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Glassy Dynamics & Mechanical Properties of Quiescent and Stressed Particle Suspensions

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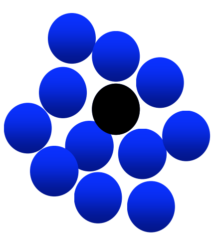
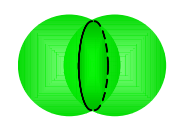
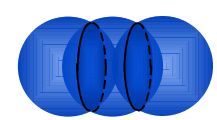
GOALS : "Simple", Microscopic, Predictive Dynamic Theory
Beyond MCT :Activated Barrier Hopping + Nongaussian Dynamic Fluctuations
Nonlinear Viscoelasticity, NONspherical Object
HARD SPHERES : Quantitative confrontation with Experiment & Simulation



Quiescent → **Driven (deformed)**



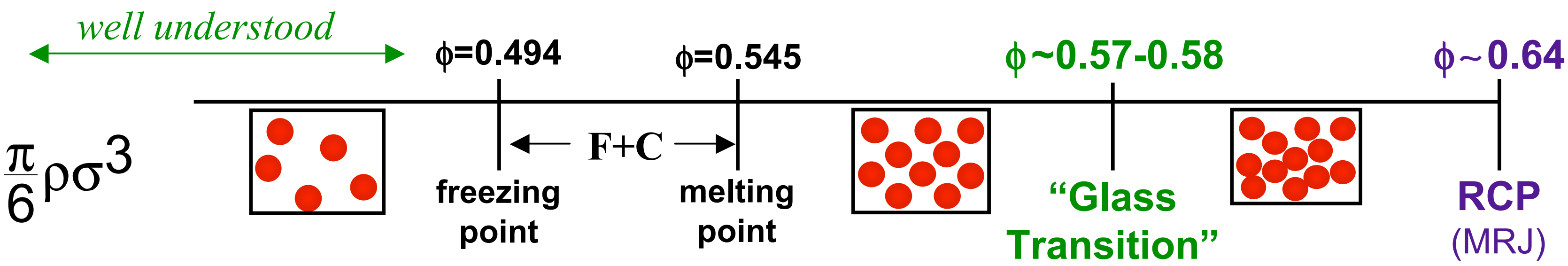
Hard Spheres → **"Colloidal Molecules"**

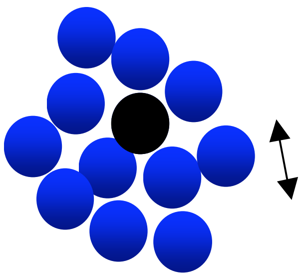


models for other systems :Atomic Liquids ; microgels, pastes, emulsions, charged,…

"Athermal" Glassy HARD SPHERE Colloidal Suspensions

$\phi \equiv \frac{\pi}{6}\rho\sigma^3$





$\sigma \sim 100$ nm -1 μm

+ ***solvent < nm***

ALL ENTROPY
Excluded Volume

Real World Complexities

Polydispersity
Gravity
Aging
Hydrodynamics

"GLASS TRANSITION" : *kinetic crossover…ala thermal glass* T_g

vs. *True Singularity ?*

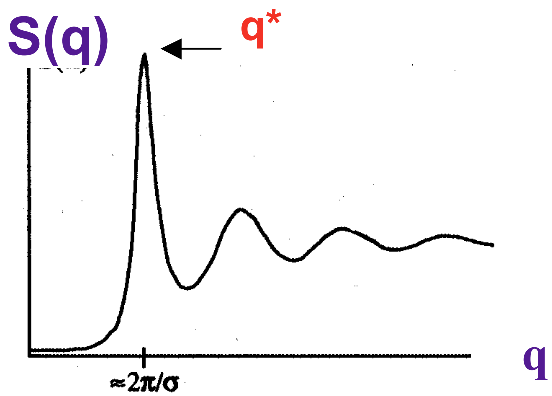
Relaxation Time > Expt time scale ~ 1000 - 10,000 secs…***.No Singularities below RCP ?***

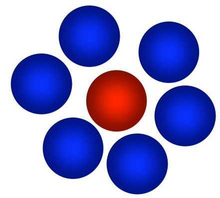
Experiments (*and simulations*) **probe "precursor" regime**

Colloids: **$10^{3\text{-}4}$** change in η, D **vs.**

Thermal liquids: **10^{14}** ***Brownian time*** $\tau_0 = \sigma^2/D \sim$ **0.01-10 sec**… *very large*

"Average" Dynamical Behavior: Ideal Mode Coupling Theory





Gotze, Sjogren, Leutheusser, ...1986-

SLOW Cage Scale $(\delta\rho)^2$

Relate Local Structure, S(q), & Dynamics

Gaussian Mean Field Theory ***for S(q,t)***

PREDICTS "ideal" dynamic glass : a strict LOCALIZATION transition << RCP

v/v EXPTS : **GOOD** for many ***AVERAGE*** properties ***if FIT*** location of singularity

$$\tau \sim \eta \sim D^{-1} \sim (\phi_C - \phi)^{-\nu}$$

$\nu \sim 2.5$, $\phi_C \sim$ 0.57-0.58

"critical power law" *over few orders magnitude*

Shear Effects : 2002- ; Fuchs/Cates, Reichman……*Useful But BUILT on Singularity*

…Divergence ("ideal glass") **NOT** real….rather signals ***Dynamic Crossover***

new mode of transport : ***Activated Barrier Hopping***…..**when important ?**

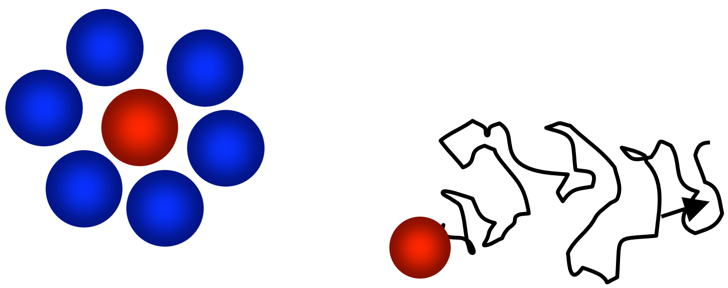
Nongaussian Effects and Rare Events

Multiple Simulations (Reichman ; Heuer; Berthier…) + ***Confocal Colloid Expts see :***

* **HOPPING processes** important ***BEFORE*** *empirically deduced* (**fit**) MCT transition

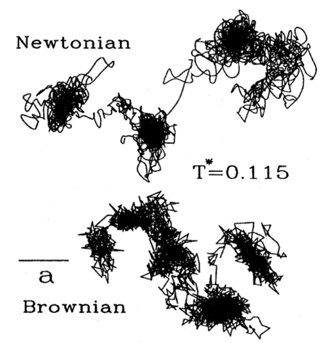
Trajectories change character

"high T", "low ϕ"



"smooth, hydrodynamic like"

"Solid - Like"…intermittent hopping



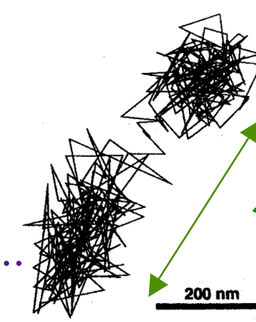
Hansen et al, 1987

~ *MCT temperature*

Weeks & Weitz

ϕ=0.56

Sillescu ; Kegel,…



~ σ/2

* Multiple Strong **"Dynamic Heterogeneity" Effects @ Single Particle level**

….***NOT predicted by MCT***

OUR GOAL : **Build on MCT but** :

treat Entropic Barriers & Hopping, ***AVOID*** *Fitting,* ***NO*** *Singularities below RCP*

Saltzman & KSS
JCP, 2003

Activated Barrier Hopping Theory

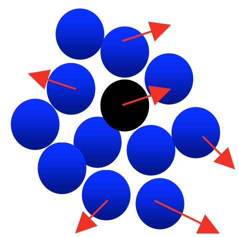
DERIVATION : KSS, JCP, 2005

Simplest **SINGLE** Particle Dynamics Level

Seek Stochastic Equation of Motion NOT *closed equation for time correlation functions*

Dynamic **DFT**

$$\hat{\rho}_s(\vec{r},t) = \delta\left(\vec{r}-\vec{r}_i(t)\right)$$



r(t) = *scalar **displacement** from initial position*

Solid State View

Local Equilibrium Approx + *"on average" Caging constraints via **S(q)***

$$\frac{\partial\hat{\rho}_s(\vec{r},t)}{\partial t} = D_s\nabla^2\hat{\rho}_s(\vec{r},t) + D_S\nabla\hat{\rho}_s(\vec{r},t)\int d\vec{r}\,'\,\hat{\rho}(\vec{r}\,',t)\nabla V(\vec{r}-\vec{r}\,') + \eta_i\nabla\hat{\rho}_s(r,t)$$

CONTRACT to lowest level **+** Average over local packings **+** Local Equilibrium Approx

$$\frac{\partial}{\partial t}r_i^2(t) = 6D_s + 2r_i(t)\eta_i(t) - 2r_i(t)\int d\vec{r}\int d\vec{r}\,'\,\overline{\hat{\rho}_s(r,t)\hat{\rho}(r',t)}\nabla V(r-r')$$

Local Equilibrium

$$\frac{\rho^{(2)}\left(\vec{r},\vec{r}\,';t\right)}{\rho^{(1)}\left(\vec{r};t\right)} \approx \rho g\left(|\vec{r}-\vec{r}\,'|\right)$$

Sum Rule →

$$-2r_i(t)\int d\vec{r}\,\bar{\rho}_s(r,t)\nabla\frac{\delta\bar{f}_{exc}}{\delta\bar{\rho}_s(r)}$$

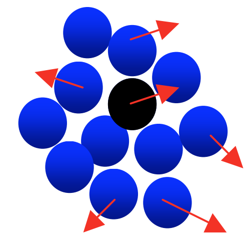
Instantaneous Caging Force

ala Ramakrishnan-Yussoff DFT ***BUT*** ***"coarse-grained"*** *NOT ensemble-averaged*

$$\bar{f}_{exc} \underset{RY}{\cong} -\frac{1}{2}\int \frac{d\vec{q}}{(2\pi)^3} C(q) \overbrace{N^{-1} \sum_{i\neq j} e^{i\vec{q}\cdot R^0_{ij}}}^{\approx \rho h(q)} e^{-q^2 r^2/3}$$

Intermolecular liquid pair correlation

ala Einstein solid
Dynamic Mean Field
"closure"



Nonlinear Stochastic Langevin Equation…force balance

$r(t=0)=0$

$$\zeta_s \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial \bar{r}} F_{eff}(r(t)) + \eta(t)$$

white noise

$$\beta F_{eff}(r) = -3\ln(r) - \frac{1}{3}\int \frac{d\vec{q}}{(2\pi)^3} C^2(q) \rho S(q) e^{-q^2 r^2/3} \equiv F_{ideal} + F_{cage}$$

Time Local
Displacement
-Dependent
Trapping
"Field"

Liquid Structure
Caging Forces

Favors :	**Delocalized** ***Liquid***	**Localized** ***Solid***

ϕ–dependent competition

Source of material specific predictive power…ala MCT

$$S^{-1}(q) = 1 - \rho C(q)$$

Analogies & Reduction to *Naïve* Ideal MCT

$$\zeta_S \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial r} F_{eff}(r(t)) + \eta(t) \qquad \langle \eta(t)\,\eta(0)\rangle = 2\zeta_S k_B T\,\delta(t)$$

Stochastic Trajectories…*destroys Ideal Glass State,* ***Dynamical Crossover..”onset”***

