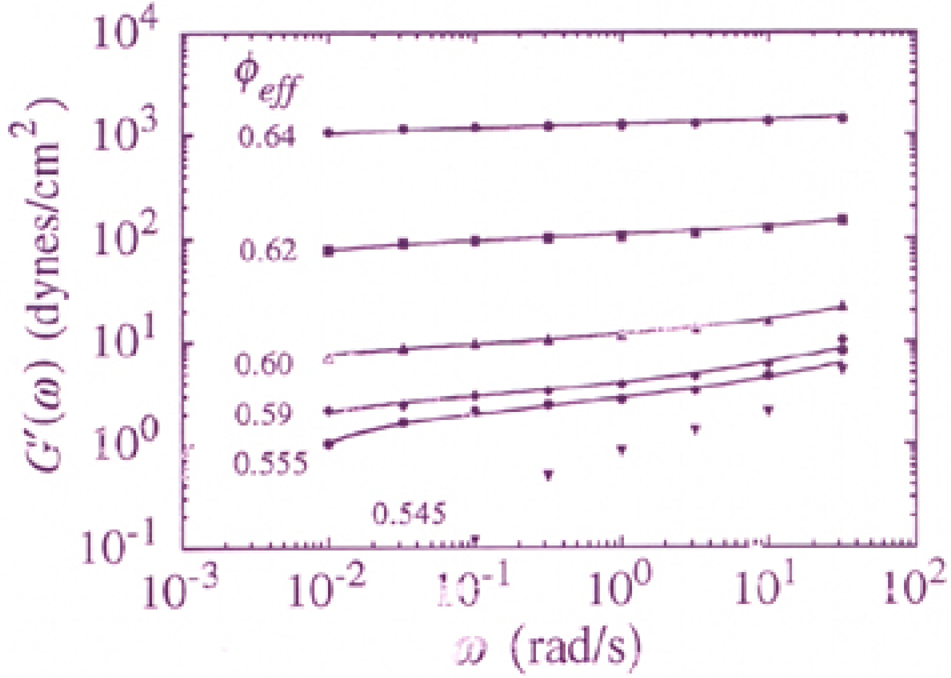
STRESS $\sim \dfrac{kT}{a^3}$ ENTROPY

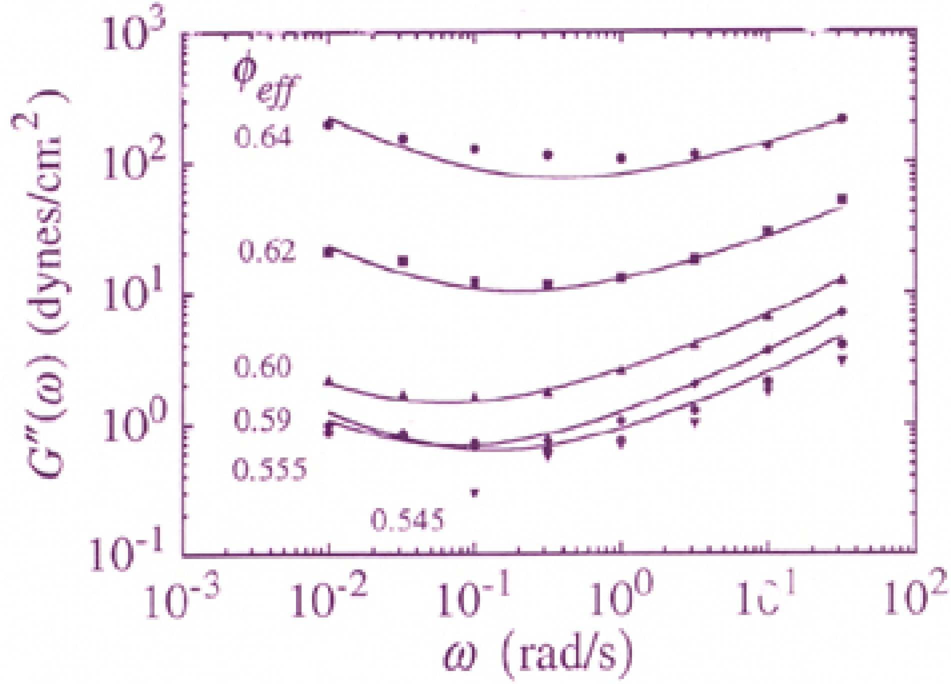
STRAIN $\sim \dfrac{1}{a}\sqrt{\dfrac{D}{\omega}}$ DIFFUSIVE MOTION

$$\text{MODULUS} = \frac{\text{STRESS}}{\text{STRAIN}} \simeq \frac{kT}{a^3}(\omega \tau_D)^{1/2}$$

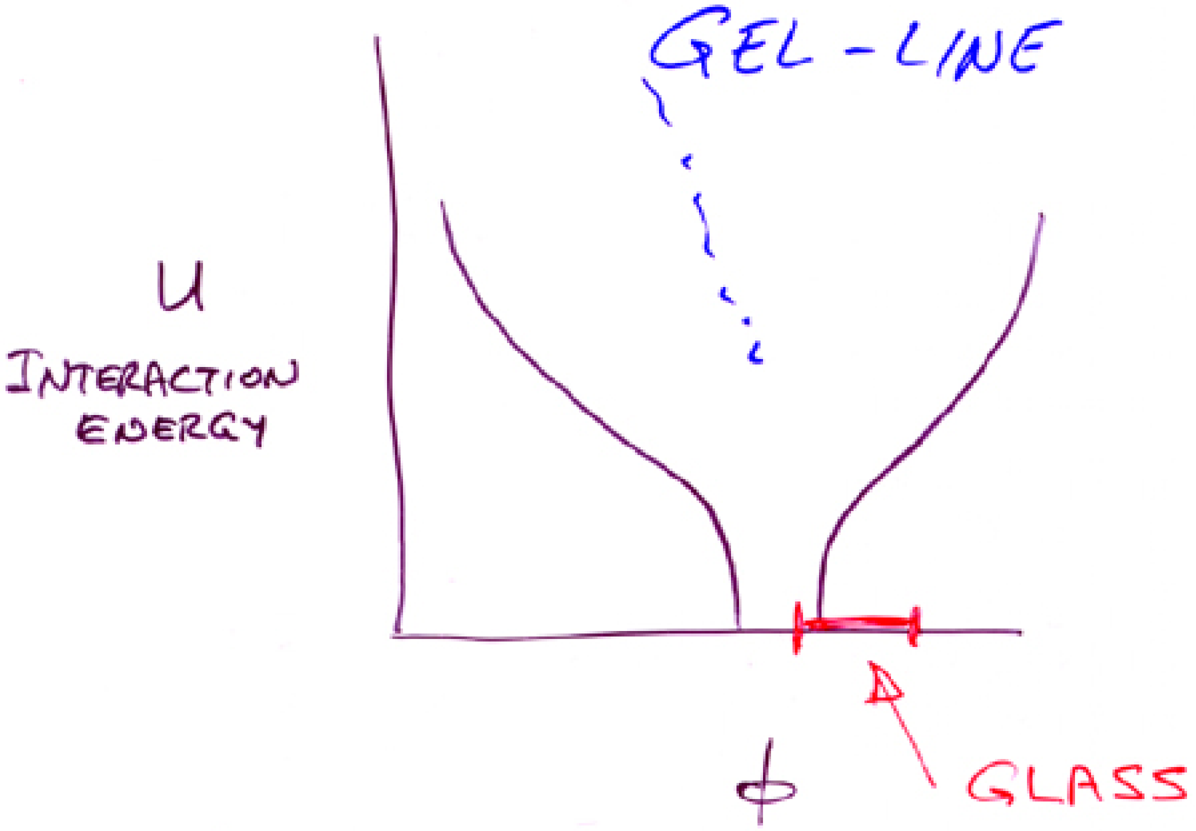
$$\tau_D = a^2/D_s$$

$$G'_{diff}(\omega) = G''_{diff}(\omega) = \frac{3}{5\pi}\,\frac{kT}{a^3}\,\phi^2 g(2a,\phi)\,[\omega\tau_D]^{1/2}$$


ϕ_{eff}
0.64
0.62
0.60
0.59
0.555
0.545
$G'(\omega)$ (dynes/cm^2)
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
ω (rad/s)


ϕ_{eff}
0.64
0.62
0.60
0.59
0.555
0.545
$G''(\omega)$ (dynes/cm^2)
10^3
10^2
10^1
10^0
10^{-1}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
10^2
ω (rad/s)

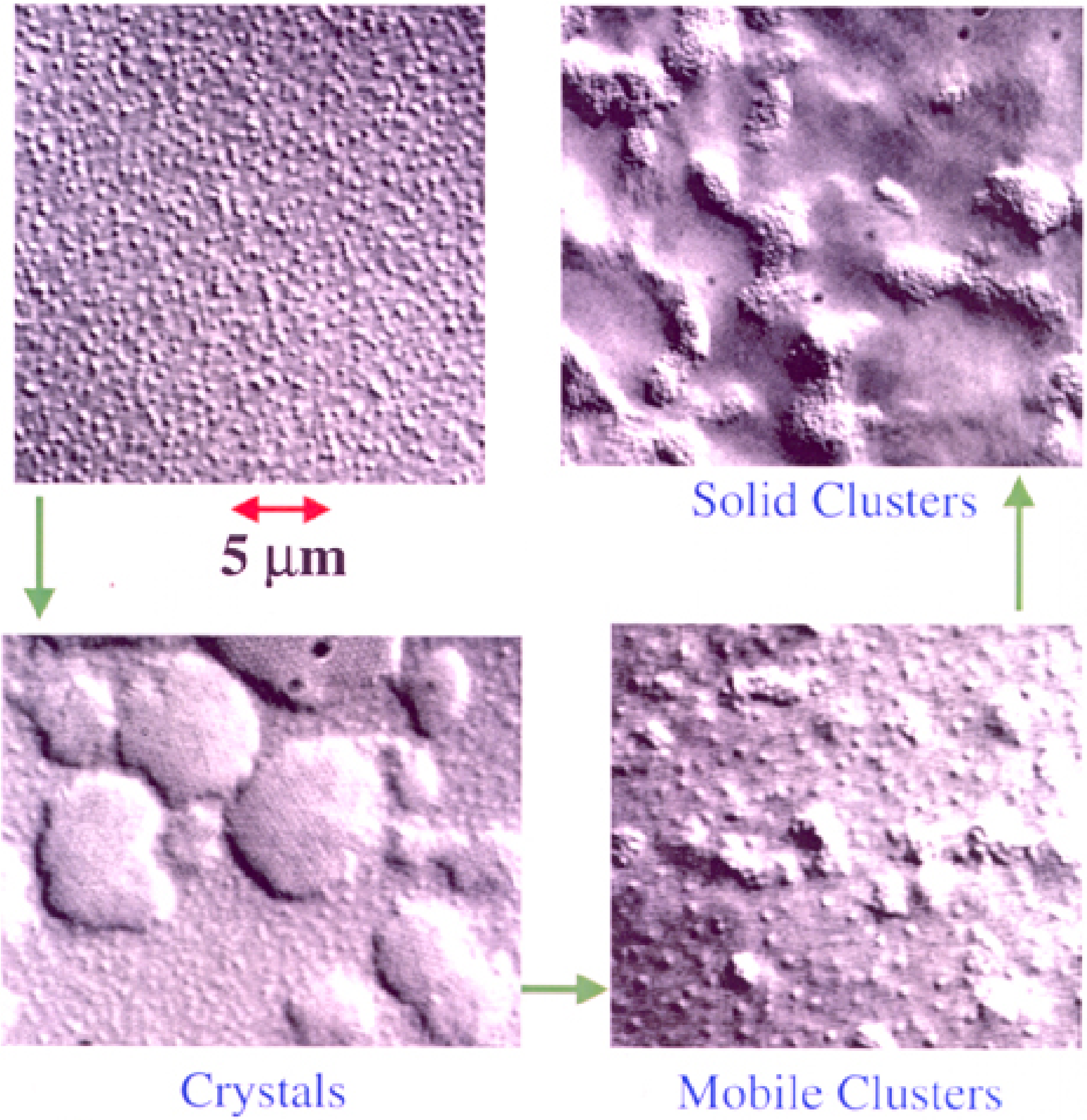
PHASE BEHAVIOR OF ATTRACTIVE PARTICLES



WHAT HAPPENS TO COLLOIDAL GLASS WHEN PARTICLES BECOME ATTRACTIVE ?