Resembles **Kramers** theory of chemical reactions, **Model A** of dynamic critical phenomena
…BUT F_{eff} *not an* ***Equilibrium*** *Free Energy nor Potential-of-Mean Force*

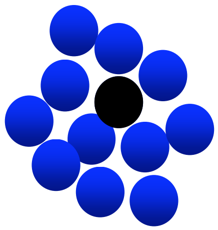
* **RECOVER** ***Naïve Ideal MCT*** *Transition* IF :

Kirkpatrick & Wolynes
PRA, 1987

Drop Noise OR Gaussian approximation for **< $r^2(t)$ >**

→ *Dynamic Order Parameter :* ***Mean Localization Length***

$$r^2_{LOC} \equiv \langle r^2(t \to \infty)\rangle$$



Debye-Waller

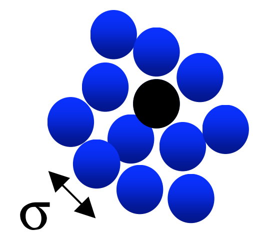
$$\frac{1}{r^2_{LOC}} = \frac{1}{18\pi^2}\int_0^\infty dq\, q^4 C^2(q)\rho S(q)\; e^{-\frac{q^2 r^2_{LOC}}{6}(1+S^{-1}(q))}$$

→ ***IDEAL GLASS at*** ϕ_C

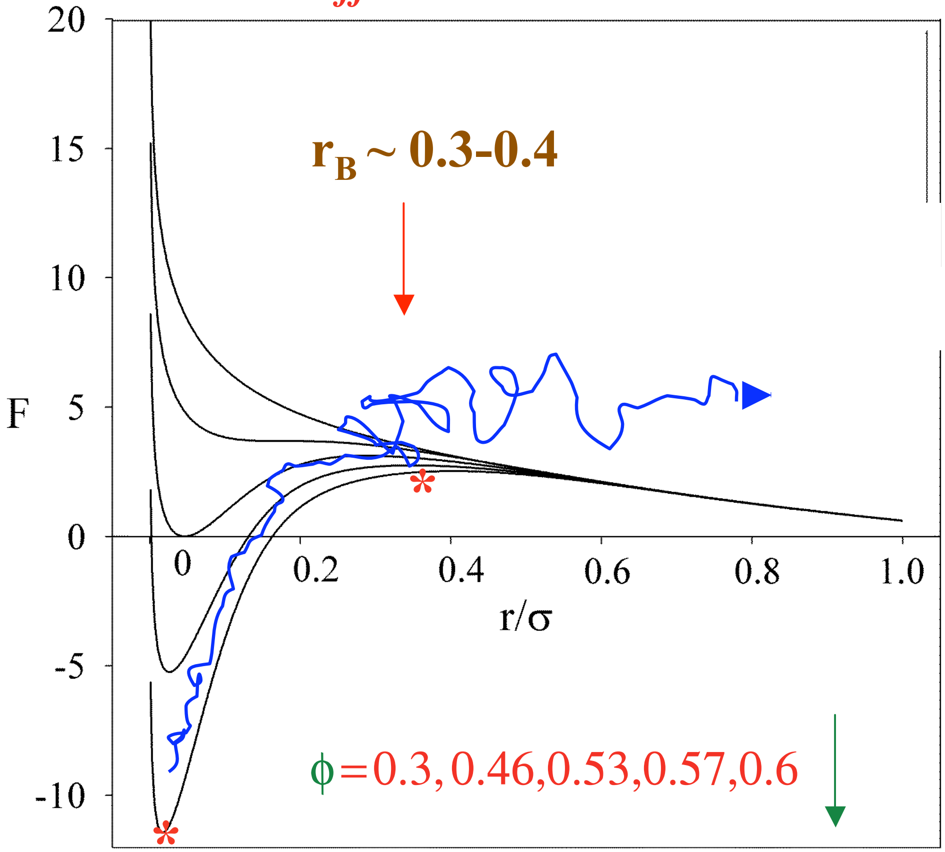
Nonequilibrium "Free Energy" and Dynamical Crossover

$\phi < \phi_C \sim$ **0.432** (PY input) → Diffusive, smooth motion

$\phi > \phi_C$ → Activated Hopping, abrupt / intermittent displacements



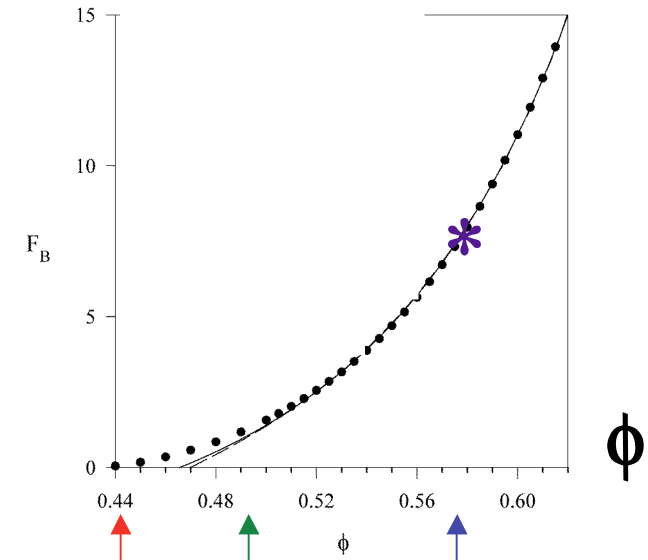
$F_{eff}(r)$ …"*scalar landscape*"



r_{LOC}

Displacement, **r(t)**

Entropic barrier $F_B(\phi)$



φ

nMCT Freezing Kinetic Vitrify

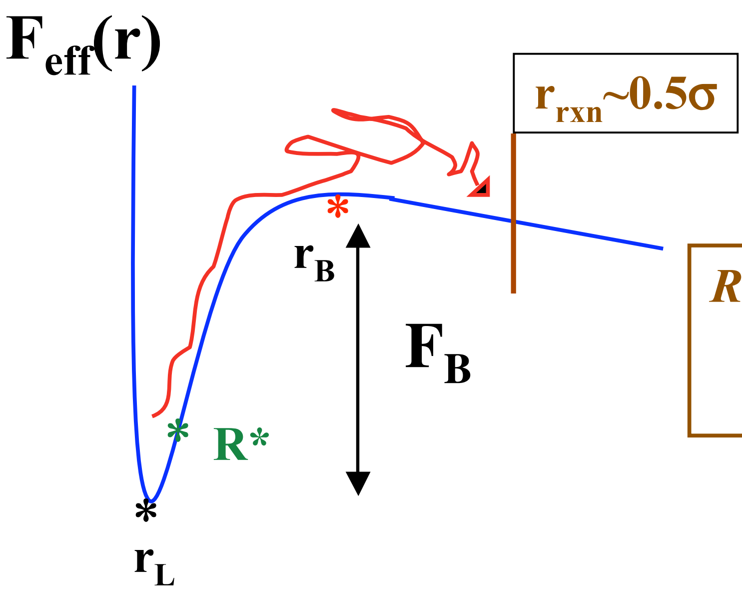
~ Negligible $\phi < 0.49$ ….normal fluid

~ 7 @ EXPT "kinetic glass transition"

Glassy Dynamics : *hopping over "low" barriers*

Rich "Self - Dynamics"

$$\zeta_s \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial r} F_{eff}(r(t)) + \eta(t)$$



4 Local Length Scales

Reaction Point :Cage Escape, *negligible localizing force*

Crossover to 3-d Fickian Diffusion

$$\zeta_{tot} = \zeta_s + \zeta_{HOP} \quad , \quad D_{HOP} = r^{+2} \langle \tau_{rxn}^{-1} \rangle / 2 \equiv k_B T \zeta_{HOP}^{-1}$$

Maximum Caging Force at R*

....related to "yielding"

Connections between : *Transient Localization*
Early Cage Escape (late β)
final Alpha Process

Average Scalars (analytic)

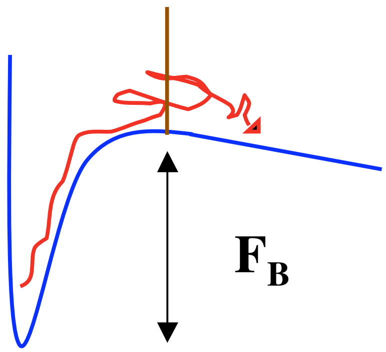
Brownian Trajectories → Time Correlations; → Nongaussian effects

Nonlinear Viscoelasticity, Colloidal Molecules,….

Purely Dynamical
NOT structure fluctuations

Quasi-Analytic Theory for Average Scalars

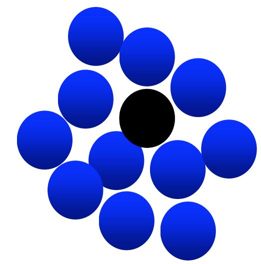
JCP, 2003



Diffusion-Controlled ***Kramers theory***

$$\frac{\bar{\tau}_{hop}}{\tau_0} = \frac{2\pi\,(\zeta_s/\zeta_0)}{\sqrt{K_0\,K_B}}\,e^{F_B}$$

~ alpha or flow time



$\tau_0 = \sigma^2/D_0$ ***Brownian time***

Transport Coefficients (*Green-Kubo*) : *Bridge multiple regimes*

$$D = \frac{k_B T}{\zeta}$$

$$\zeta = \zeta_s + \frac{1}{3}\beta^{-1}\int_0^\infty dt \int \frac{d\vec{q}}{(2\pi)^3}\, q^2\, C^2(q)\, \rho S(q)\, \Gamma_s(q,t)\, \Gamma_c(q,t)$$

$$\eta = \eta_\infty + \frac{k_B T}{60\pi^2}\int_0^\infty dt \int d\vec{q}\, q^4 \left(\frac{\partial}{\partial q}\ln S(q)\right)^2 \Gamma_c^2(q,t)$$

Cohen et al theory (PRE, 1997)

"binary collision in a mean field cage approximation"

works well in **"normal fluid"** regime : $\phi < 0.5$

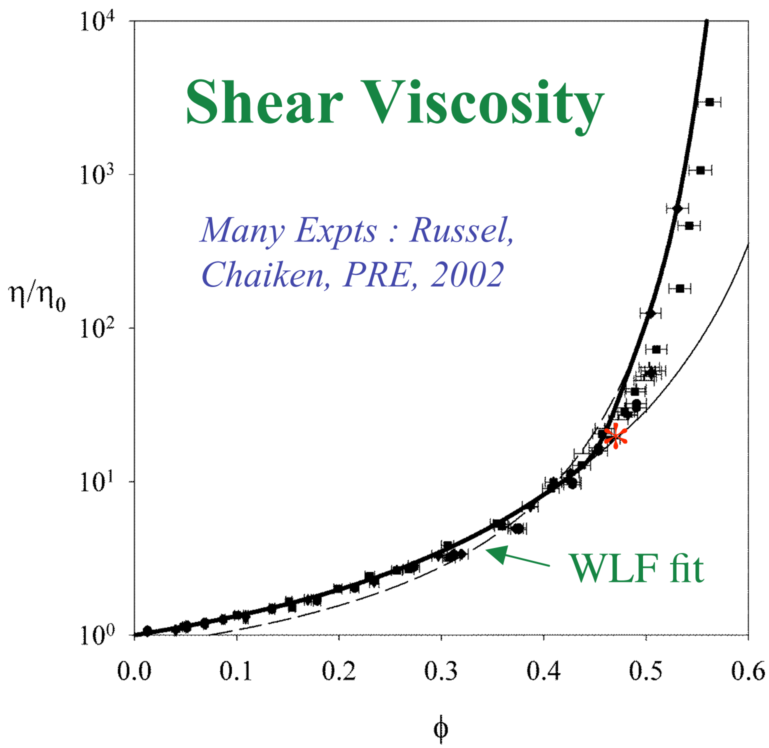
Include "hopping friction" : $\zeta_s \rightarrow \zeta_s + \zeta_{HOP}$

NOT rigorous, but introduces NO adjustable parameters

Theory vs. Experiment

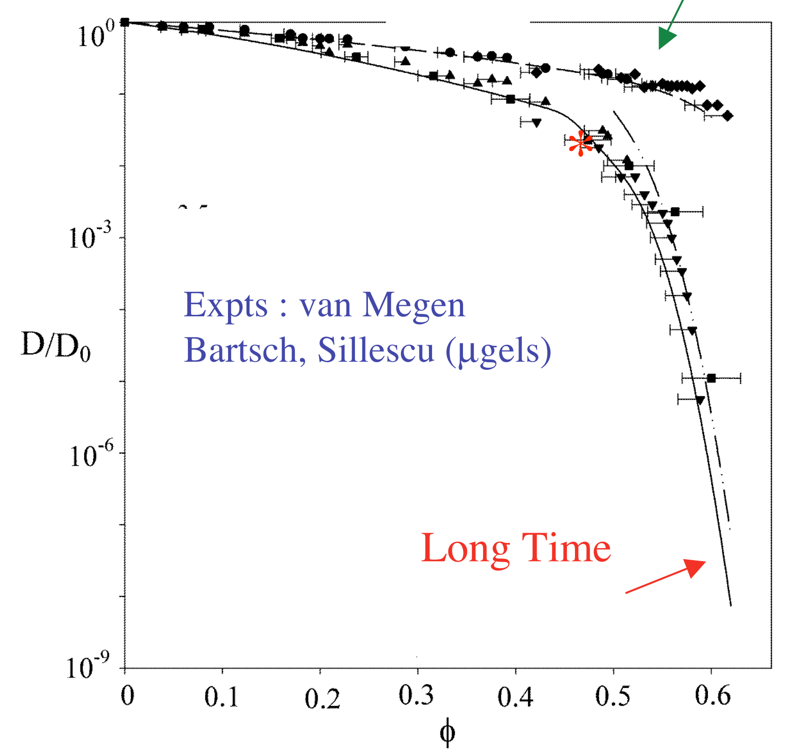
NO fitting Parameters

Single Theory for ALL Volume Fractions



“low” Barriers Control $\phi > 0.5$

Self-Diffusion



FITS to *(essential)* ***Singular*** forms

Adams-Gibbs Entropy

Free Volume

Ideal MCT

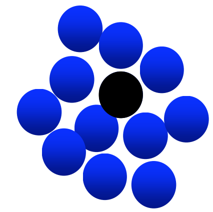
$$\exp\left(\frac{C}{\Delta S_{config}}\right), \quad \exp\left(\frac{B}{\phi-\phi_C}\right), \quad (\phi_c-\phi)^{-2.5}$$

FIT ϕ_c

Full Numerical Solution

Saltzman & KSS

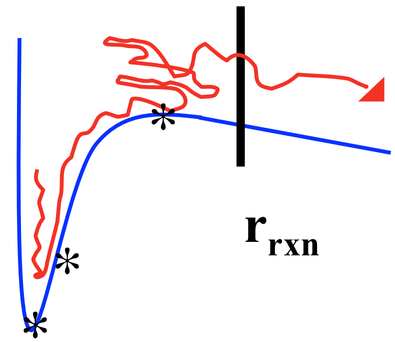
JCP & PRE, 2006



Brownian Trajectories

$$\zeta_s \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial r} F_{eff}(r(t)) + \eta(t)$$

F_{eff}(r)



Relaxation Time Distribution

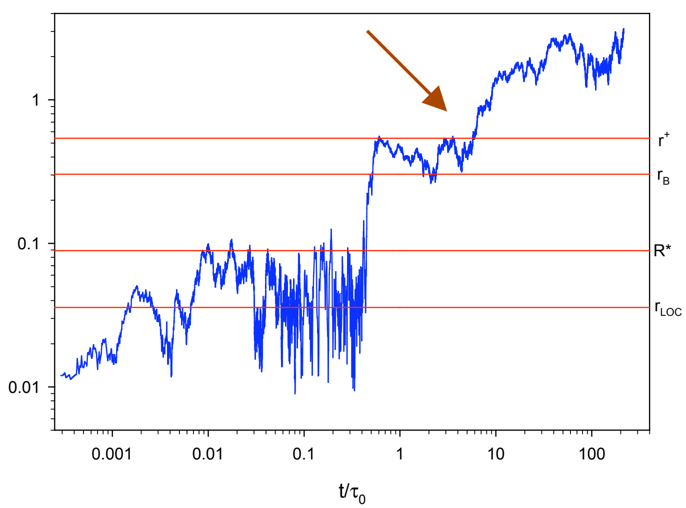
"Heterogeneity"

Intermittent dynamics

→ **ALL Single Particle Time Correlations**

r(t)/σ

ϕ=0.55 ; Barrier ~ 5



Reaction point

Barrier

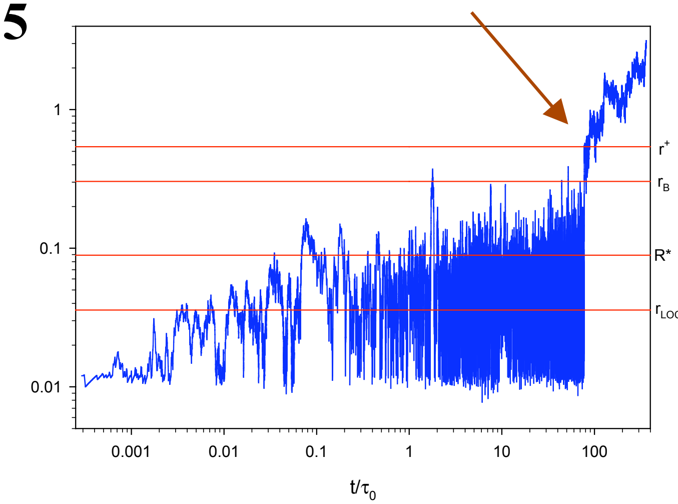
Maximum force

Localization length

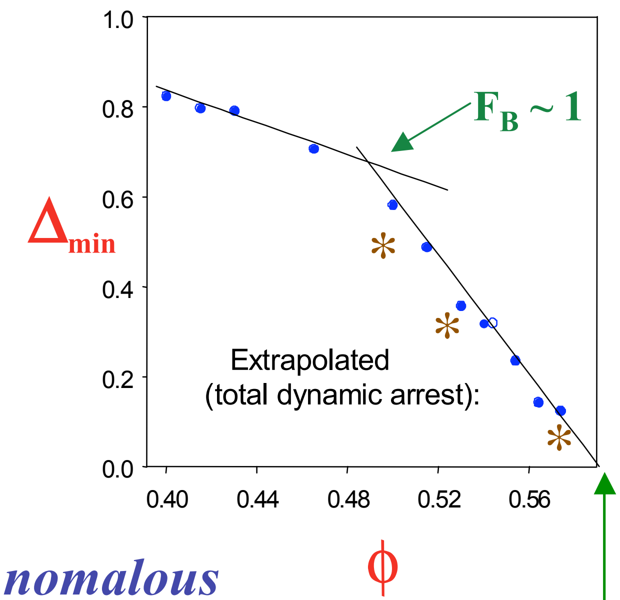
Re-crossings

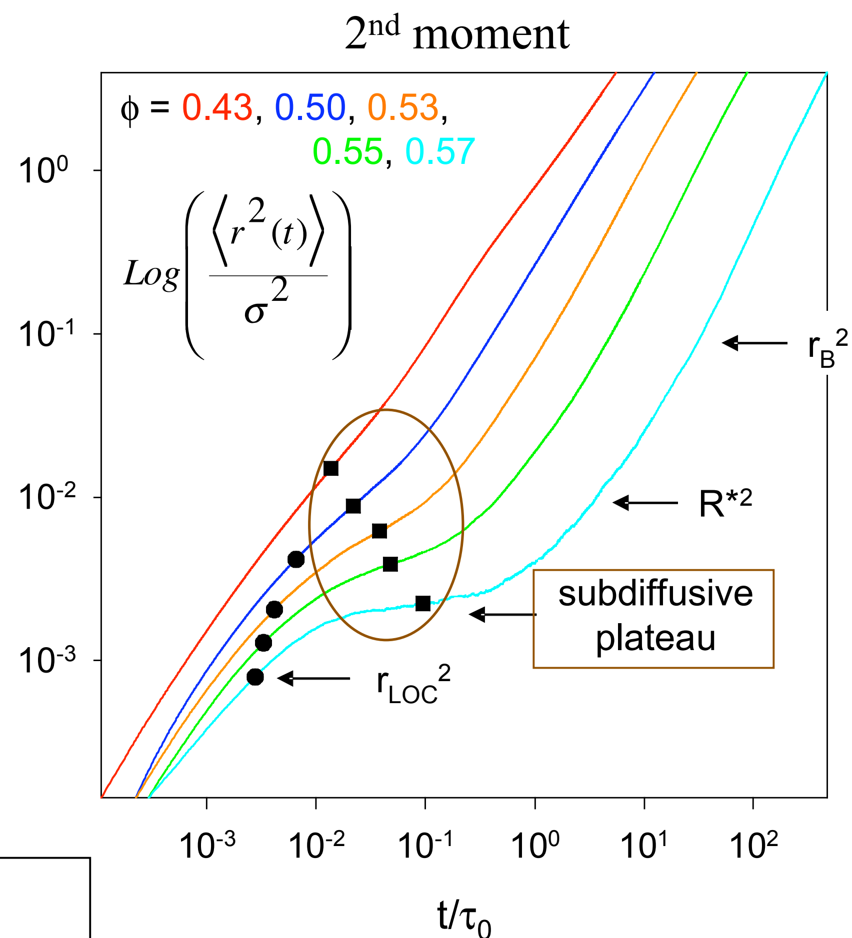
Large Fluctuations

FAST "reaction"