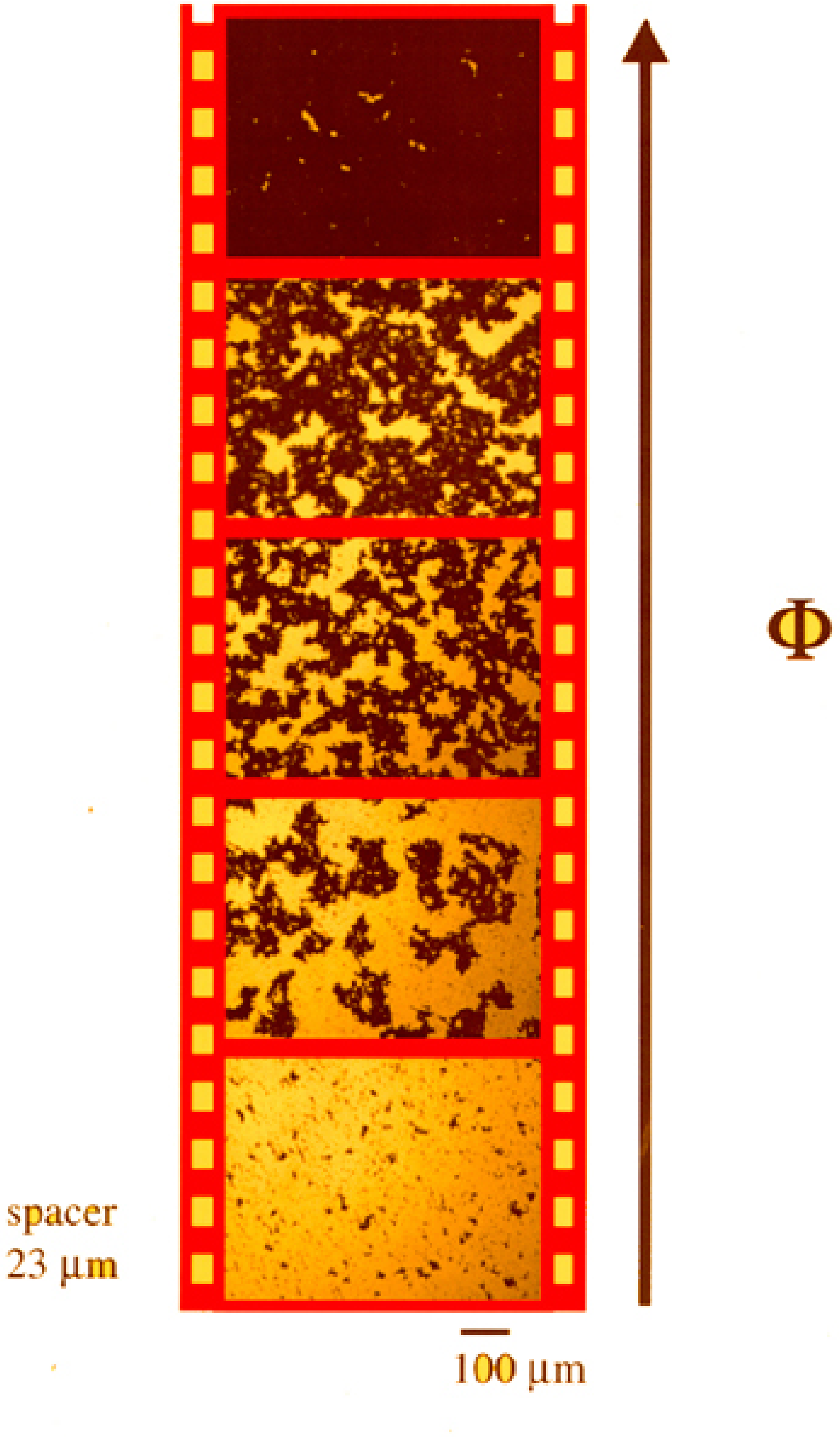
Self Assembly

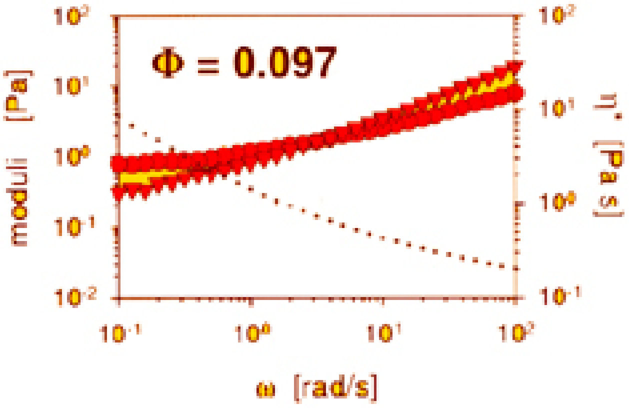
Attractive Colloidal Spheres



Carbon Black in Oil

$U \sim 10 \pm 2\ kT$

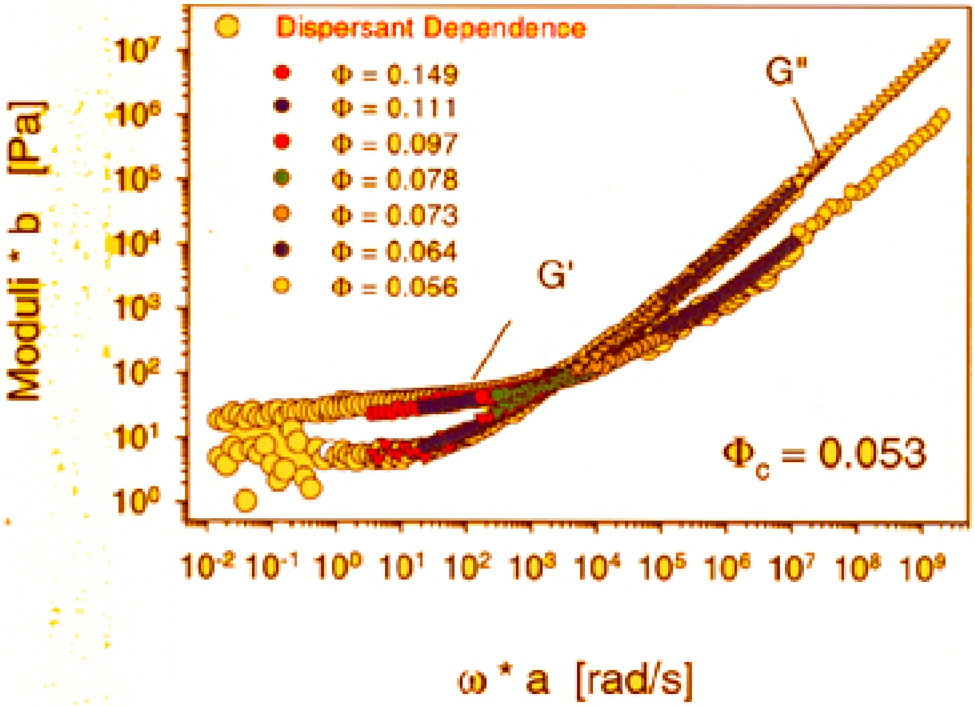



Φ = 0.097
moduli [Pa]
10^2
10^1
10^0
10^-1
10^-2
η* [Pa s]
10^2
10^1
10^0
10^-1
10^-1
10^0
10^1
10^2
ω [rad/s]

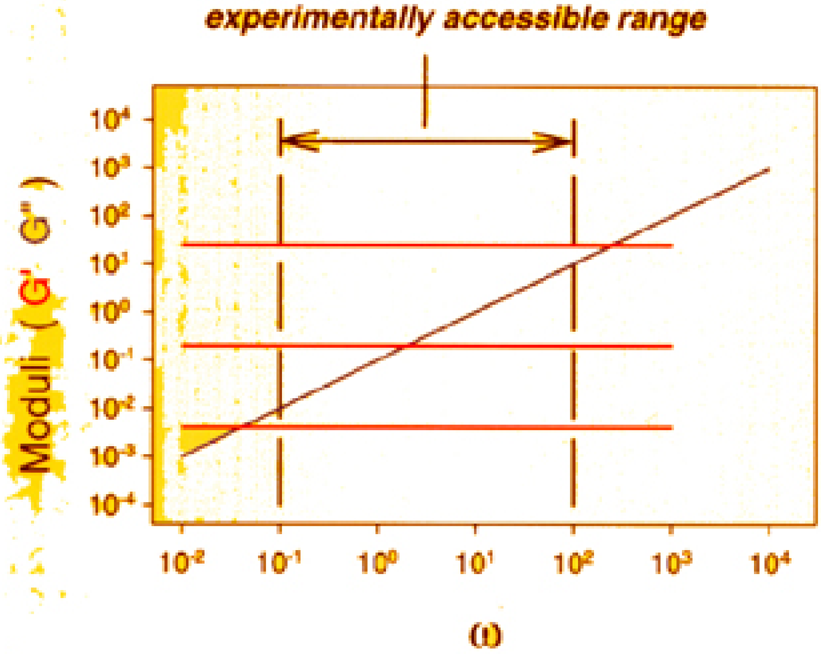
Scaling

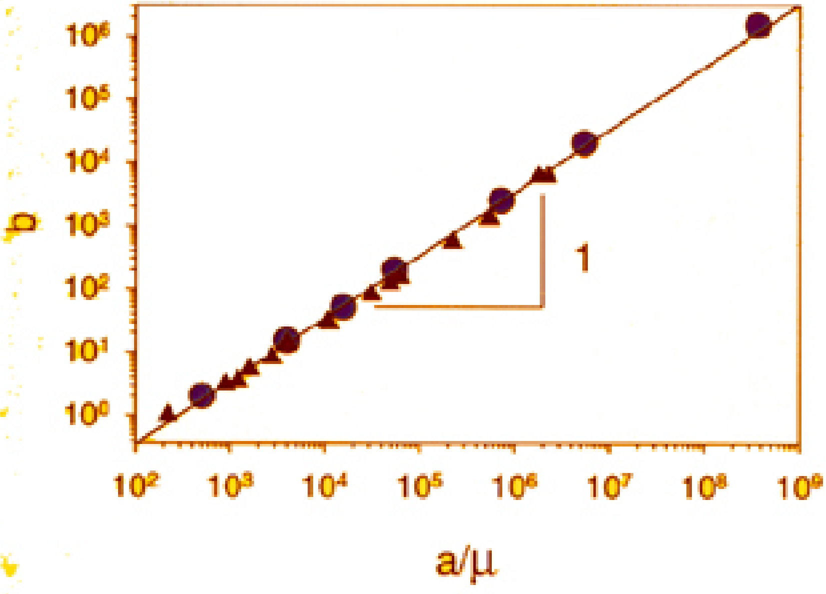
Φ-Dependence

Carbon Black in Oil $U \sim 10 \pm 2\ kT$



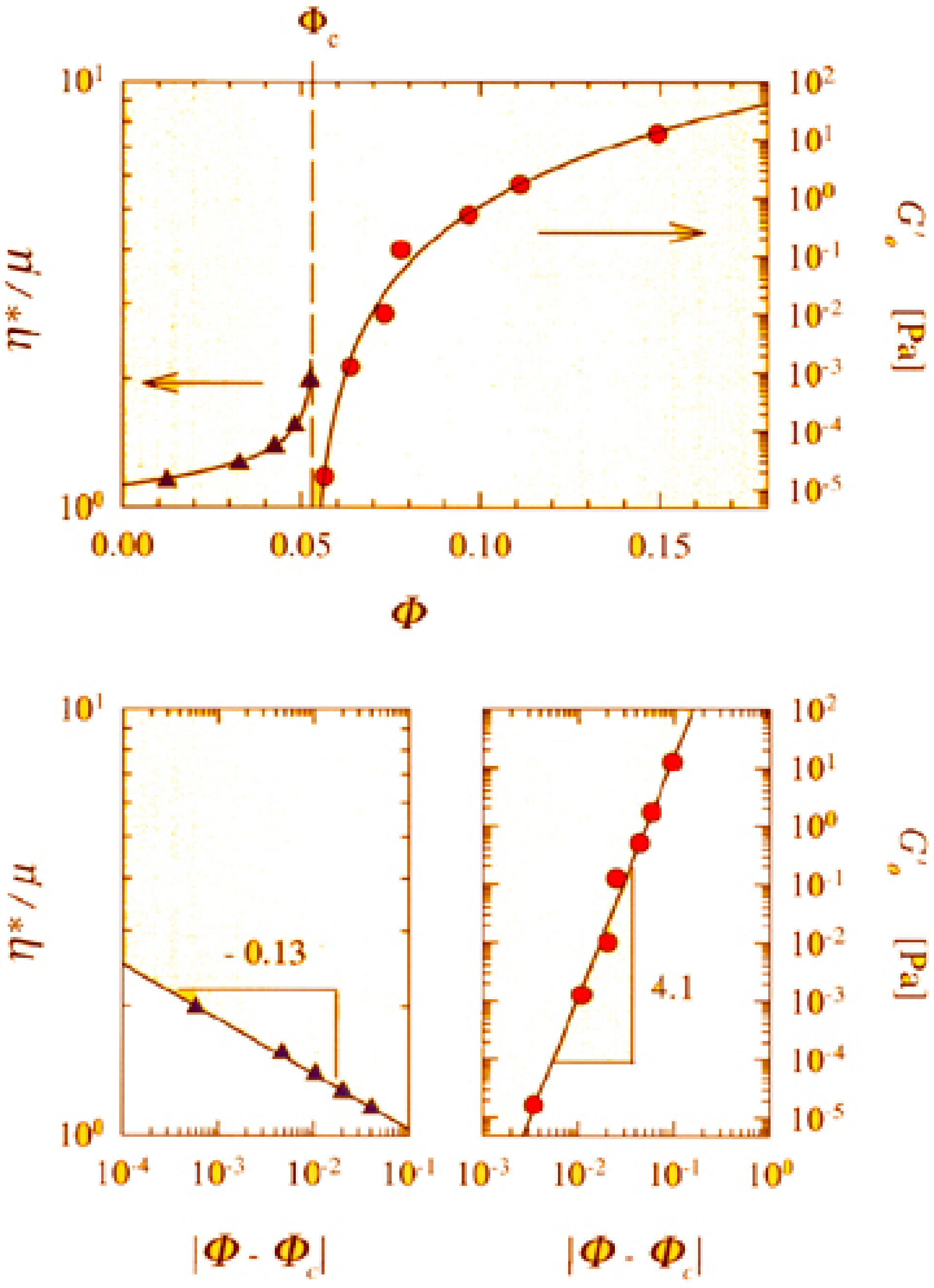
Scaling along the Background Viscosity





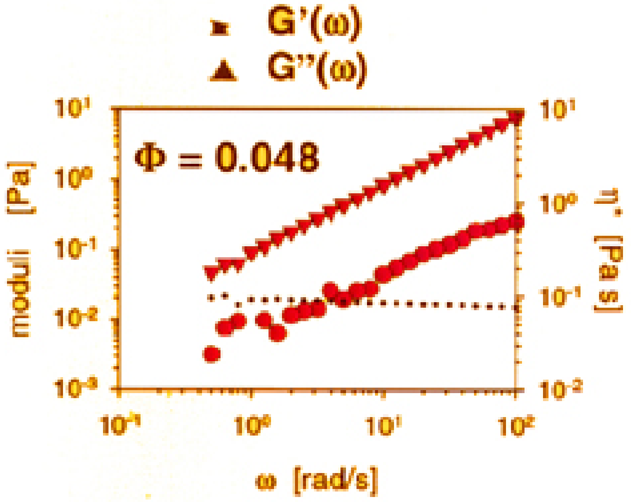
Fluid-Solid-Transition   Carbon Black in Oil