Mean Square Displacement & Anomalous Diffusion





Anomalous Diffusion

$$\langle r^2(t)\rangle \propto t^{\Delta_{min}}$$

$\phi_c \sim 0.58$

~ EXPT + MCT empirical fits

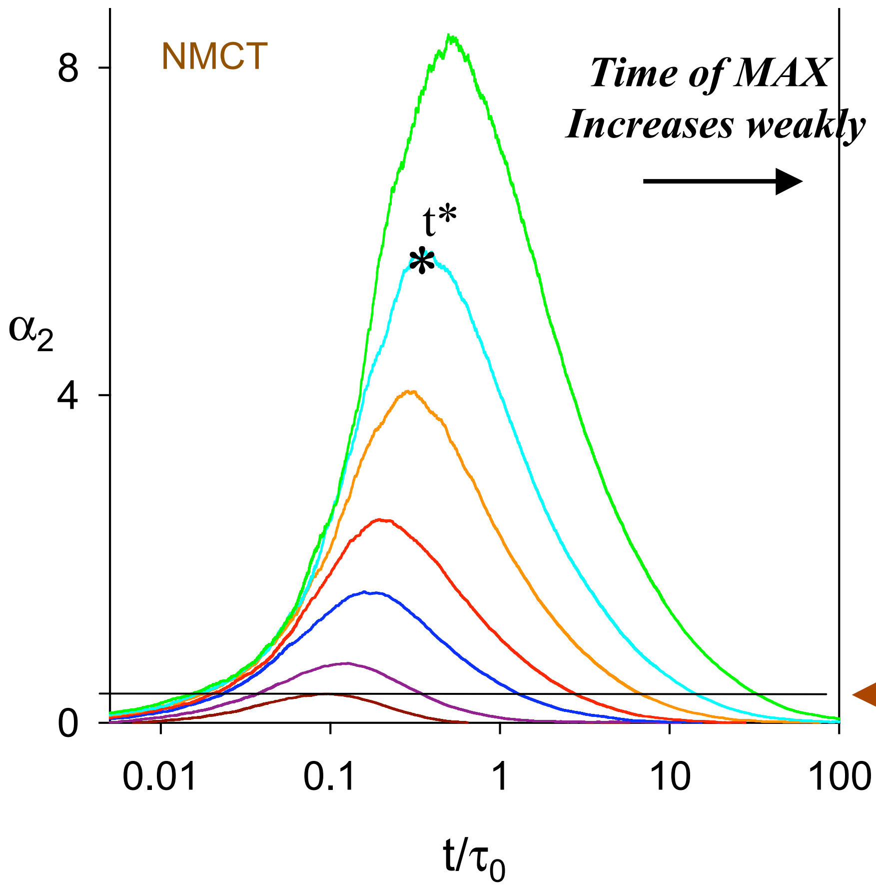
van Megen Dynamic Scattering Expts *

PRE, 2005 *~ linear reduction of minimum* $\Delta(\phi)$

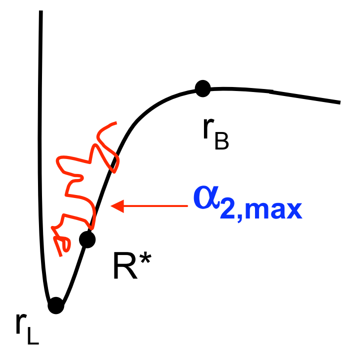
NONgaussian Parameter

$$\alpha_2(t) \equiv \frac{3}{5}\frac{\langle r^4(t)\rangle}{\langle r^2(t)\rangle^2} - 1$$

ϕ = **0.43**, 0.465, 0.5, 0.515, 0.53, 0.54, **0.55**

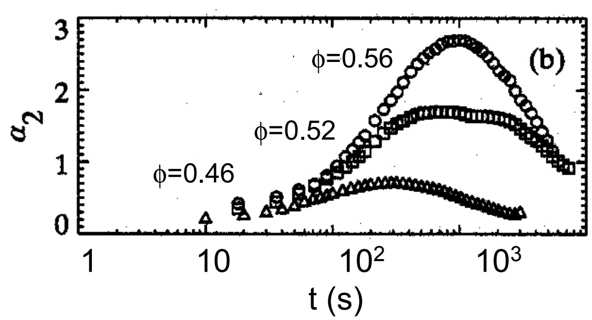


Time of MAX Increases weakly →



Full MCT :
$\alpha_{2,max}$ ~ **0.33**
~ OUR result at NMCT

EXPTS : Weeks, Weitz, PRL, 2002

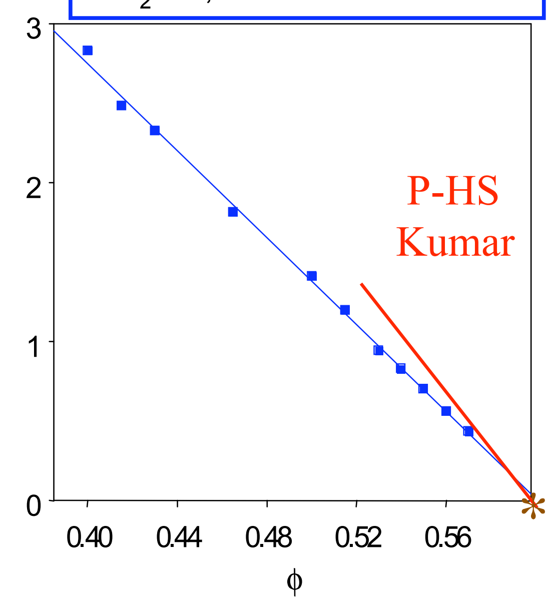


P-HS Simulations
Reichman et. al.
$\alpha_{2,max}$ ~ **5**, ϕ ~ 0.55

Max NGP correlated with

* Late β / early α (Weitz expt)
  r(t*) ~ 0.3 --> 0.1
* Cage-Restoring Force :
  $$\alpha_{2,max} \sim \left(f^*\right)^{7/4} \sim e^{31\phi}$$

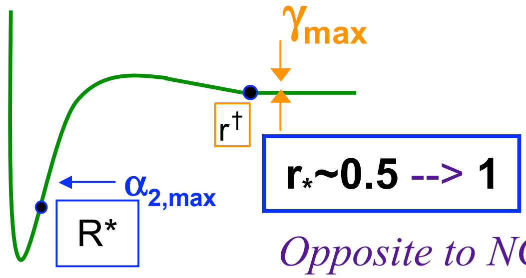
$\{\tau_{\alpha_2}\alpha_{2,max}\}^{-1/4}$ vs. ϕ



NEW Nongaussian Parameter

$$\gamma(t) = \frac{1}{3}\left\langle r(t)^2 \right\rangle \left\langle \frac{1}{r(t)^2} \right\rangle - 1$$

Flenner & Szamel PRE, 2005

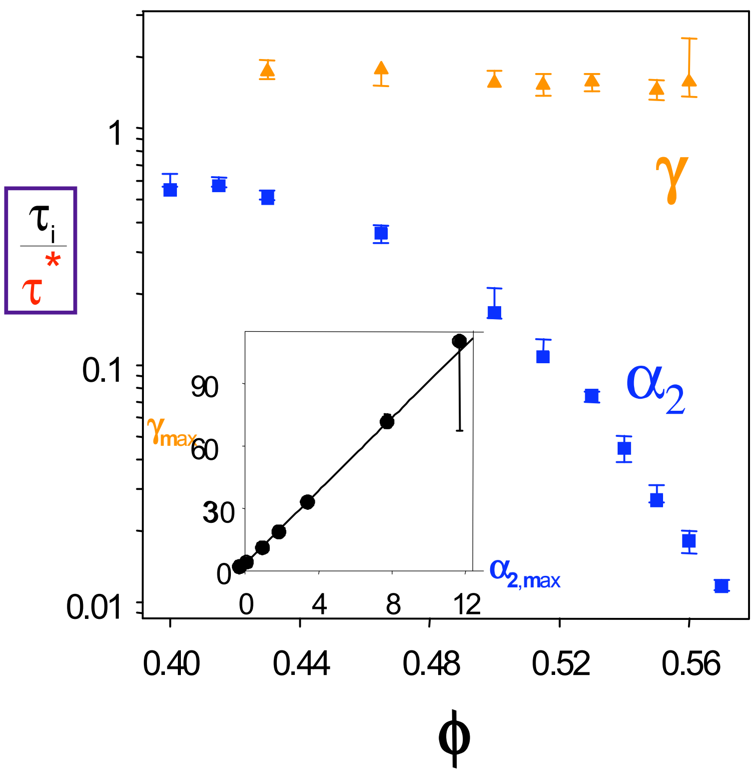


Opposite to NGP trend

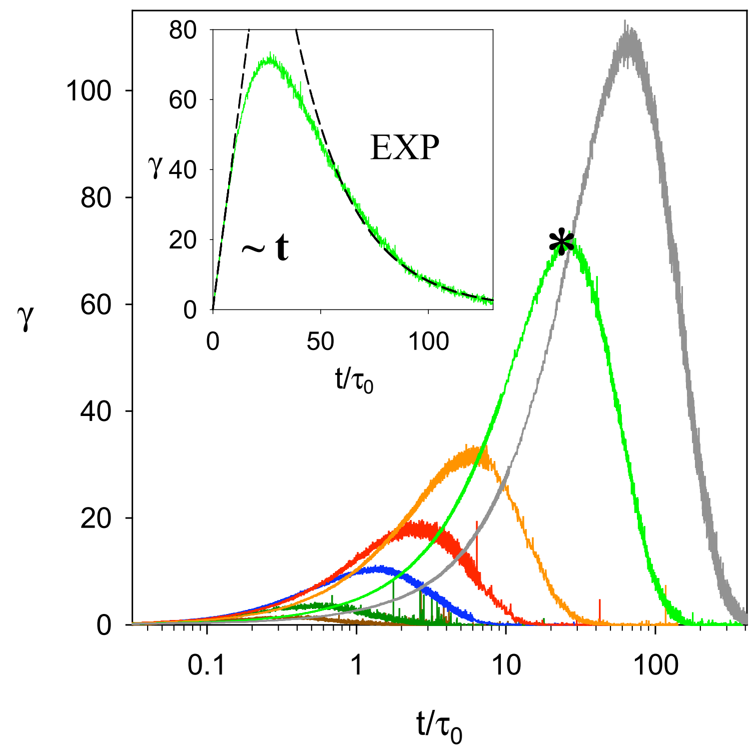
Probes LONG time alpha process

Full Simulations find :

- Timescale of MAXIMUM tracks ~2τ^* *...ala $\chi_4(t)$*
- Amplitude LARGER than classic NGP
- **Different Shape** : *sharp long time cutoff*

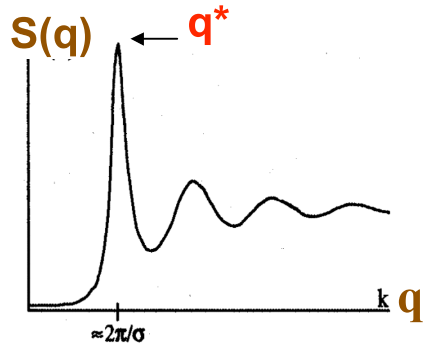


ϕ = 0.43, 0.465, 0.5, 0.515, 0.53, 0.55, 0.57

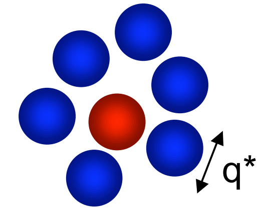


"Heterogeneity" of EARLY Cage Escape
& FINAL Alpha Relaxation strongly COUPLED

Incoherent Dynamic Structure Factor :



CAGE Scale



$$F_S(\vec{q},t) = \langle \exp[i\vec{q}\cdot\vec{r}(t)] \rangle = F.T.\langle \delta(\vec{r}-\vec{r}_j(t)) \rangle$$

Mean **Alpha Time**

$$F_S(q^*, \tau^*(\phi)) \equiv e^{-1}$$

Power Law fit $\tau \sim (\phi_C - \phi)^{-\gamma}$

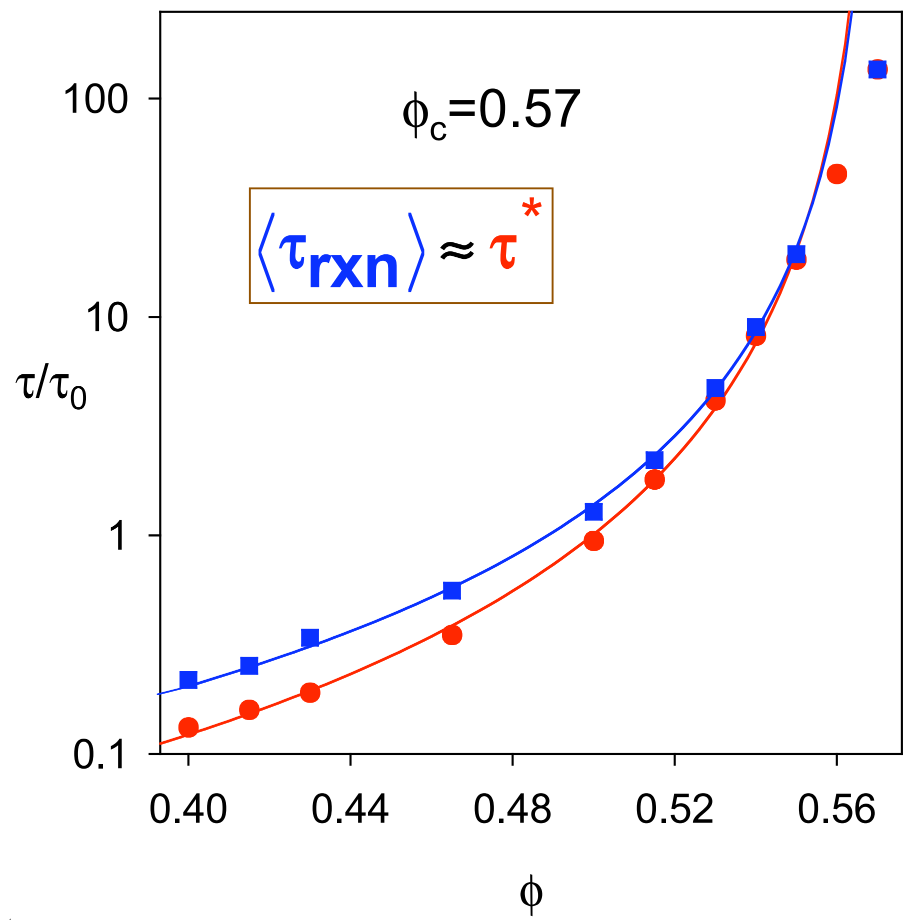
assume : $\phi_c = 0.57, 0.58$

γ **= 2.4 – 3.0**

vs. ***full MCT* :** γ **= 2.6**

Free Volume : "Perfect" FIT

$$\tau \sim e^{B/(\phi_C - \phi)} \quad , \phi_C \approx 0.62 \pm 0.02$$



Theory: *No Divergence below RCP* $\tau \sim e^{F_B(\phi)}$

Fluctuation effects ?

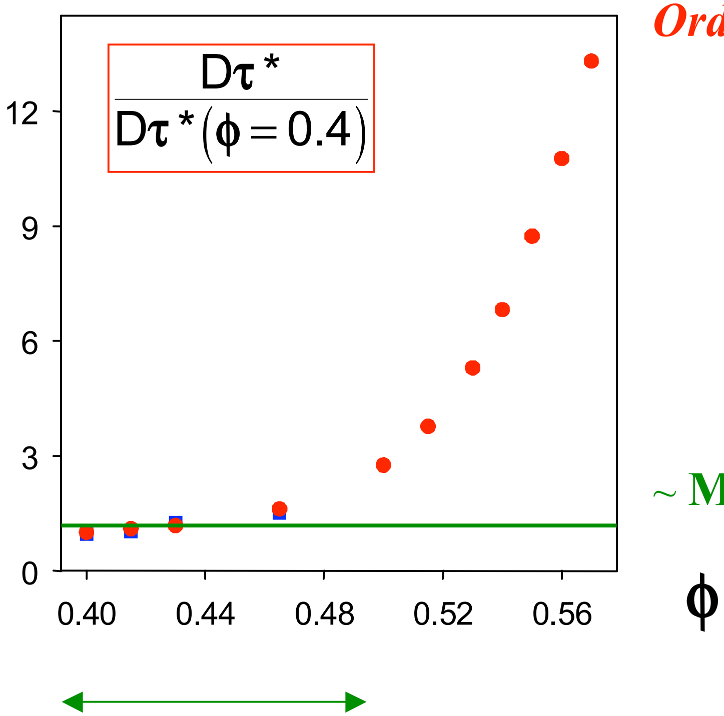
Diffusion vs. Relaxation Decoupling

Stochastic Hopping
Distribution of Relaxation times

$$\left\langle \tau_j^{-1} \right\rangle > \frac{1}{\left\langle \tau_j \right\rangle}$$

$$\left\langle \tau_{rxn}^{-1} \right\rangle \propto \left\langle \tau_{rxn} \right\rangle^{-0.77}$$

Faster Rate



Order of Magnitude

Kumar et al ; Truskett et al
polydisperse-HS SIMULATION

$$\frac{D\tau^*}{(D\tau^*)_0} \approx 10-20 \; ; \; \phi = 0.58-0.59$$

~ **MCT** ….tiny …..< ***10-15% effect***

NOT activated
~ Stokes-Einstein

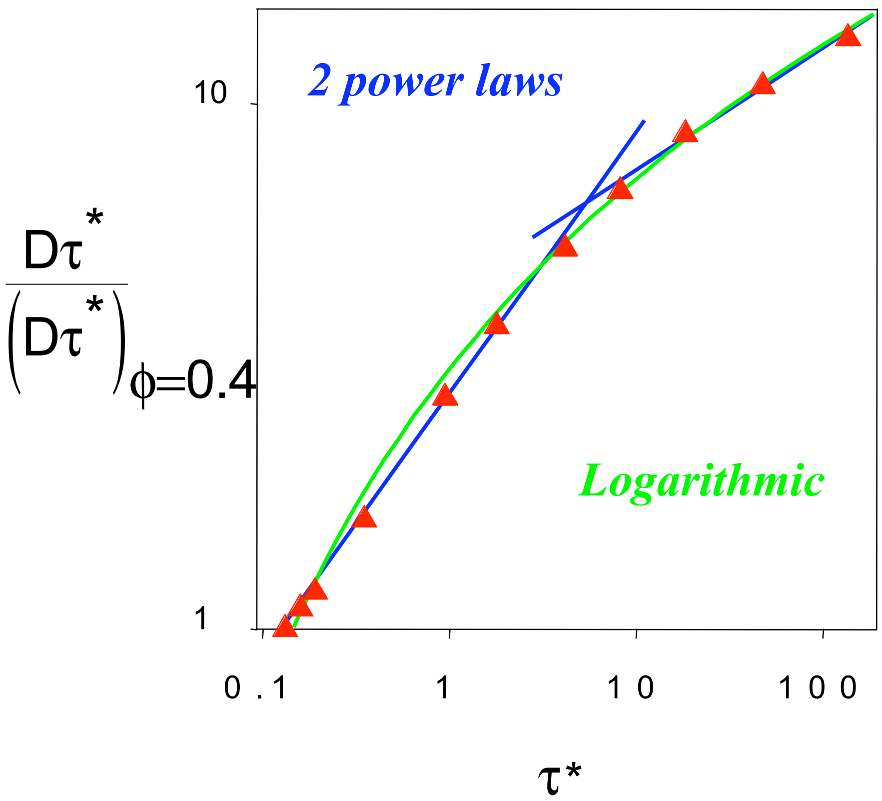
Mean Square Displacement @ τ*

$$\sqrt{\left\langle r^2\left(\tau^*\right)\right\rangle} \cong 0.4 \quad , \; \phi \leq 0.5$$
$$\rightarrow 0.9, \quad \phi = 0.57$$

Mass transport enhanced at fixed "relaxation" time

Diffusion vs. Relaxation Decoupling : Length Scale

Scaling with Relaxation time



$$\xi \equiv \sqrt{D\tau^*} \propto \ln\left(\tau^*\right) \propto F_B(\phi)$$

or

$$\propto \left(\tau^*\right)^{0.25} \quad \text{lower } \phi$$

$$\propto \left(\tau^*\right)^{0.115} \quad \text{high } \phi$$

WEAK Growth

ala BLJM Sims
Szamel, Yamamoto,….

implies $D \sim (\tau^*)^{-0.77}$

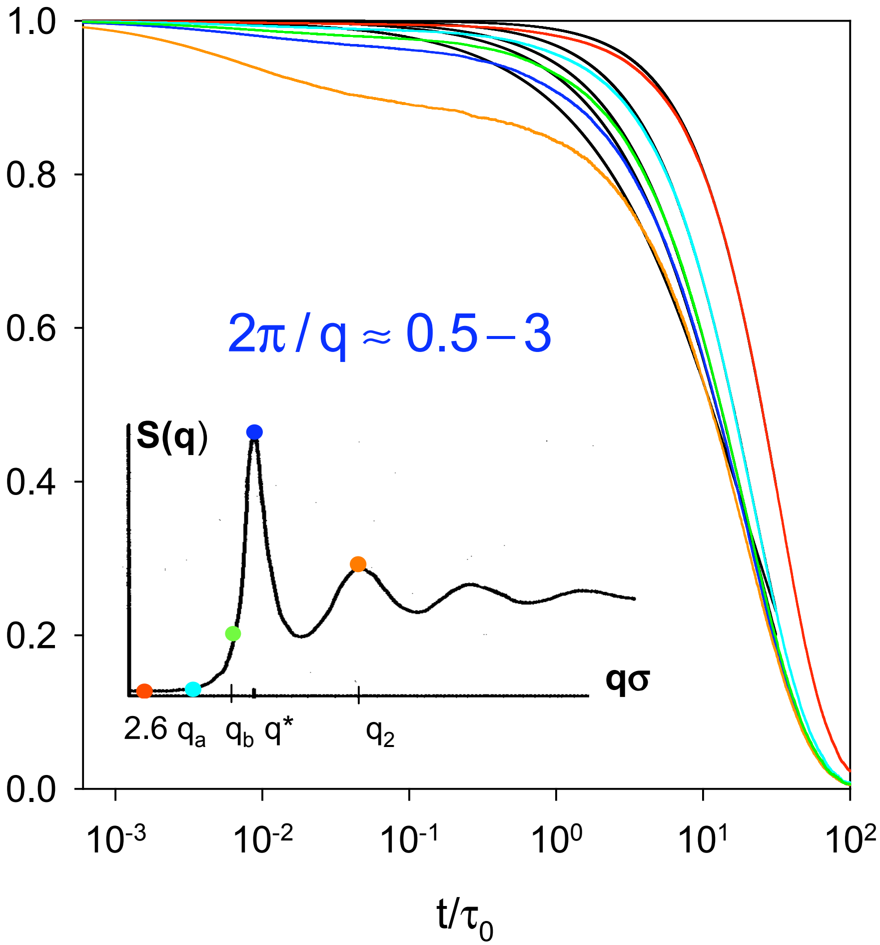
Fractional Stokes-Einstein behavior

Spatial Dependence of Relaxation

$$F_S(q,t) = \left\langle \exp\left[i\vec{q}\cdot\vec{r}(t)\right]\right\rangle$$

$\phi = 0.55$ **q-dependence**

$$\boxed{F_S(q,\tau(q)) \equiv e^{-1}}$$



Relaxation Times

Extremely ***NON****diffusive, NonFickian*

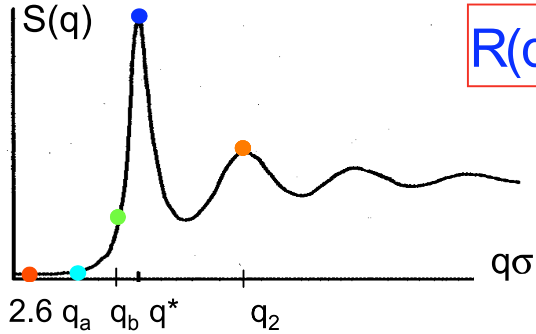
not $\exp(-q^2Dt)$

Slow Relaxation ~ q-INdependent

Why ?....intermittent "hopping"

Length Scale for Crossover to Fickian ?