U ~ 10 ± 2 kT

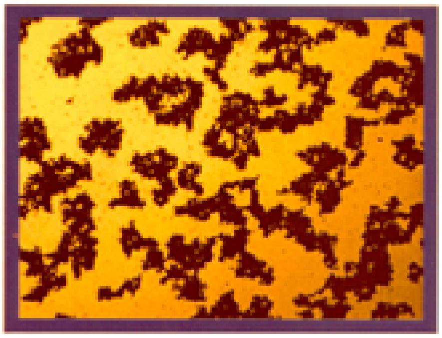


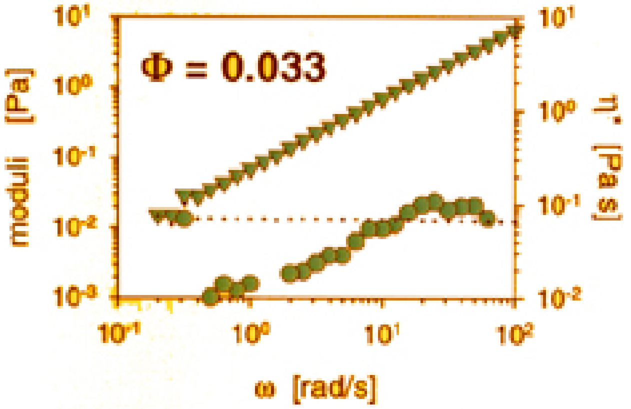
Fluid Side

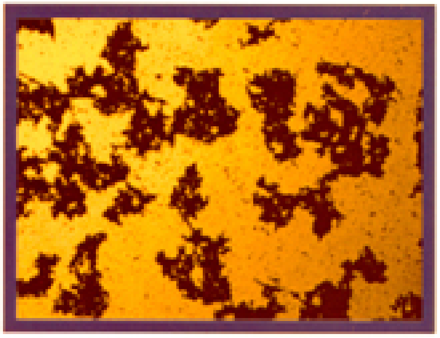
Carbon Black in Oil

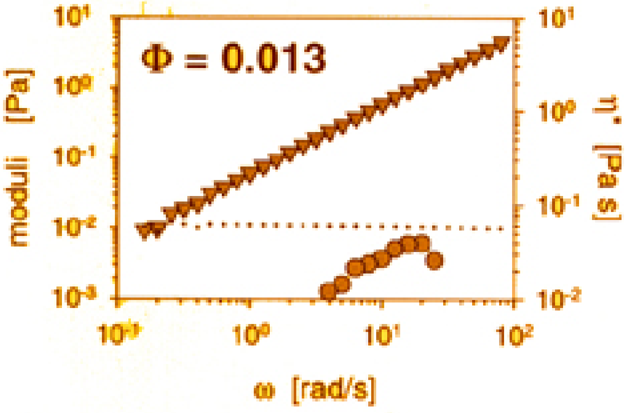


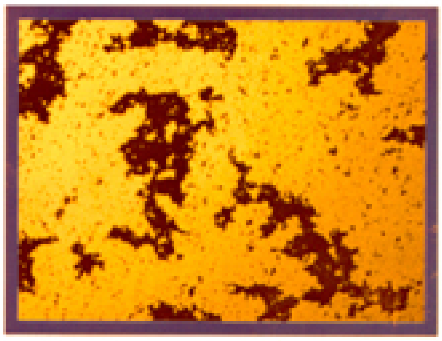
23 μm thick







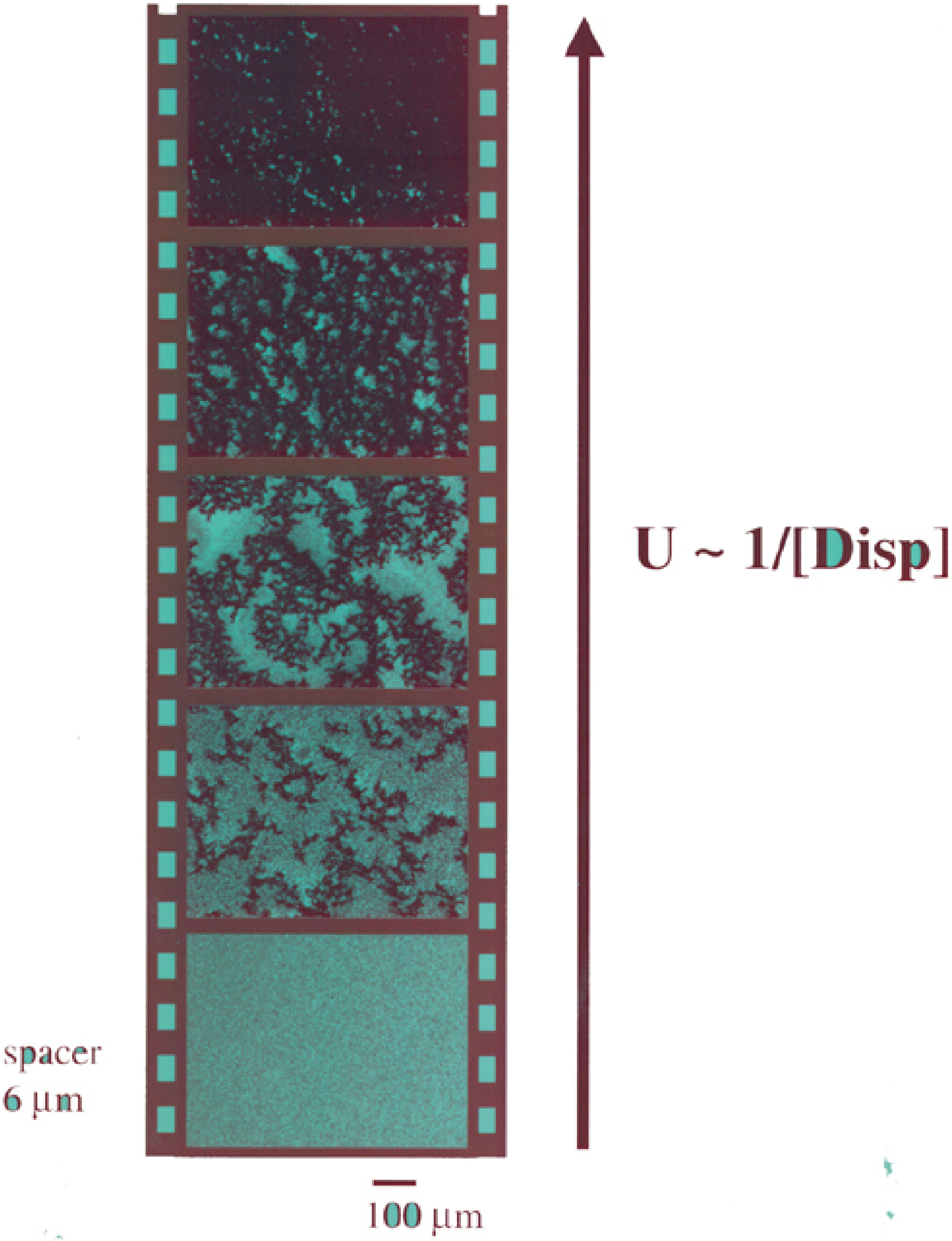




100 μm

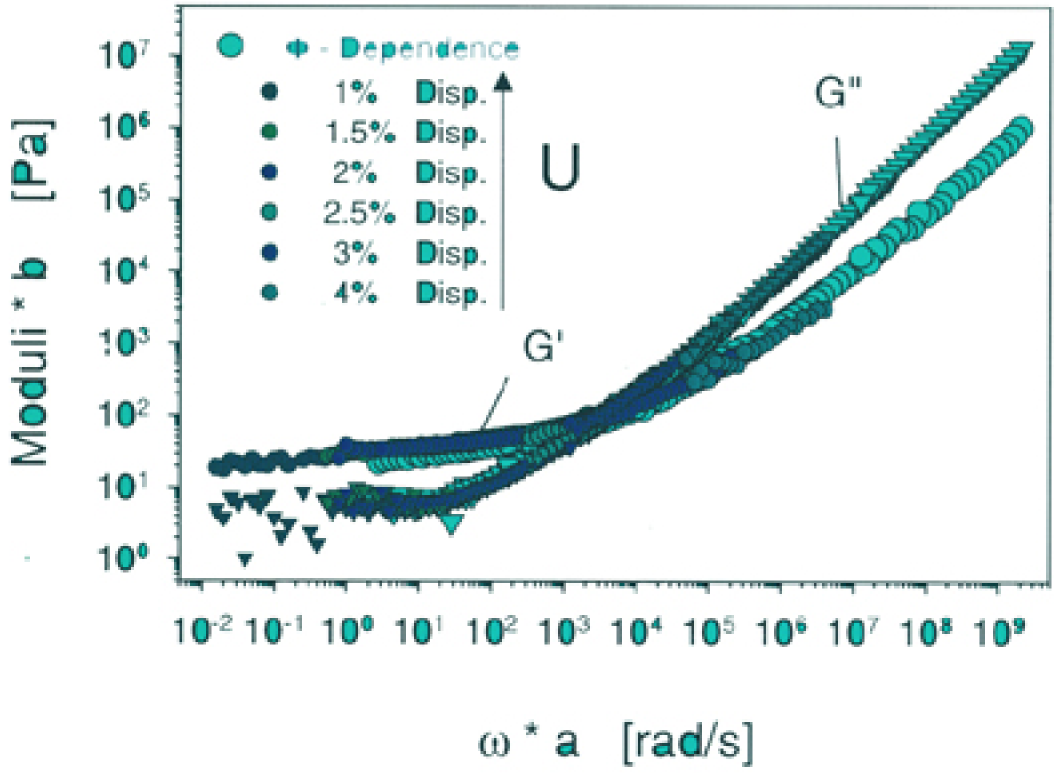
Carbon Black in Oil

$\Phi = 0.14$



Scaling

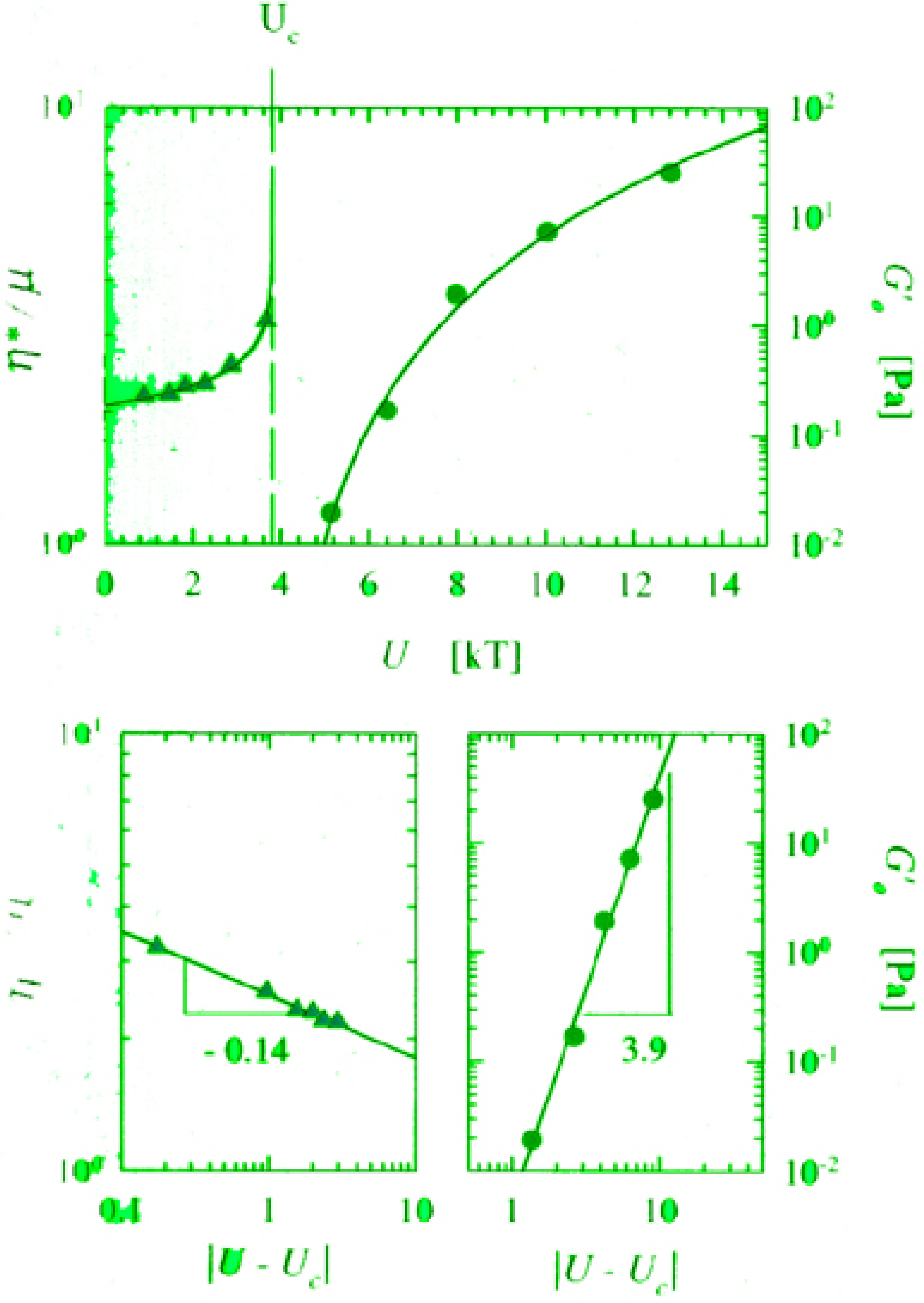
U-Dependence
Carbon Black in Oil   Φ ~ 0.14