Quantify Space-Time NONgaussian Aspects



$R(q) \equiv q^2 D\tau(q) \to 1$, Gaussian $\approx$ MCT

Growing length scale for recovery of Fickian diffusion

Derived ***ANALYTIC*** ***"Jump Diffusion" model***

$$\frac{1}{\tau(q)} = \frac{q^2 D}{1+(q\xi_D)^2}$$

Viscoelastic Length scale

$$\xi_D \propto \sqrt{D\tau^*}$$

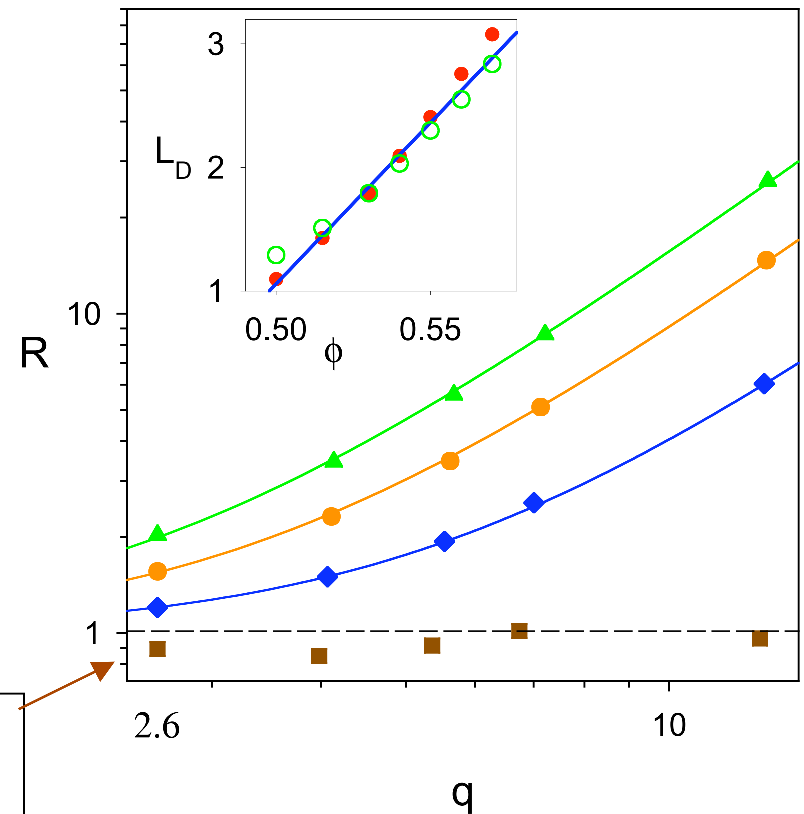
....*use to fit numerical theory*

$$R(q) \sim 1+\left(\frac{L_D q}{2\pi}\right)^2$$

$$L_D \propto \sqrt{D\tau^*} \propto \phi \approx 1-3$$

agrees with analytics

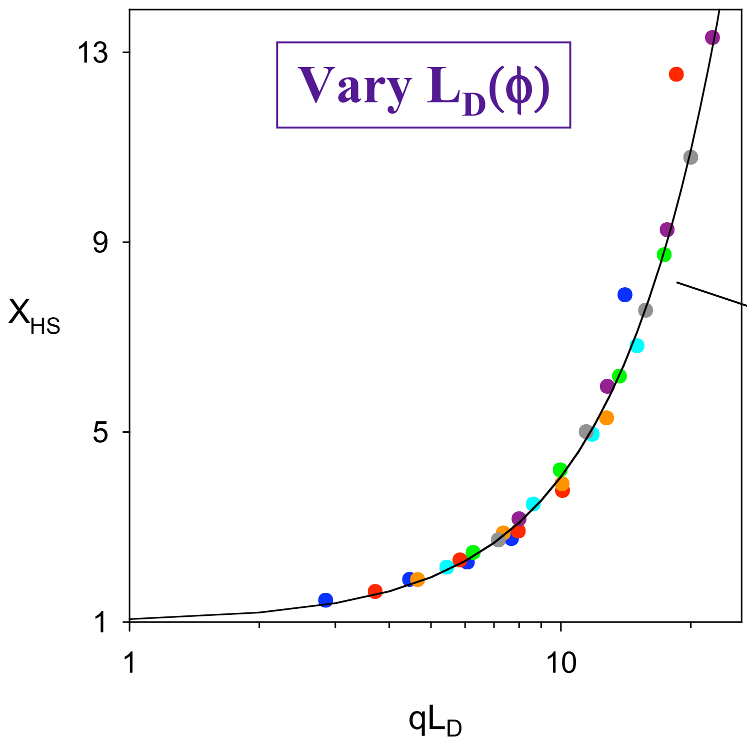
ϕ = **0.43**, 0.5, 0.53, 0.55



Fickian
ala MCT
~10% effect

Consistent with BLJM Simulations, Flenner & Szamel, PRE, 2005

Dynamical Scaling : *Collapse of ALL ϕ and q dependences*



$$X_{HS} = \frac{\tau(q,\phi)D(\phi)}{\tau(q,\phi=0.4)D(\phi=0.4)}$$ ← *normal regime*

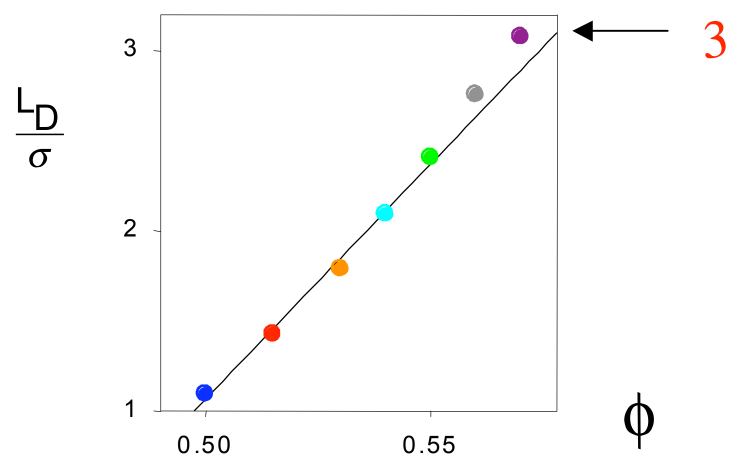
For $\phi>$ 0.5 ($F_B > 1$)

$$X(qL_D) \cong 1+(qL_D/2\pi)^{\beta}$$

$\beta \sim 1.8 \pm 0.2$

(best fit)

dynamic length scale

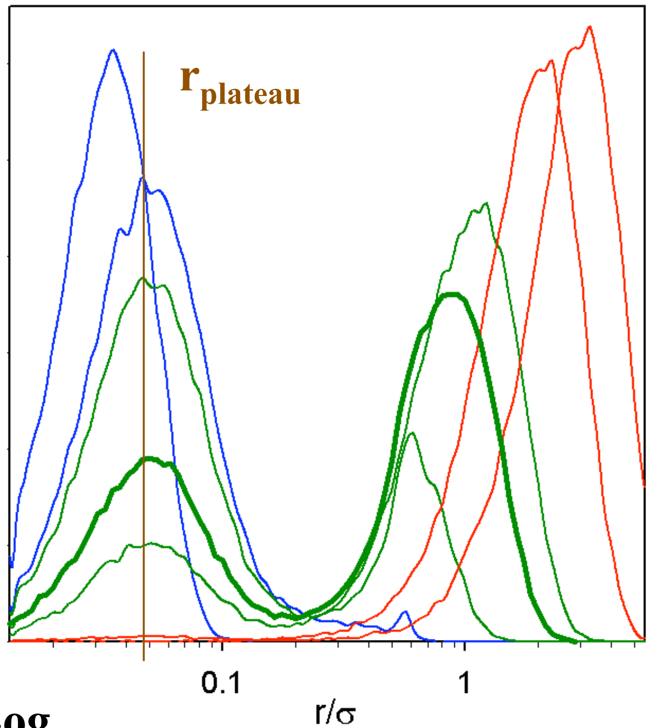


ala BLJM thermal liquid Simulation
L. Berthier, PRE (2004)

$$X(q,T) = \frac{\tau(q,T)D(T)}{\tau(q,T_0)D(T_0)}$$

Displacement Distribution P(log|r(t)|) & Mobility Bifurcation

$\phi = 0.55$ $F_B \sim 5$



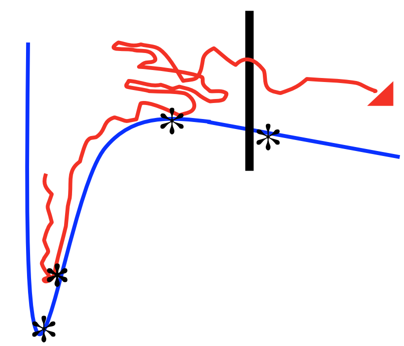
Log

increasing time

r_{loc}, R*, r_B , **τ*, σ, 2σ, 3σ**

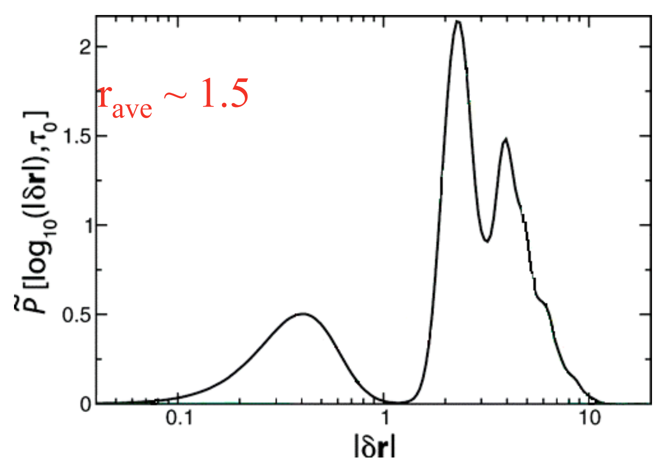
- **Gaussian** (Fickian) **at short & long times**
- ***Intermediate times***: BIMODAL..*more so as* ϕ *increases*
- **Strongest** near $\mathbf{t = \tau^* \sim \tau_{rxn}}$

Fast & Slow ***Populations***



* *Slow population ~ pinned at MSD plateau location (max anomalous diffusion)*

* *Fast population diffuses*



ϕ **= 0.55**

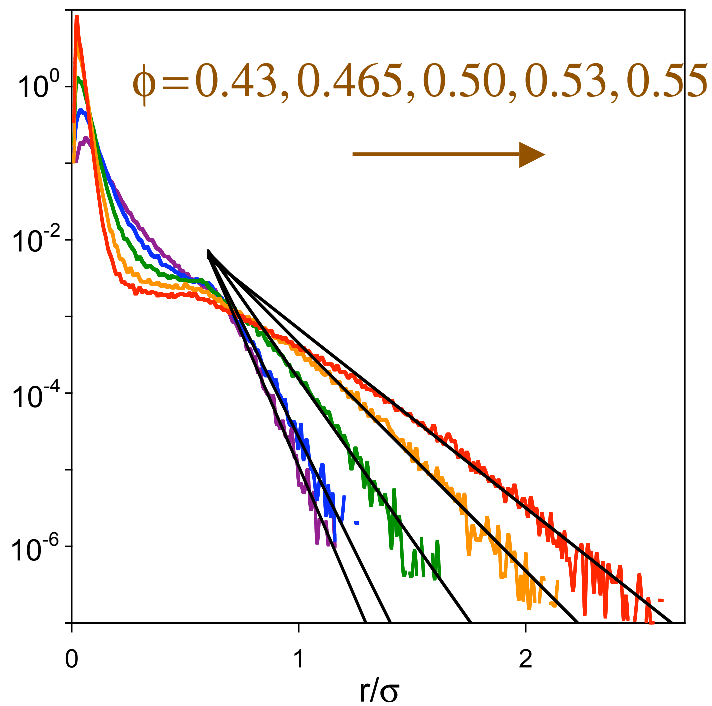
P-HS
simulation

Reichman et al, JPCB, 2005

Exponential Tails of $G_s(r,t)$ ***…..van Hove***
predicted by "Jump Diffusion" model
Underlies Decoupling,……

Van Hove Representation and Exponential Tails

Log{$G_s(r,t=\tau^*)$} @ mean α–time



Exponential Tail

ξ=Length scale ~ 0.06-0.20

Analytic "Jump Diffusion"

$$F_s(q,t) \cong \exp\left(-q^2Dt/(1+q^2\xi^2)\right)$$

$$\xi \propto \sqrt{D\tau^*}$$

$$\tau_\alpha \equiv \xi^2 D^{-1} \propto \tau^*$$

$t < \tau^*$

r NOT too small

$$G_s(r,t) \cong \delta(\vec{r})\, e^{-t/\tau_\alpha} + \frac{1}{4\pi\xi^2}\frac{t}{\tau_\alpha} e^{-t/\tau_\alpha}\frac{e^{-r/\xi}}{r}$$

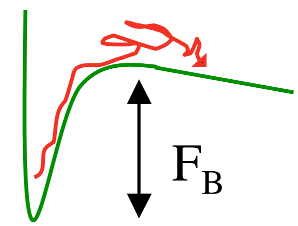
slow localized particles

fast particles

~ Exponential Tail

Comments

- "“MCT-like” aspects…***BUT hopping over low barriers & NO singularity***
- **MANY** NonGaussian, Non-MCT effects even in “***precursor regime***”
  all emerge from stochastic activated dynamics on LOCAL scales
- Connections between dynamics on different time & (local) length scales
- Consistent with Simulations & Expts, **BUT** NEED more for Hard Spheres

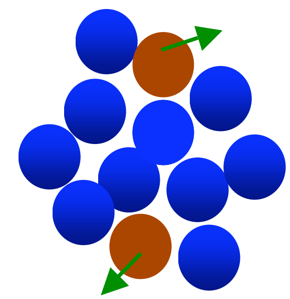


Theory Simple / Multiple Limitations

……*addresses only self-dynamics*

* Generalization to ***Collective*** Dynamic Fluctuations, **S(q,t)** ?

* ***Many Correlated Hops*** , Space-Time Mobilities, 4-point Susceptibilities ?



ξ_{coop}

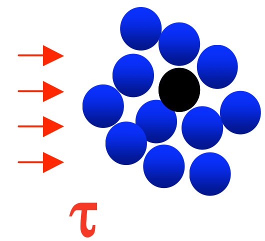
Virtues of Simplicity

SAME *predictive & experimentally testable approach applies to* :

Colloid Gels **Polymer Melts & Glass**

External Stress / Mechanics ***“Molecules”***

Nonlinear Viscoelasticity : *Stress Rheology Perspective*



Classic *Idea : External Deformation Reduces Barriers to Flow*

* ***Eyring*** *(1936)* *Arrenhius viscoplastic flow*

Frenkel (crystals)

Mechanical Work

$$E_B(\tau) \approx E_B(0) - \tau V_A$$

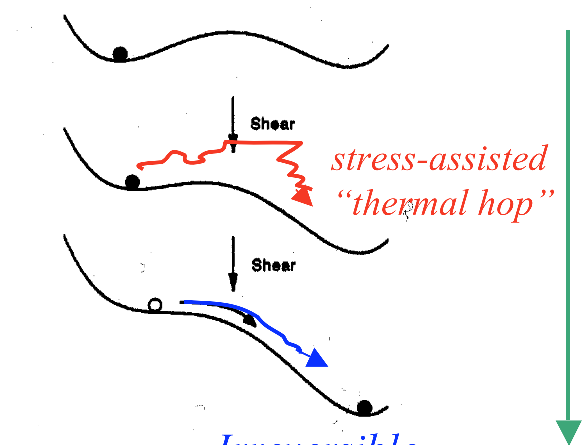
- *Phenomenological* ***"Soft Glassy Rheology" or "Trap" models***

  irreversible "barrier hops", … …Cates, Sollich, Bouchaud, …

- ***Inherent Structure / Landscape simulations…*** *Dan Lacks*

  stress, strain reduce and destroy barriers… ***ala Eyring***

Deformation



Macroscopic Rheology ⟷ local, cage scale physics

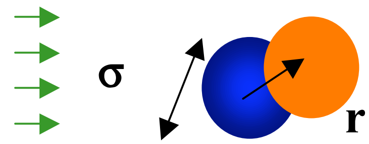
usual "mean field" assumption ala ***"MicroRheology"***

- **Simulations** *: Dynamics ~ Isotropic on CAGE scale*

SIMPLE Incorporation of External Stress

Instantaneous Mechanical work

τ=Applied Stress



$$-\tau\,\Delta V(r) \cong -\lambda\sigma^2\tau\, r \propto -f\cdot r$$

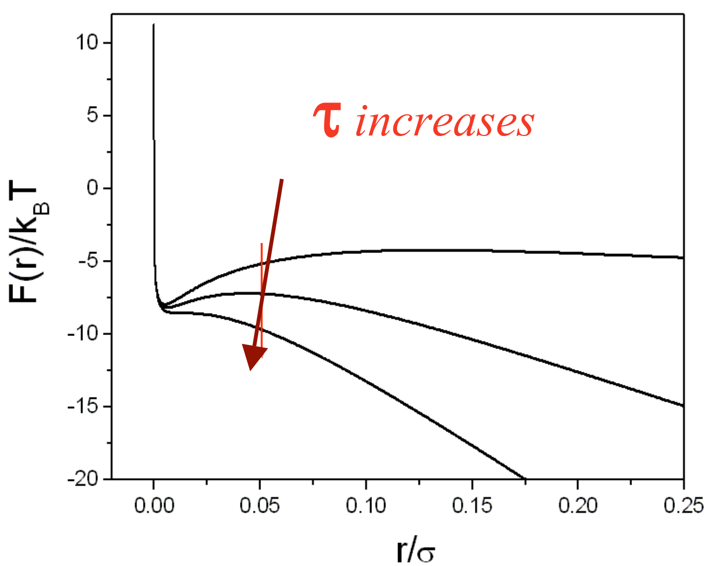
force on particle

S(q) remains quiescent

O(1) "stress transmission" factor

...factor ~2 uncertainty in local τ

$$F(r;\tau) = F(r;\tau=0) - \lambda\sigma^2\tau\, r$$



Stress softens localization, Reduces Barrier

NONlinear $\mathbf{F_B(\tau)}$ *vs. linear Eyring*

Reduces Modulus & Accelerates Relaxation

→ **"Absolute YIELD"** ↔ **Barrier destroyed**

$$\frac{\bar{\tau}_{hop}}{\tau_0} = \frac{2\pi\,(\zeta_s/\zeta_0)}{\sqrt{K_0(\tau)\,K_B(\tau)}}\, e^{F_B(\tau)}$$

Glassy Shear Modulus

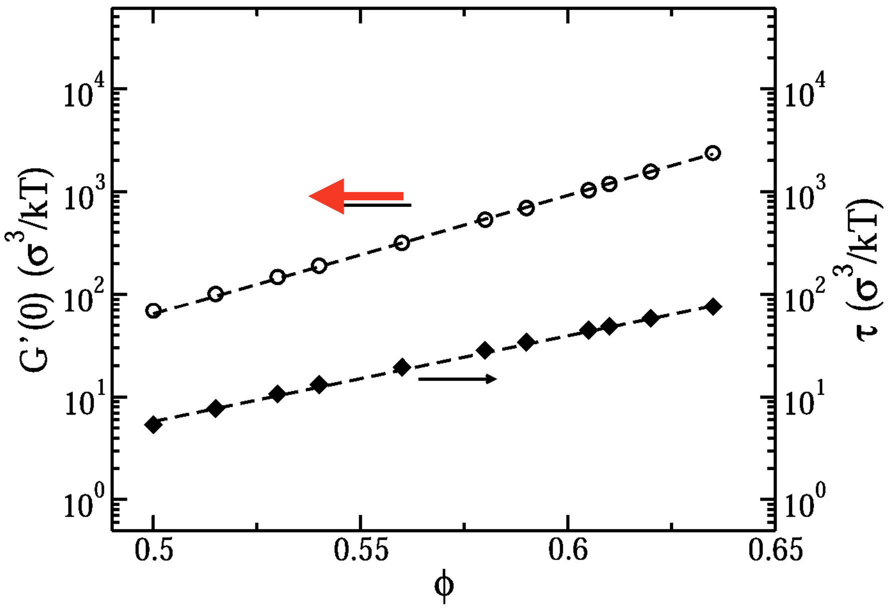
$$G'(\tau) = \frac{1}{60\pi^2}\int_0^\infty dq\, q^4 \left(\frac{\partial \ln S(q)}{\partial q}\right)^2 e^{-q^2 r_{LOC}^2(\tau)/3S(q)}$$

Shear Modulus, Absolute Yield Stress, Alpha Time

Units : kT/σ^3 = 4 Pa for 100 nm

Linear Shear Modulus & Absolute Yield Stress

hopping NOT an issue



Exponential or **High Power Laws**

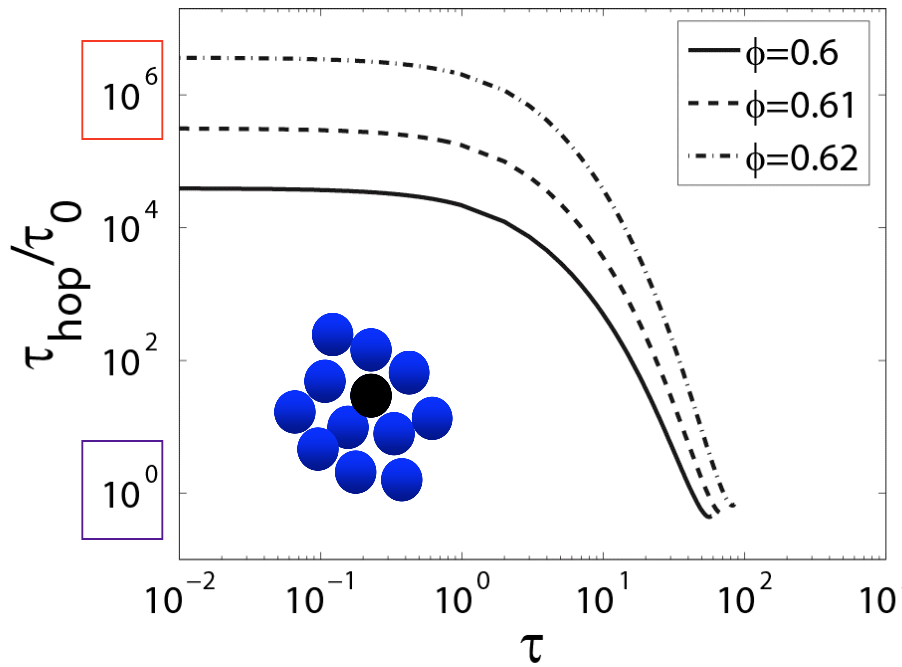
$$G' \propto e^{27\phi} \propto \phi^{14} \quad , \quad \tau_{y,abs} \propto e^{19\phi} \propto \phi^{11}$$