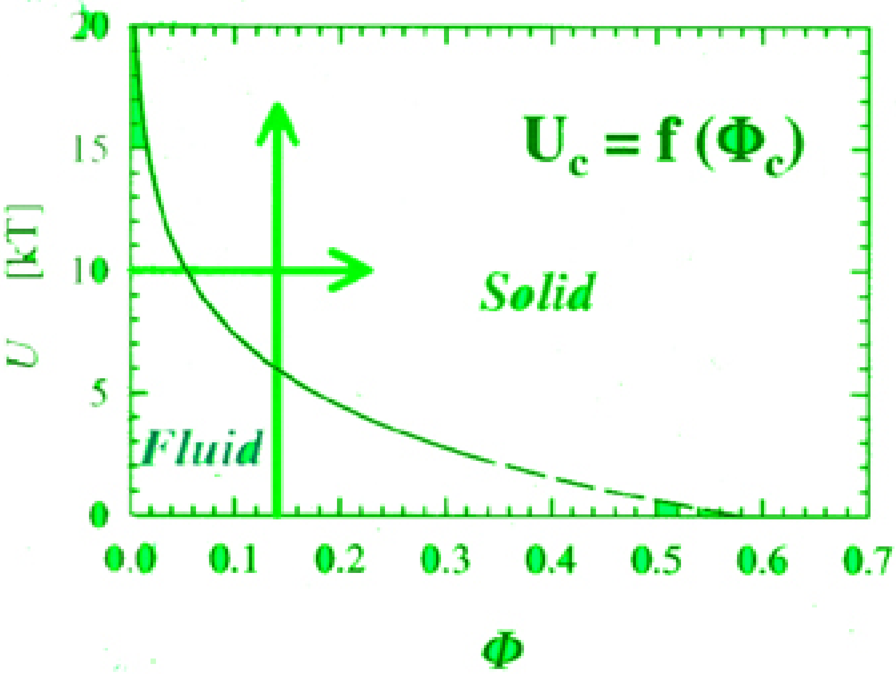
Fluid-Solid-Transition

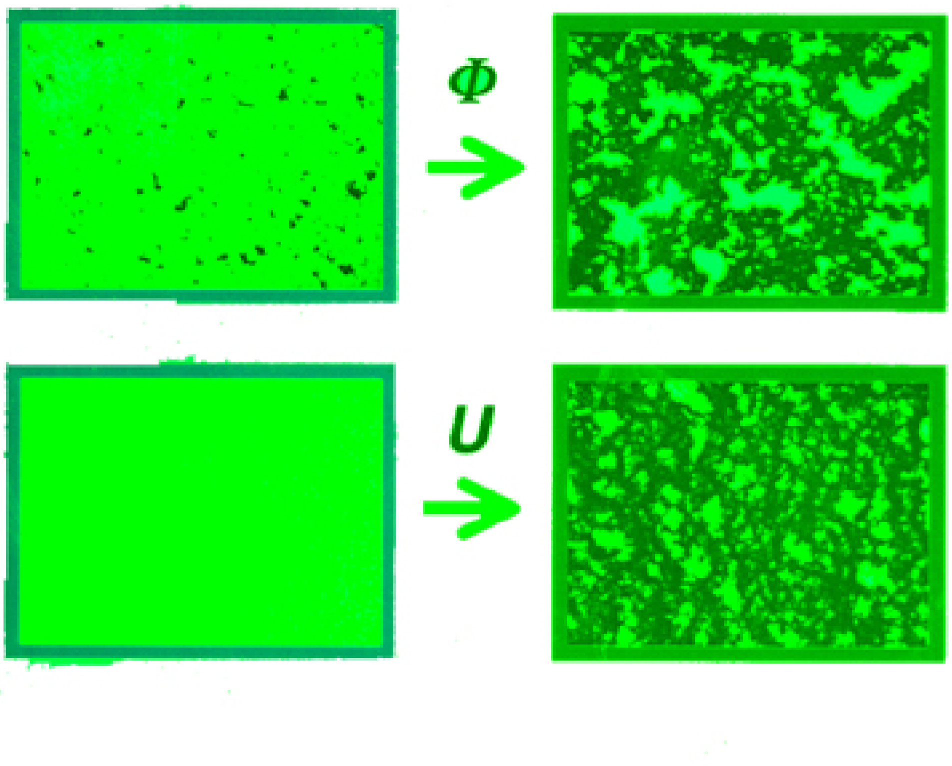
Carbon Black in Oil

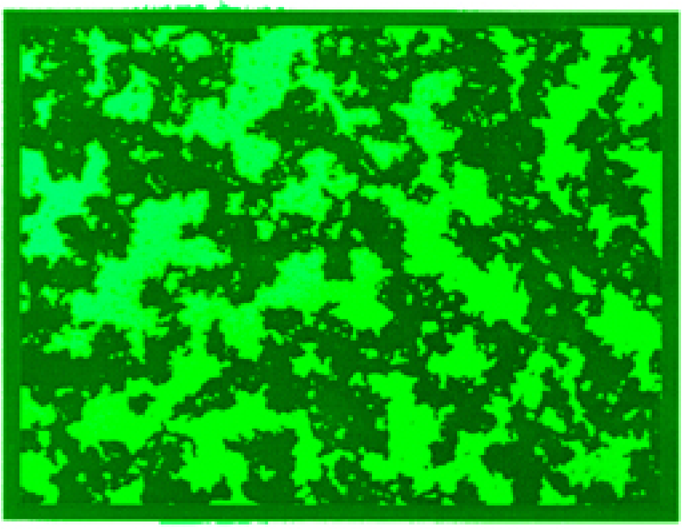
$\Phi = 0.14$



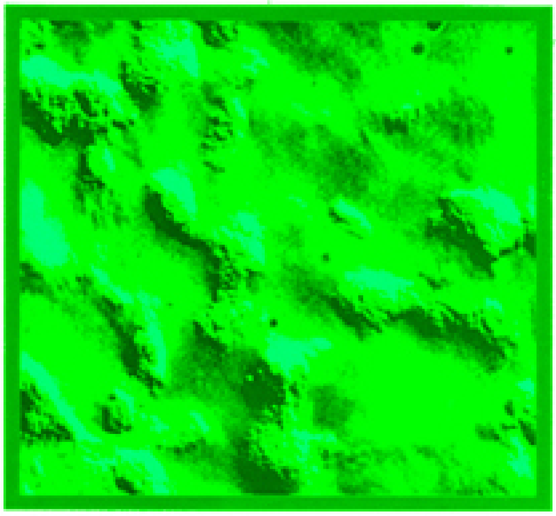
Fluid-Solid Transition
Weakly Attractive Systems



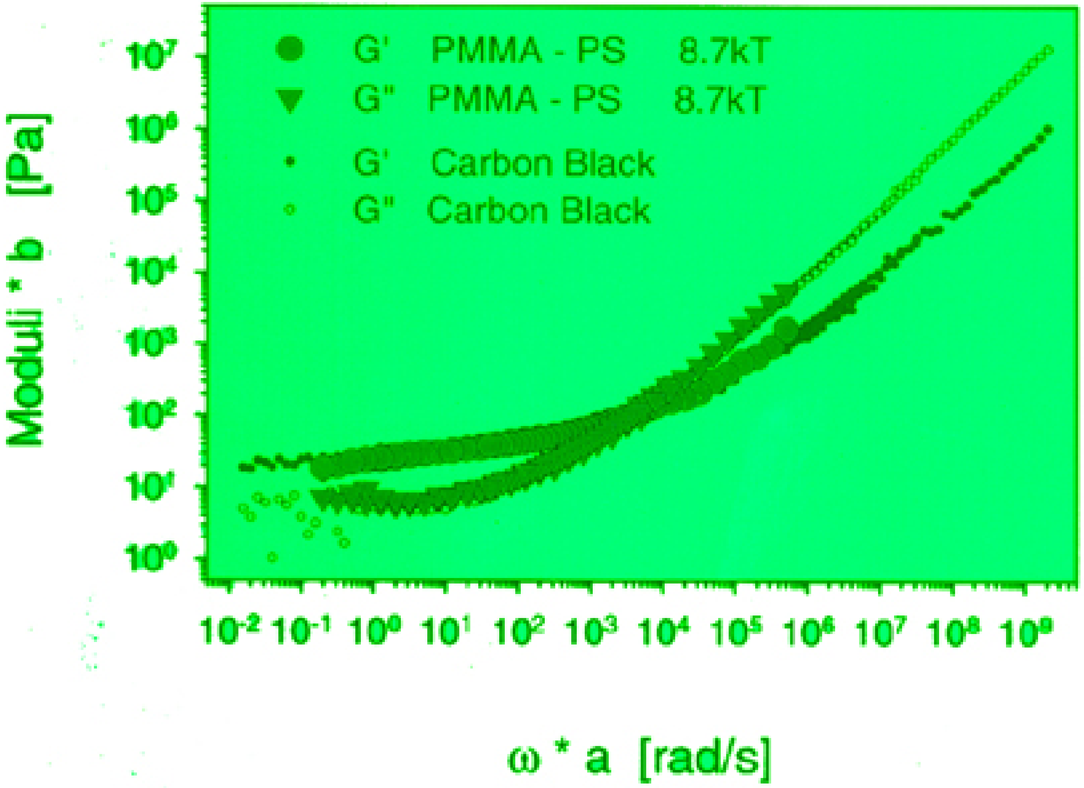




Carbon Black



PMMA - PS



Light Scattering with a CCD Camera

For Large Aggregate Structures, need Low angles

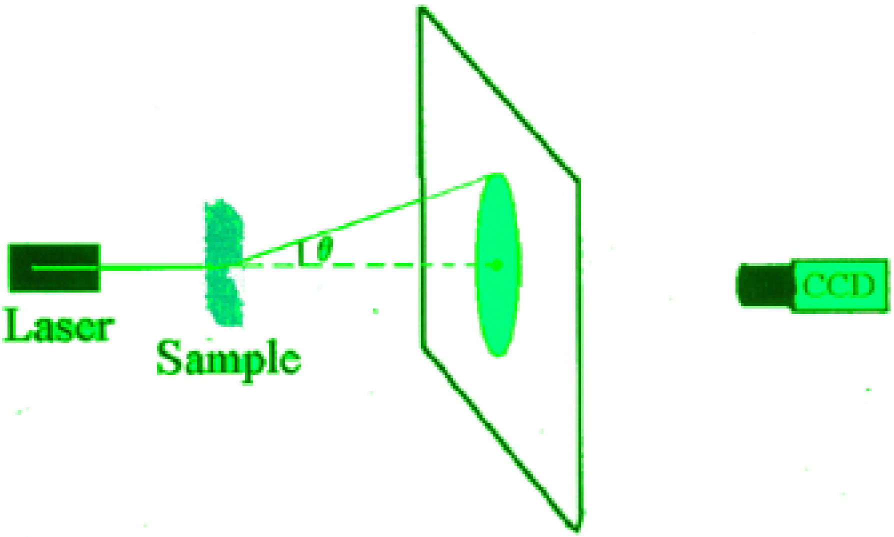
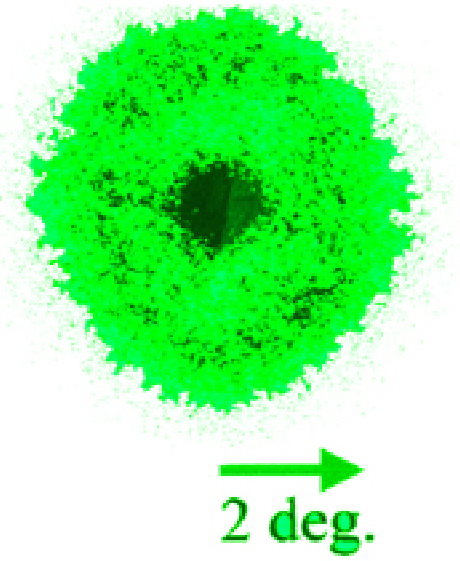
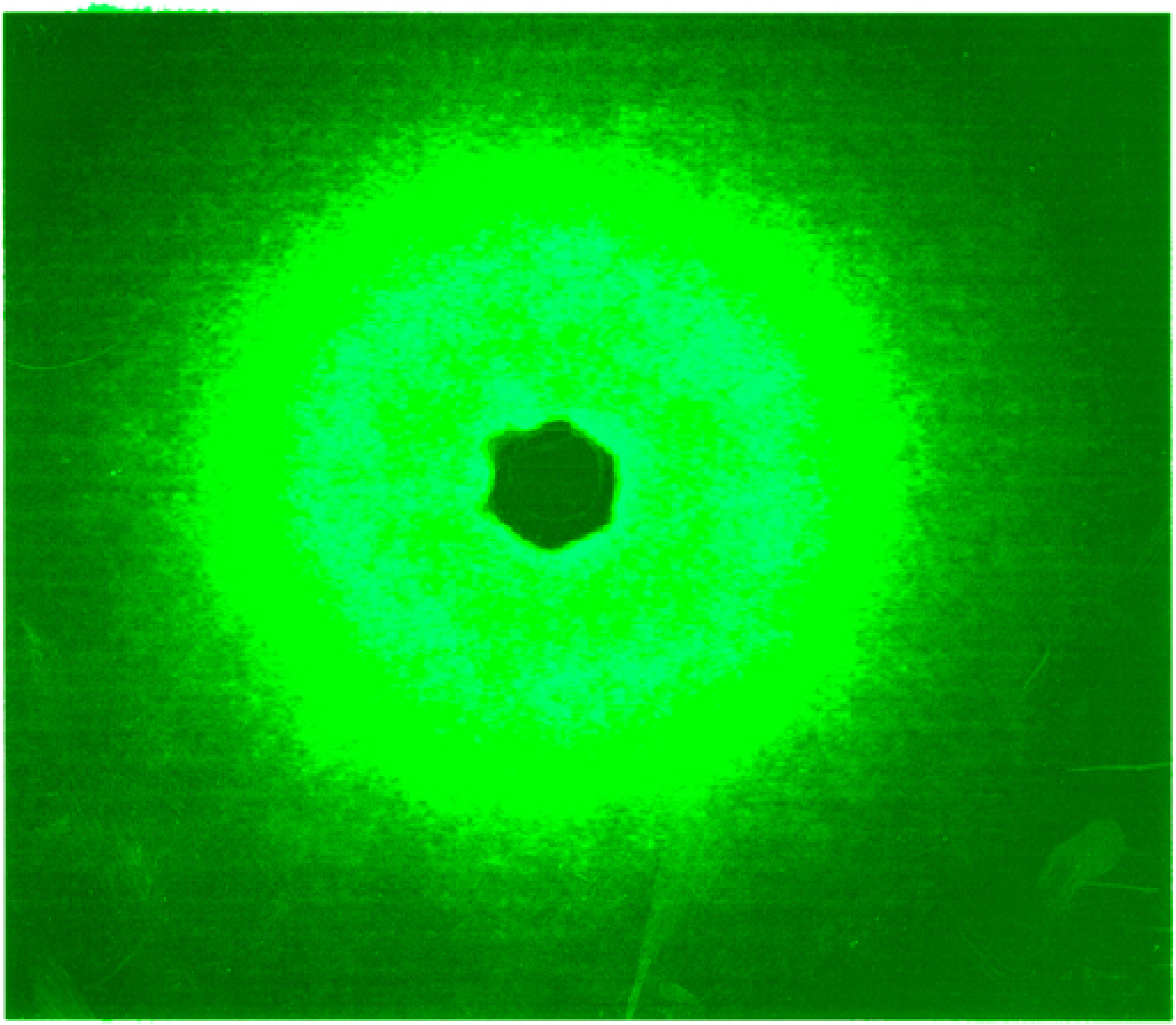
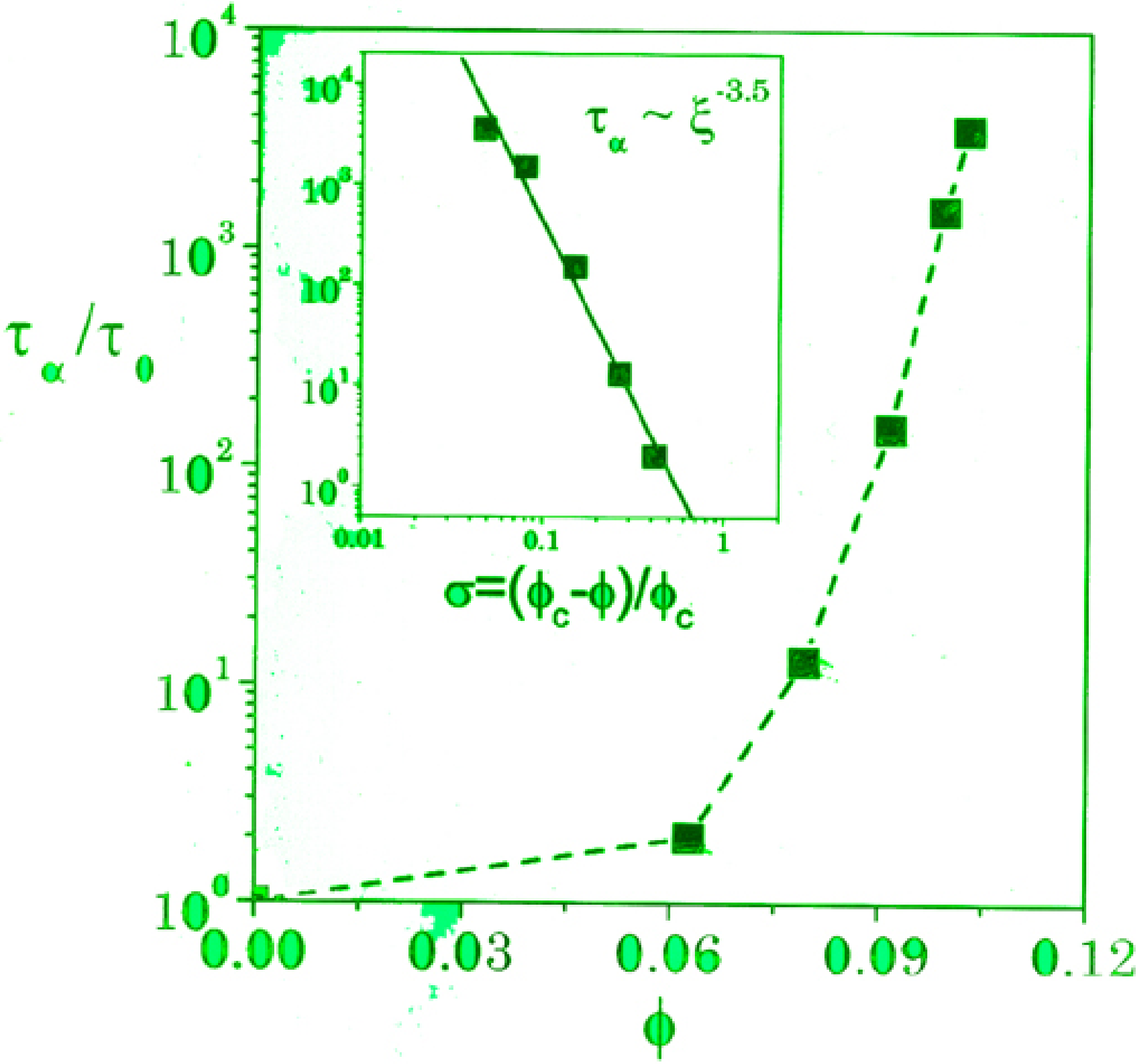


Image from Ordering Clusters



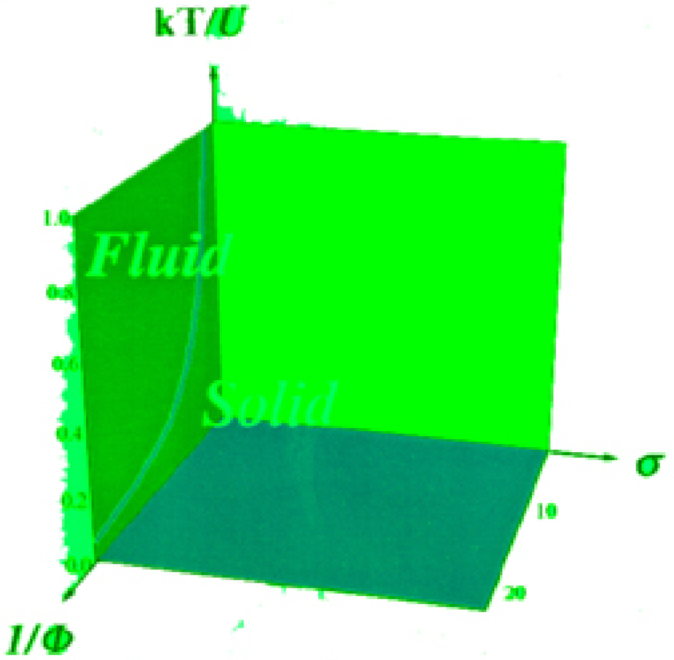


Decay Time of Cluster Dynamics

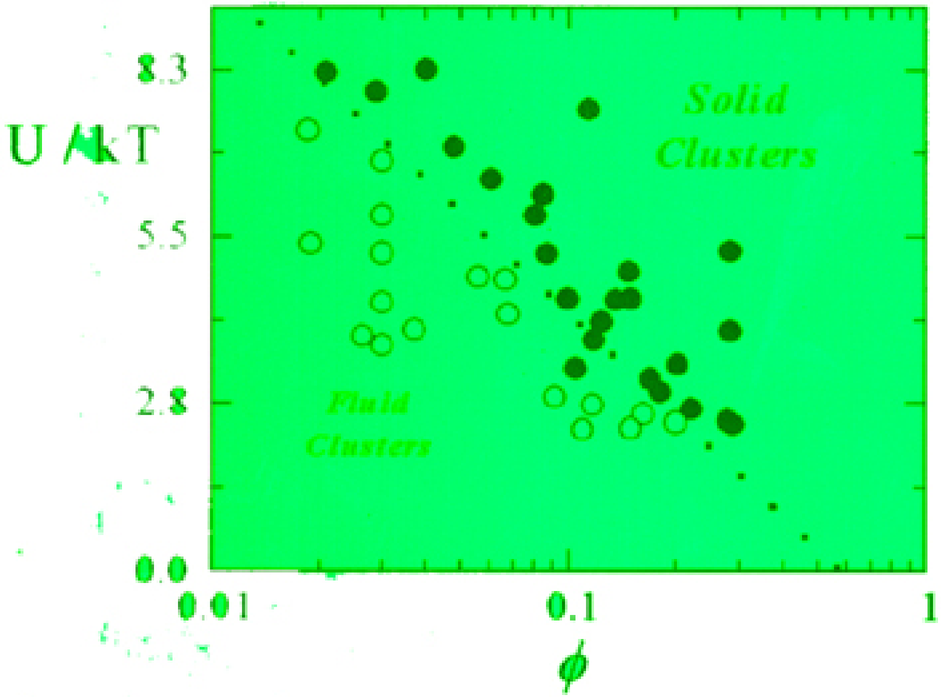


Critical Slowing Down

$\Phi - U$ Plane $\sigma = 0$

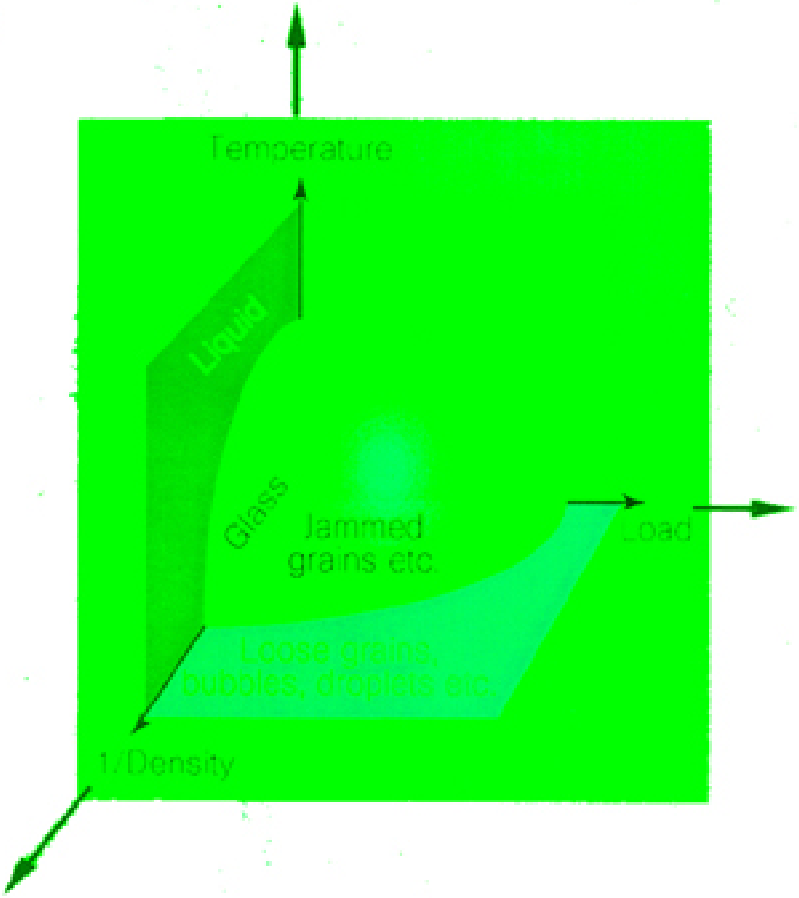


$$\Phi_c = \Phi_o \exp\{-U_c/\alpha kT\}$$



Depletion
PMMA - PS

Jamming Transition – Arrest of Motion



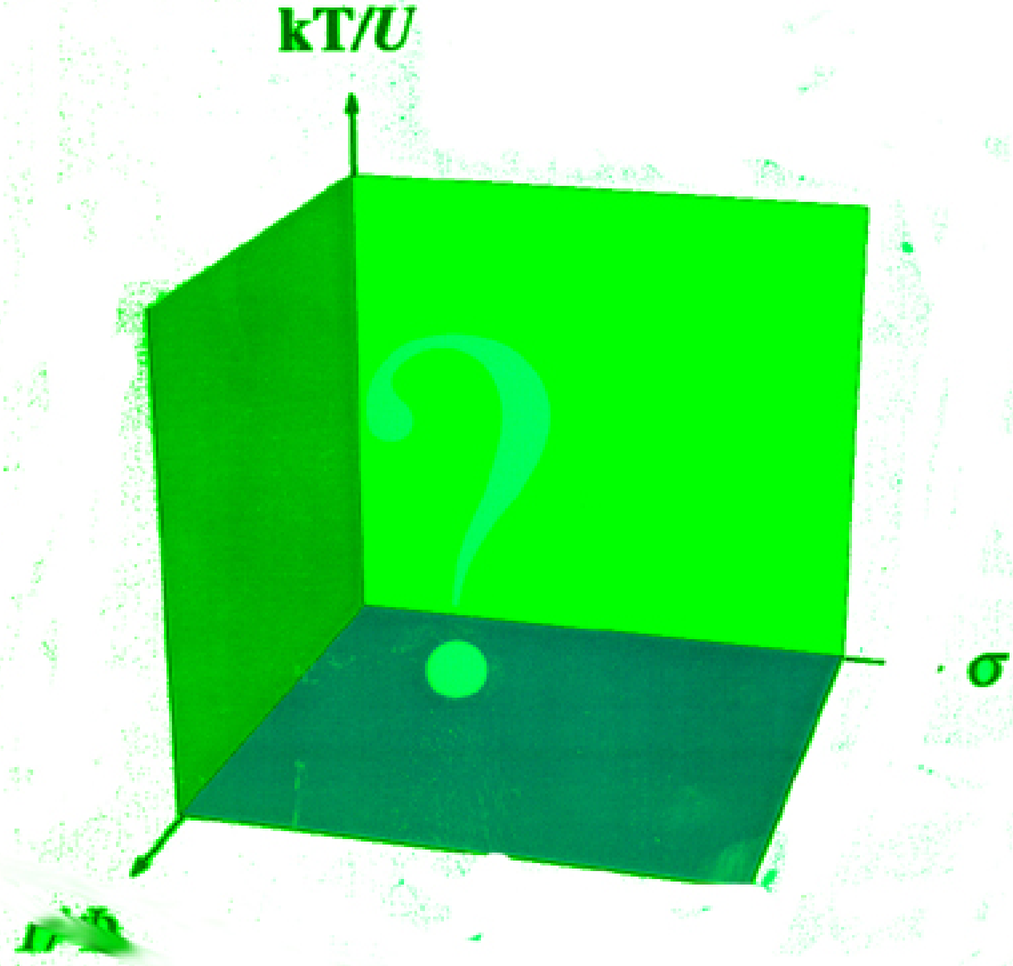
Temperature
Vibration, Shaking

Load
Incompatible Stress
Stress

Density
Compatible Stress
Pressure
Osmotic Pressure
Attractive Potential

Andrea Liu, Sidney Nagel
Nature 386 (1998) 21

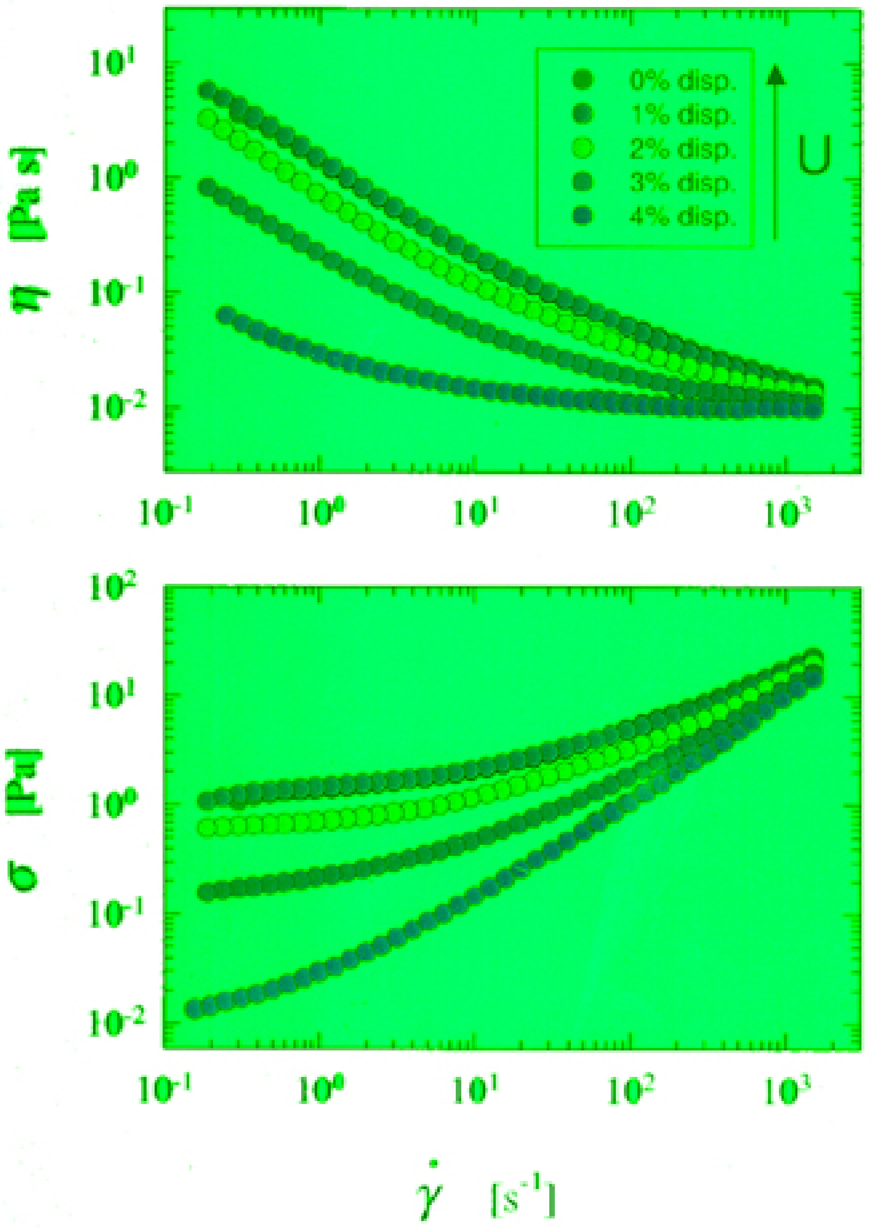
Jamming Transitions for Colloidal Systems with Attractive Interactions

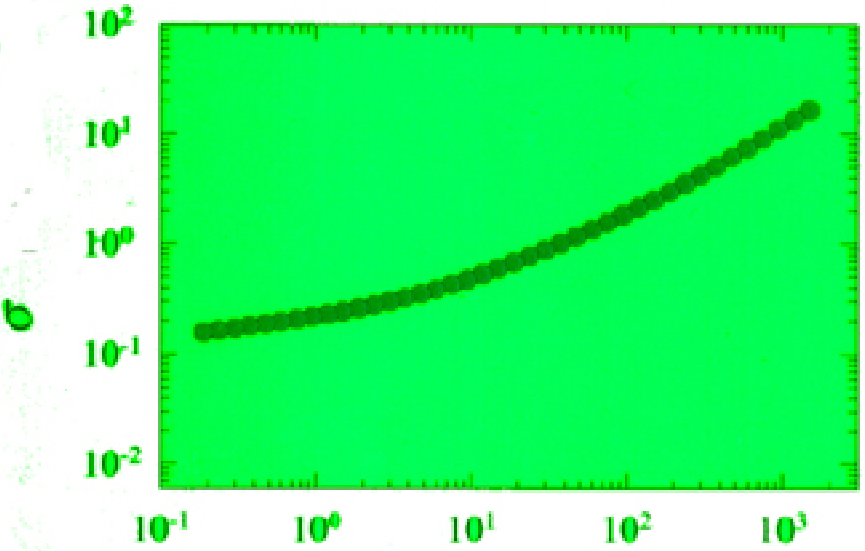


Non-Linear Rheology: Shear-Thinning

U-Dependence

Carbon Black in Oil $\Phi \sim 0.14$

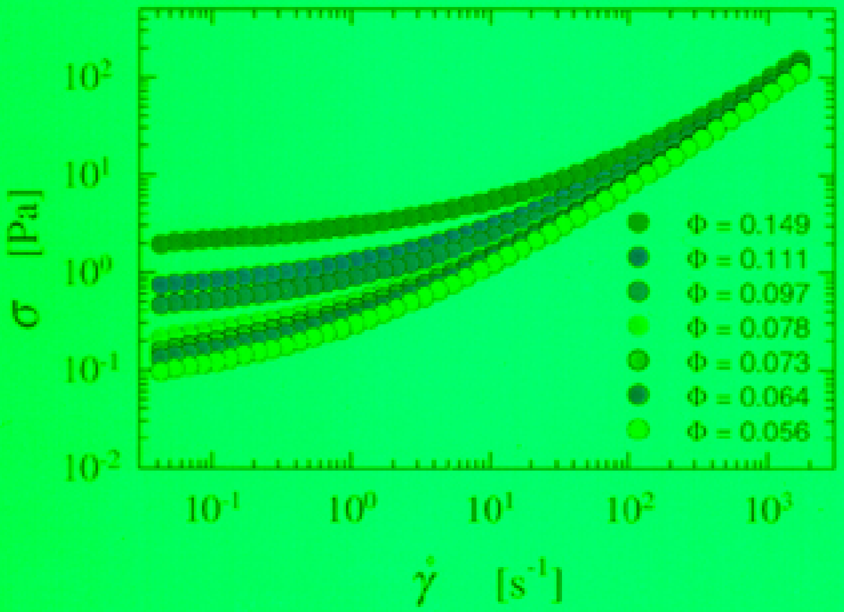


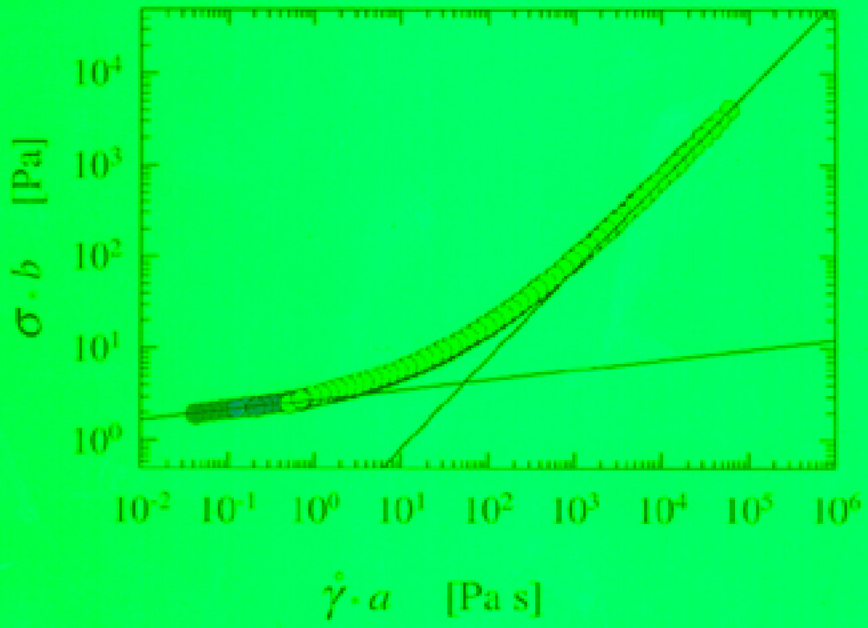

10^2
10^1
10^0
10^{-1}
10^{-2}
σ
10^{-1}
10^0
10^1
10^2
10^3

Non-Linear Rheology: Shear-Thinning

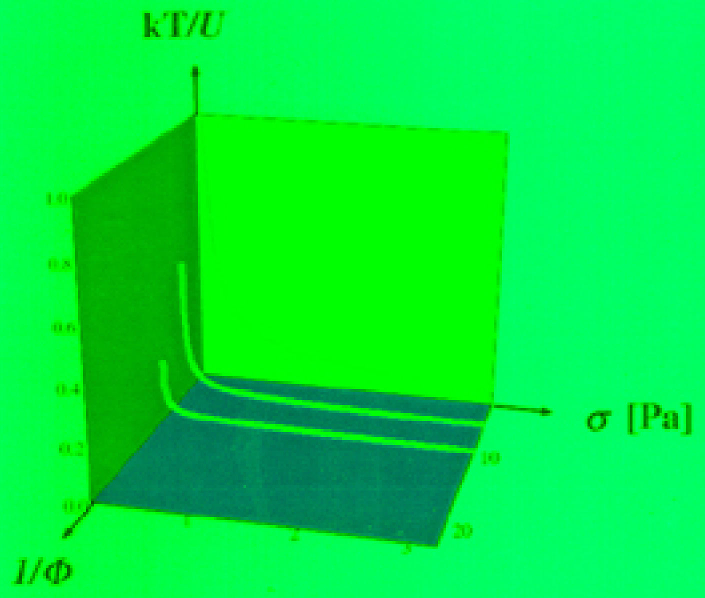
Φ-Dependence

Carbon Black in Oil U ~ 10 ± 2 kT

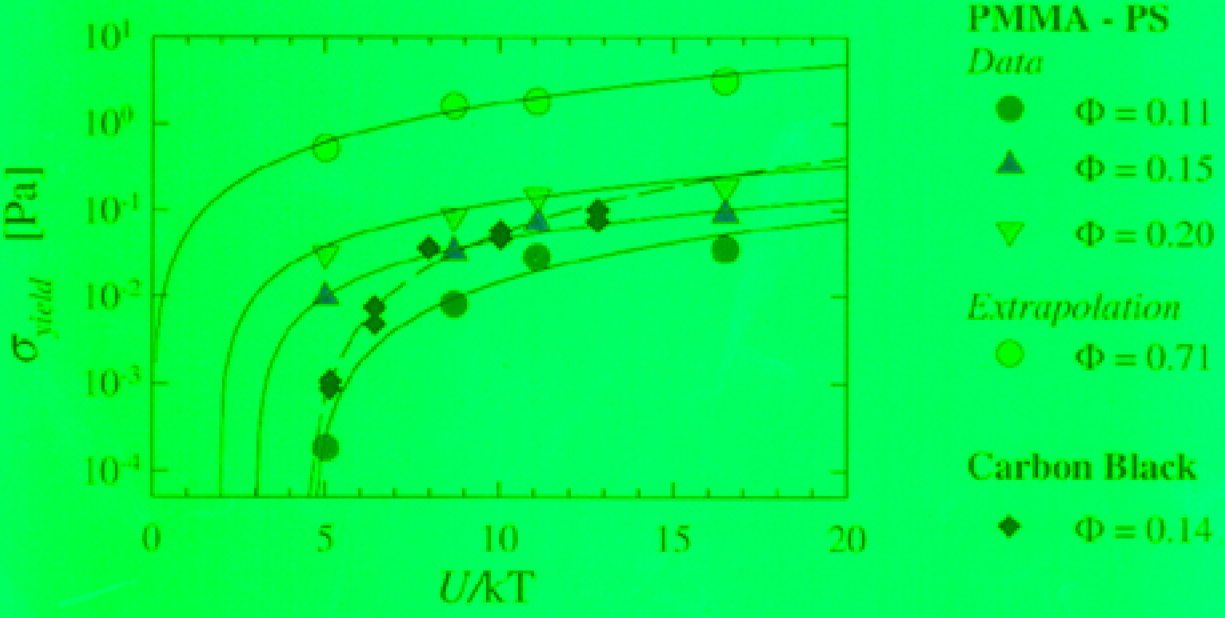




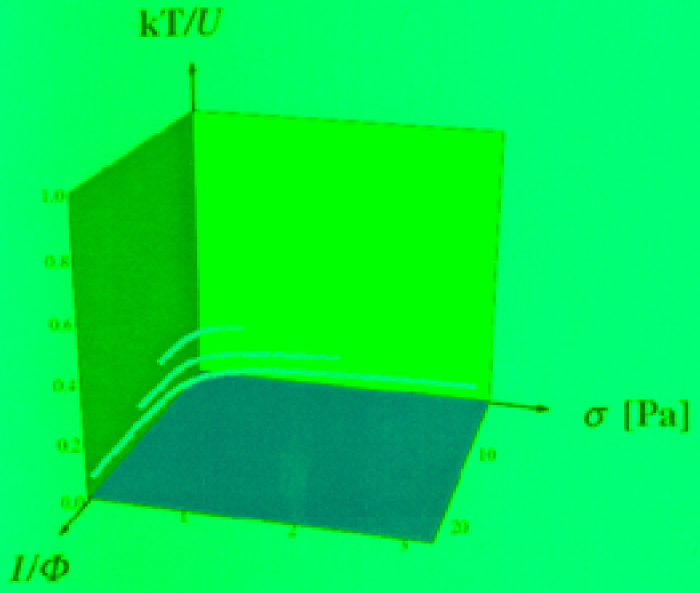
U – σ Plane   Φ = const



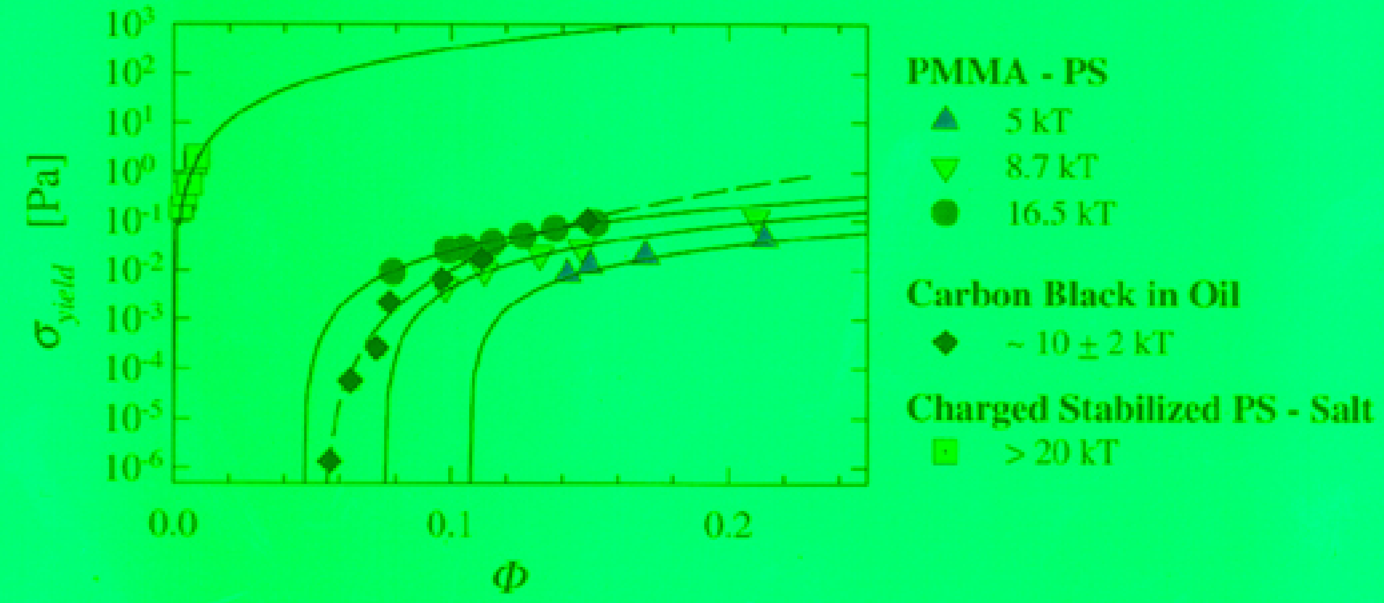
$$\sigma_y = \sigma_o \, (U - U_c)^{\nu}$$



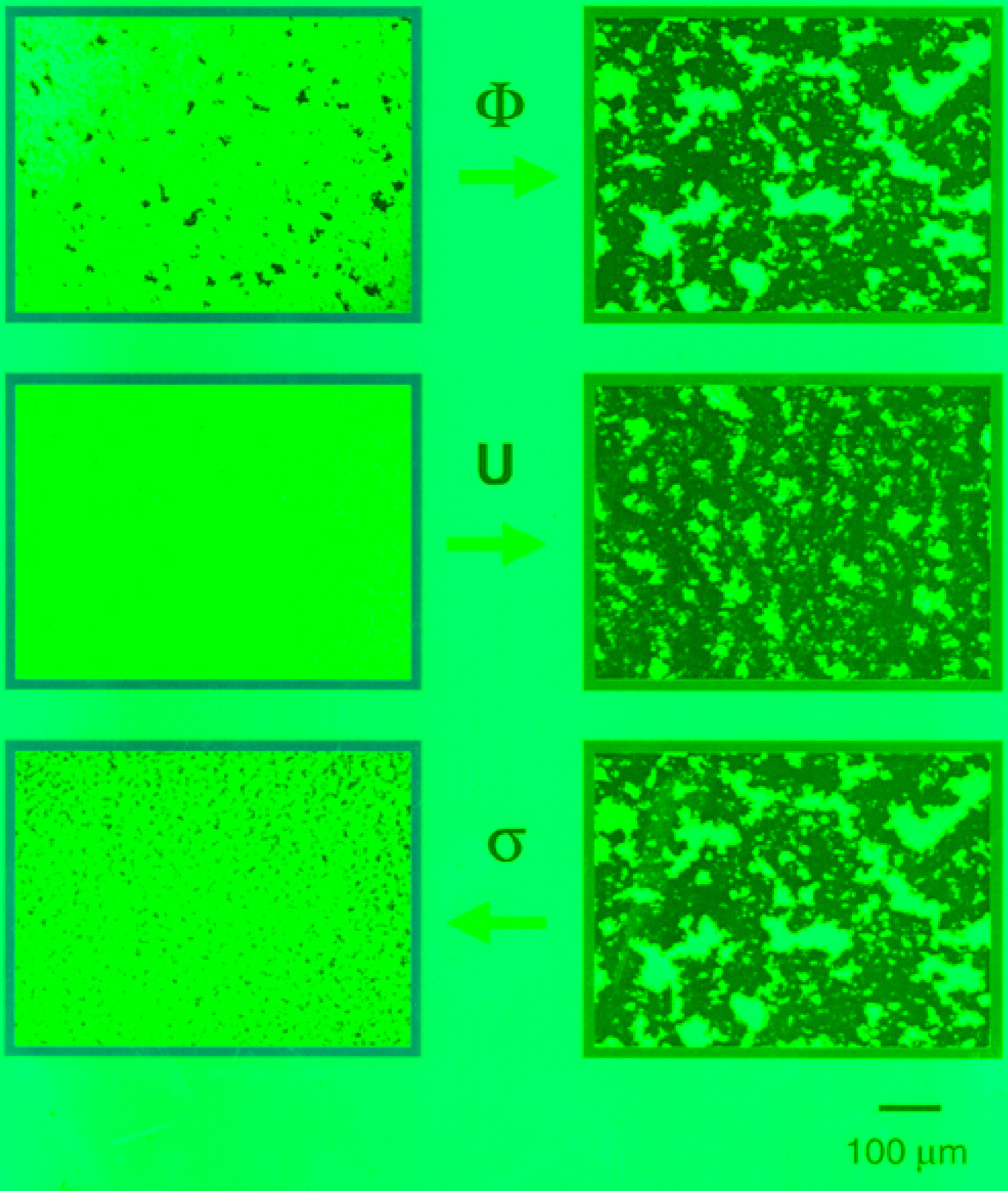
$\Phi - \sigma$ Plane   U = const



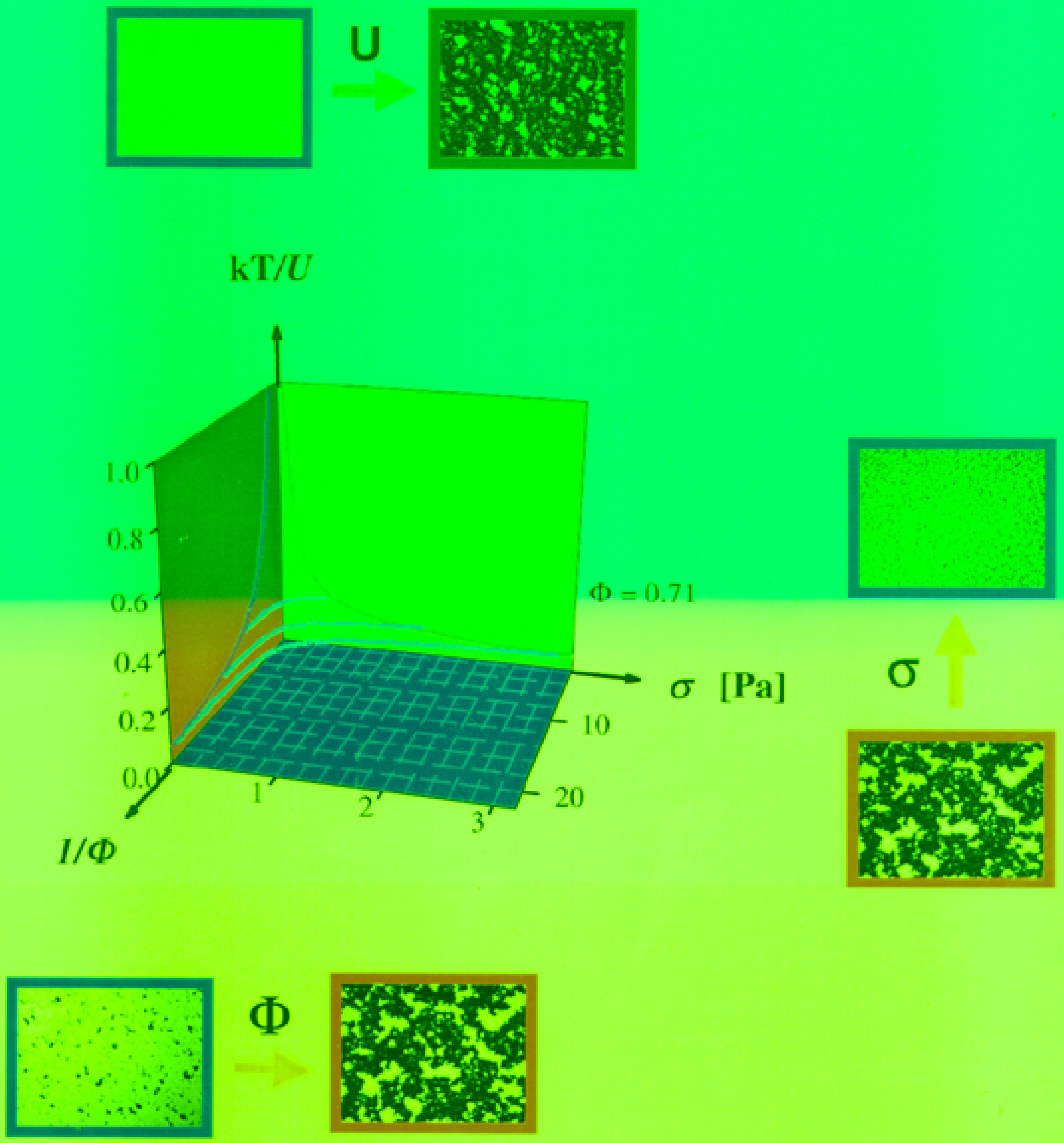
$$\sigma_y = \sigma_o (\Phi - \Phi_c)^{\mu}$$



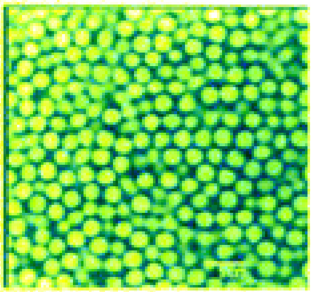
Fluid-Solid Transitions   Carbon Black in Oil



Fluid-Solid Transitions in Attractive Systems

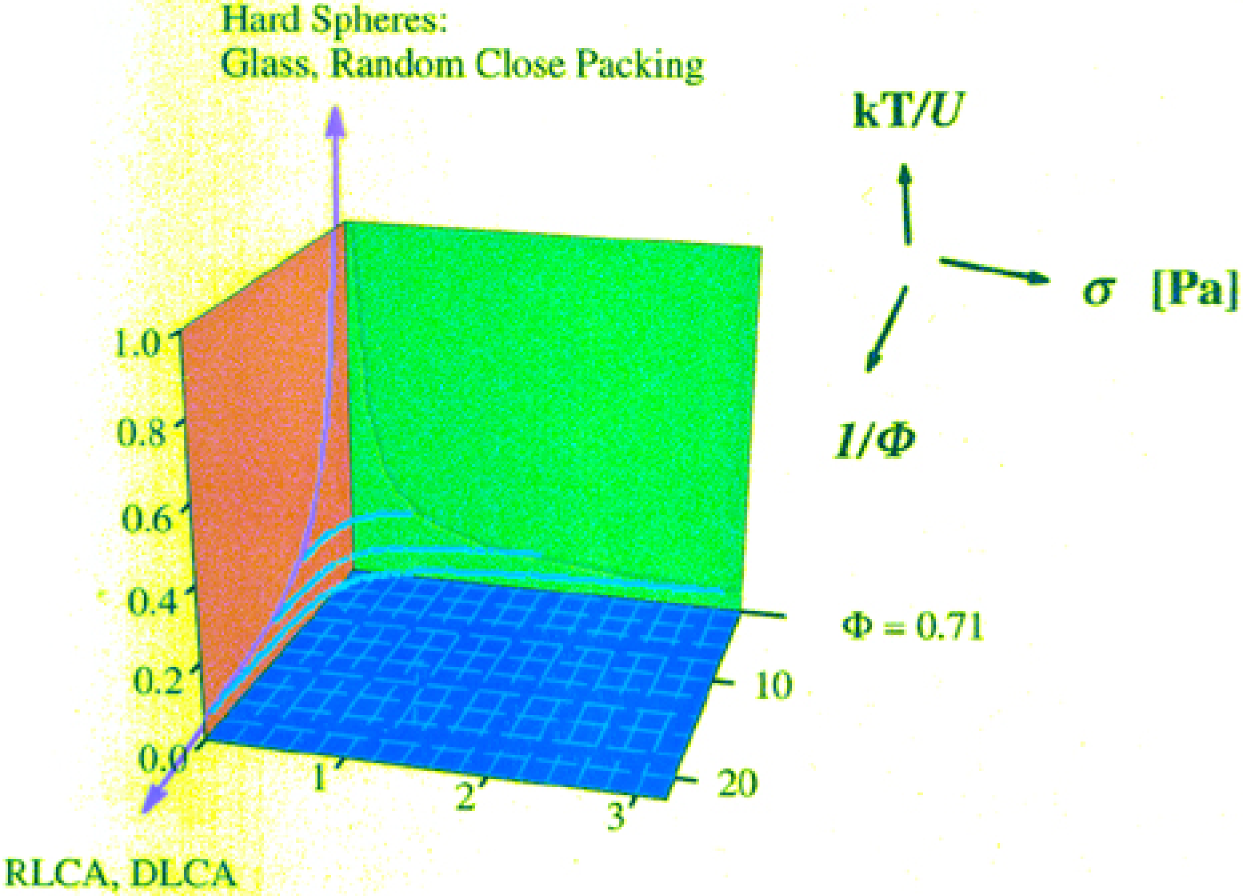


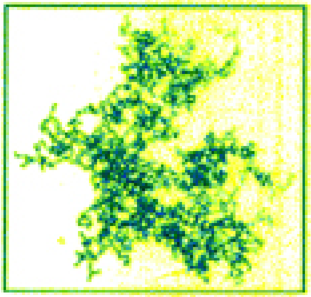
Jamming in Colloidal Suspensions



$\Phi \sim 0.6$

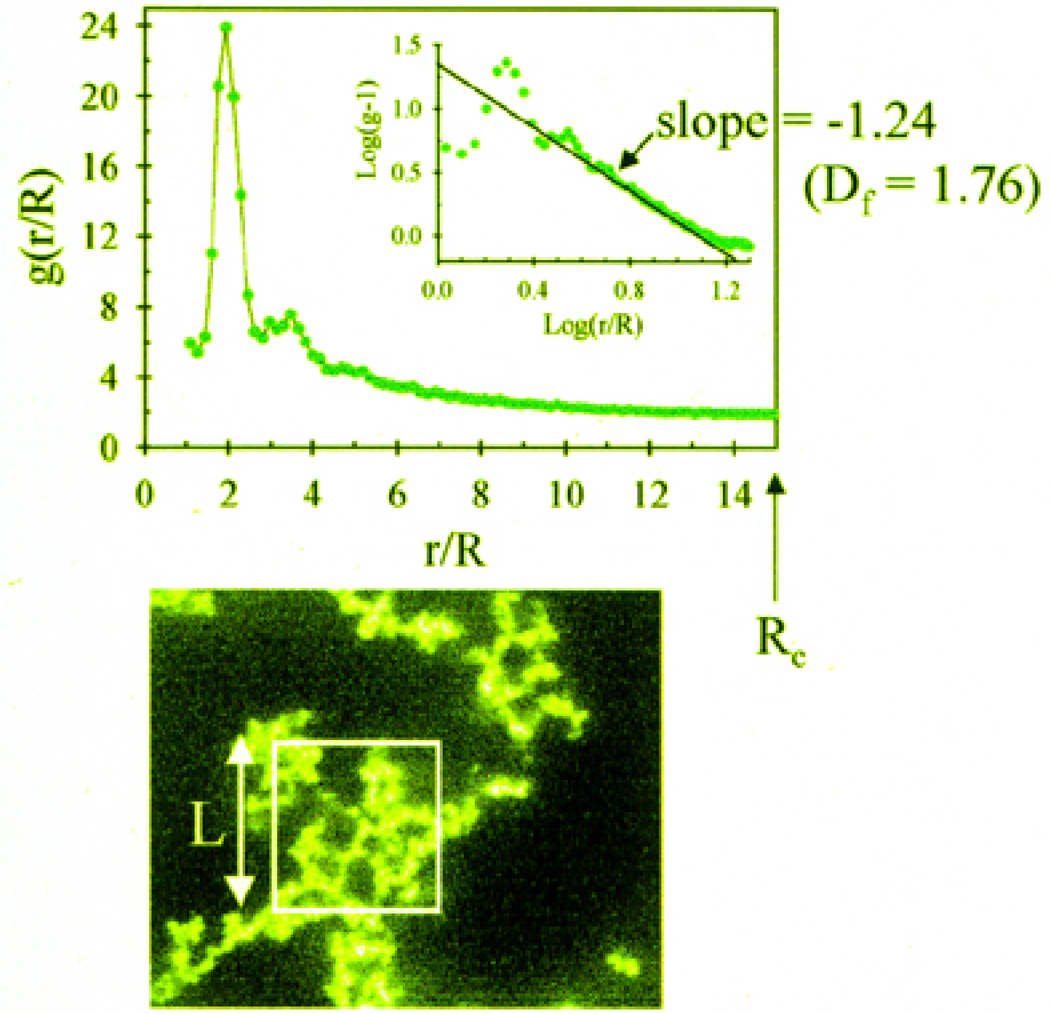
Eric Weeks





$\Phi \sim 10^{-6}$

Fractal scaling



$M \propto L^{D_f}$

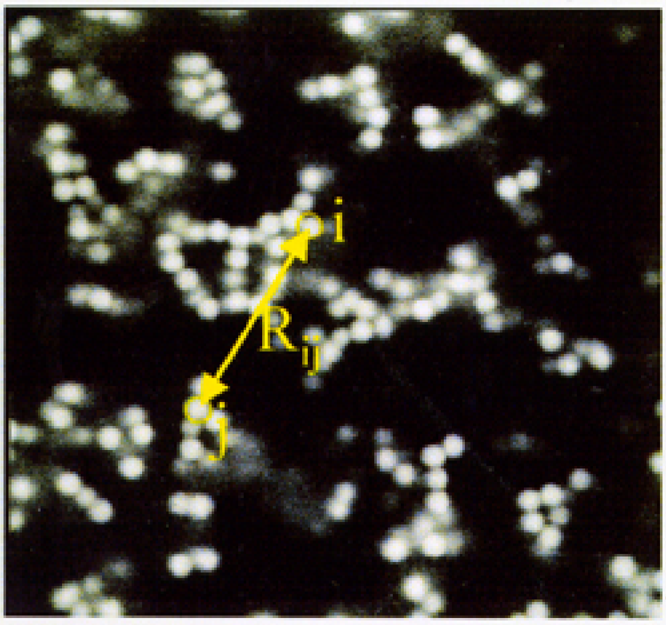
$\phi(L) \propto L^{D_f - 3}$

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

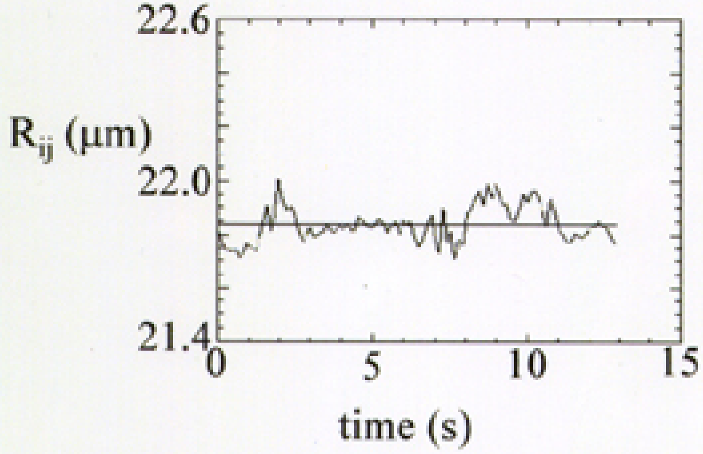
$R_c = \phi^{(1/D_f\text{-}3)}$

Review: Poon *et al*, Curr. Op. Coll. Int. Sci., '98

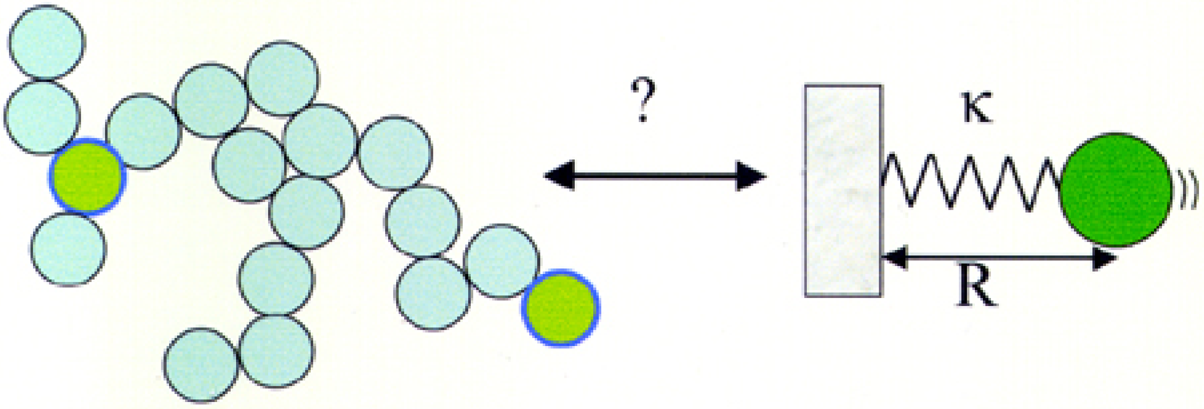
Dynamics (thermal motions)



$U = 13.6\ k_BT$,
$\alpha = 8$
$\phi = 0.04$



Spring model

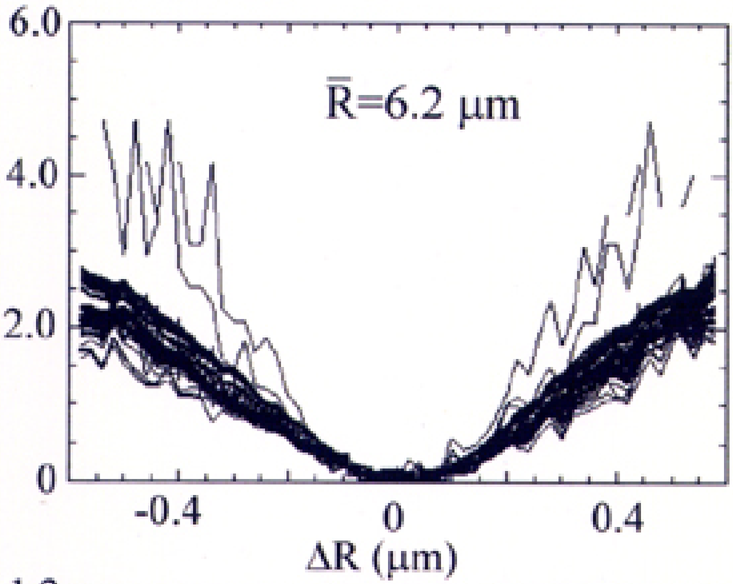


κ depends on local structure

Gel-mediated interactions

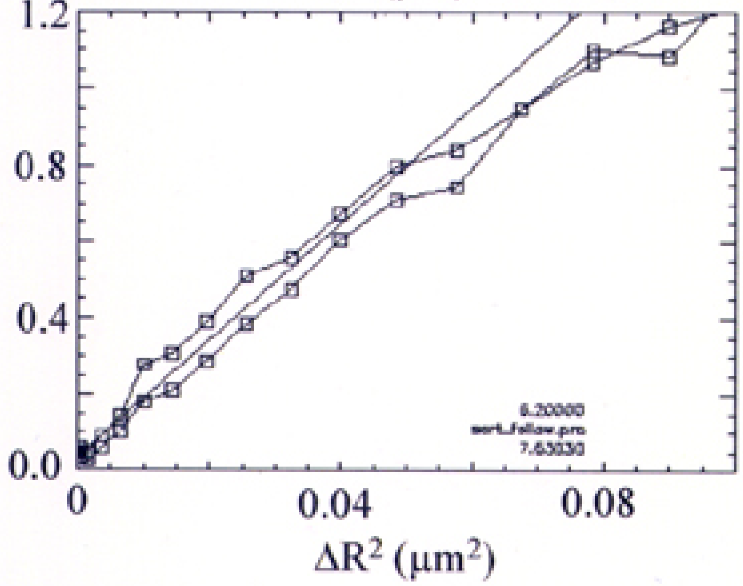
$$P(\Delta R) \propto e^{-U(\Delta R)/k_B T}$$

-ln (P)= U/k_BT



all pairs
of
particles
with
$\bar{R}$=6.2
(~100)

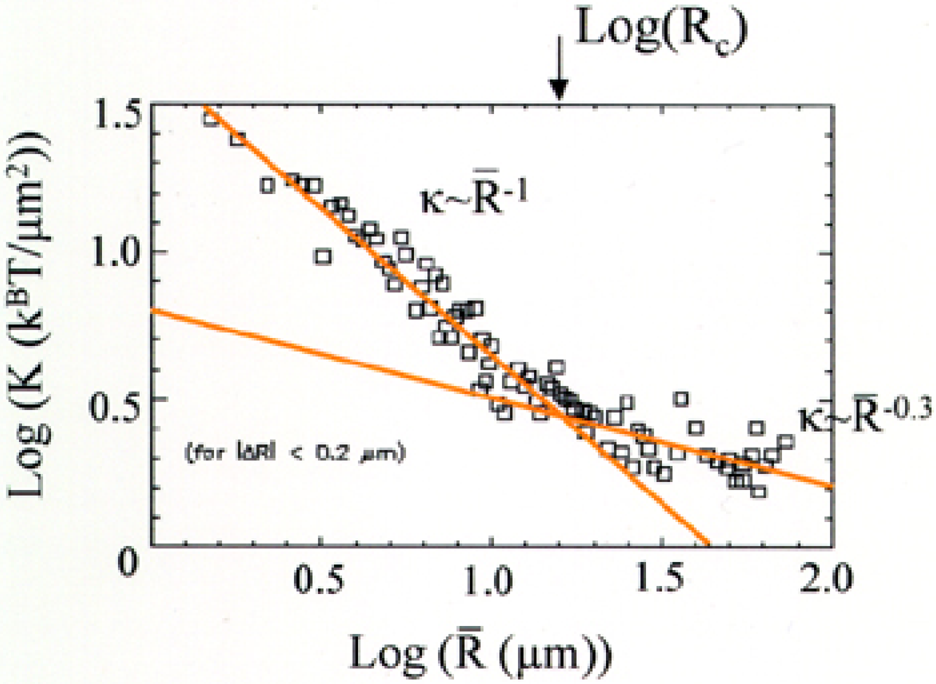
-ln (P)= U/k_BT



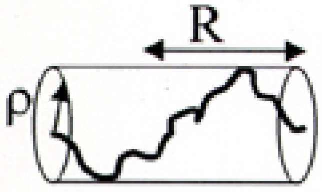
average
over all
pairs with
$\bar{R}$=6.2

- spring-like potential

κ vs. $\bar{R}$



- Kantor & Webman, PRL **52**, 1891 ('84)
  - $\kappa \sim R^{-3}$
    (single fractal chain, bending resistance)
  - $\kappa \sim R^{-1}$
    (single fractal chain, no bending resistance)



$k_c \propto G\rho^2/R$

$k_b \propto G\rho^4/R^3$

- First direct view of origin of gel's elasticity