Yield STRAINS ~ 20%

Broadly consistent with variety of Expts

Stress-Accelerated Relaxation

barrier hopping event ~ α −time



Entropic Barriers Massively Reduced

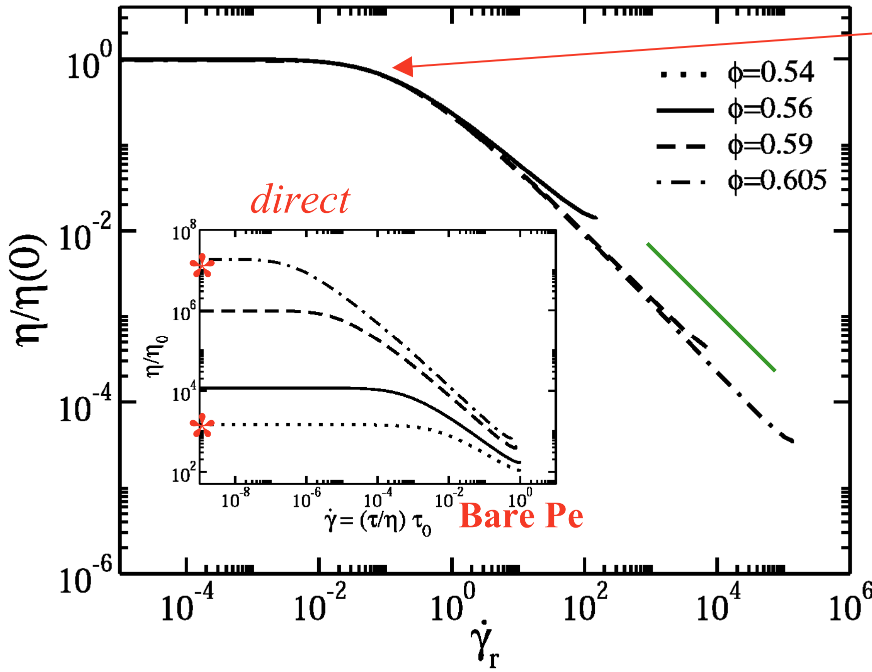
Viscosity Thinning & Flow Curves *: beyond MCT…hopping*

$\tau = \eta(\tau)\dot{\gamma}$

ϕ
0.54
0.56
0.59
0.605

η/η_s

10^3-10^7



$\dot{\gamma}_{r,crit} \approx 0.3 - 0.4$ ~ **Expts**

$\dot{\gamma}_r \equiv \dot{\gamma}\left(\beta R^3 \eta(0)\right)$ ***Dressed Peclet***

"stress relaxation time"

Near collapse

FLOW CURVES

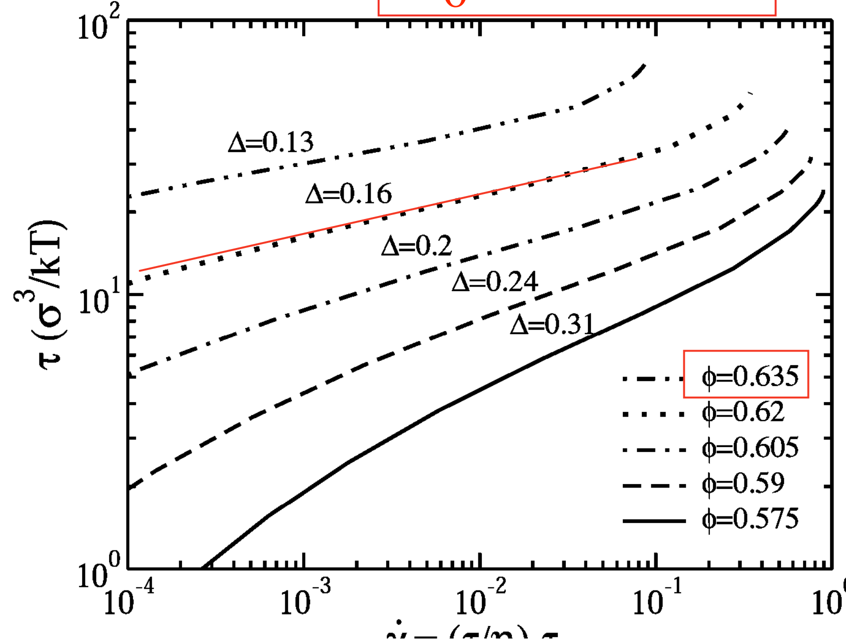
No true plateau (hopping)

APPARENT power law regime

$\tau \equiv \dot{\gamma}^{\Delta}$

$\Delta \sim 0.1$ - 0.3

$\dot{\gamma}\tau_0 = Bare\ Peclet$



SELF-Motion Under Shear

Besseling, Weeks, Poon, PRL, July,2007

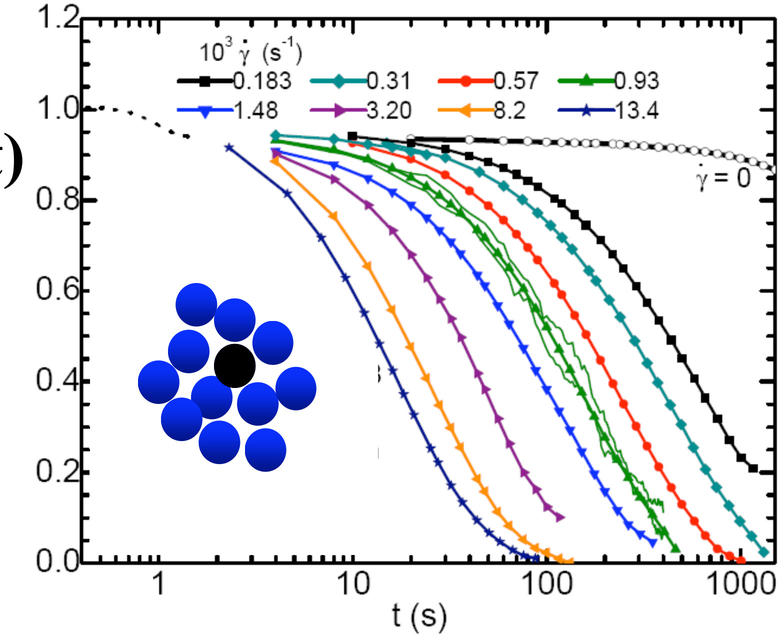
***Confocal :** direct microscopic probe of theory*

$\phi = 0.62$

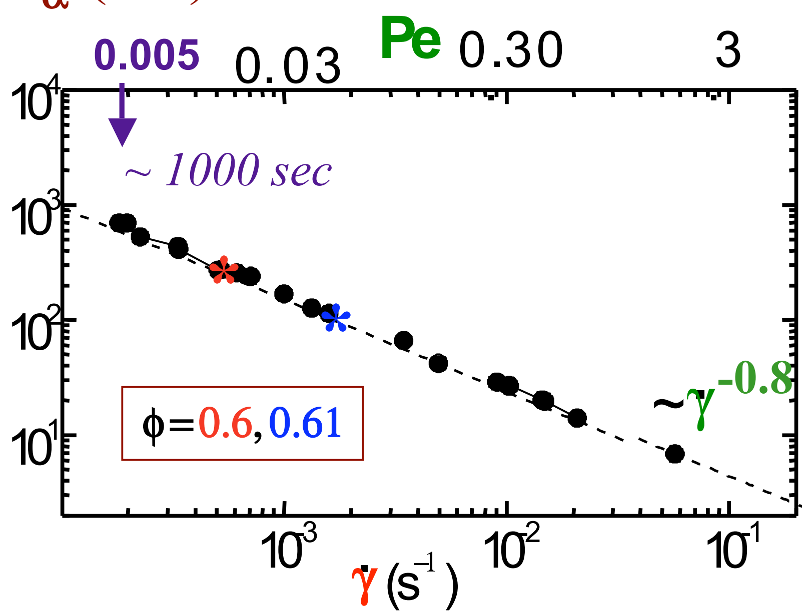
Alpha Time ~ 1/(shear rate)$^{0.8}$

for bare $Pe \equiv \dot{\gamma}\tau_0 \approx 0.005-1$

$F_s(q^*,t)$



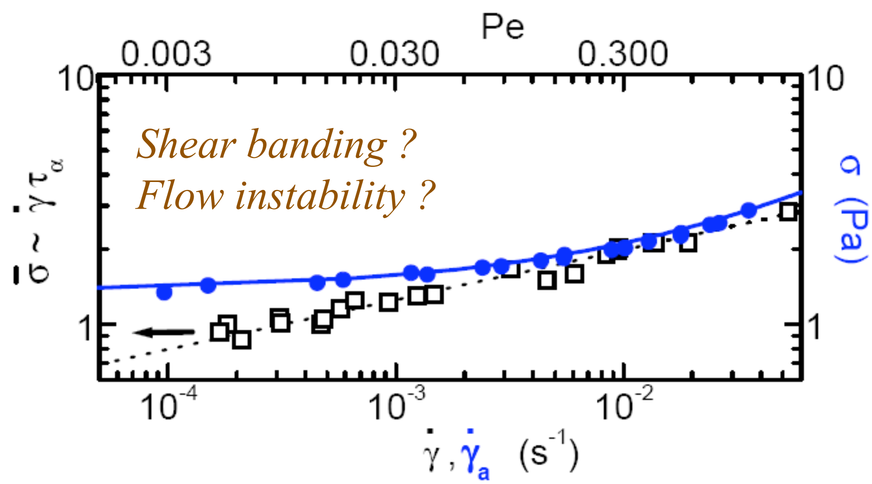
τ_α (sec)



"microscopic flow curve"…NO plateau

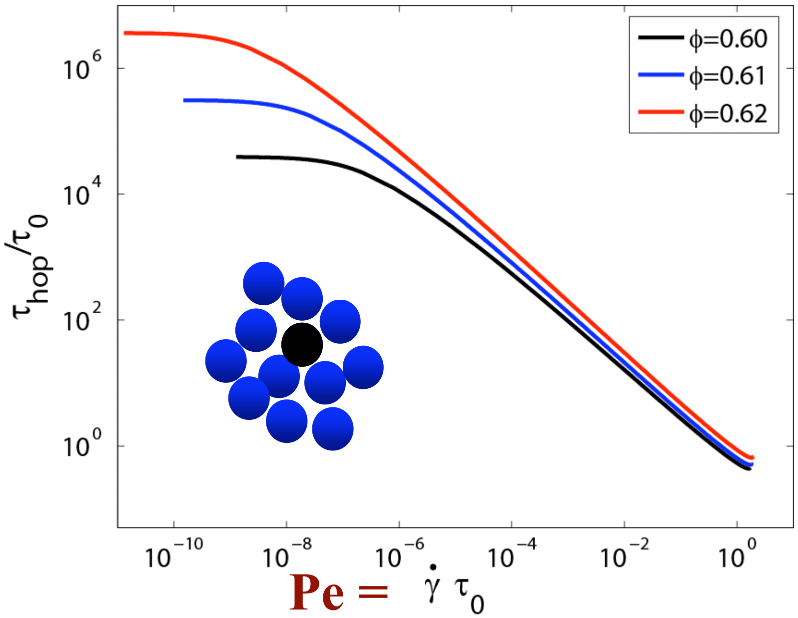
Disagrees with Bulk Rheology

Hershel-Buckley….yield stress ?



Theoretical Predictions

Kobelev & KSS, PRE,2005



Hopping

τ_0 ~ 30 secs → φ=0.62 **τ_α ~ 60 million secs**
~ 2 Years

AT *lowest* **Pe = 0.005 : 900 secs ~ EXPT**

"shear thins" by ~ 5 orders of magnitude !

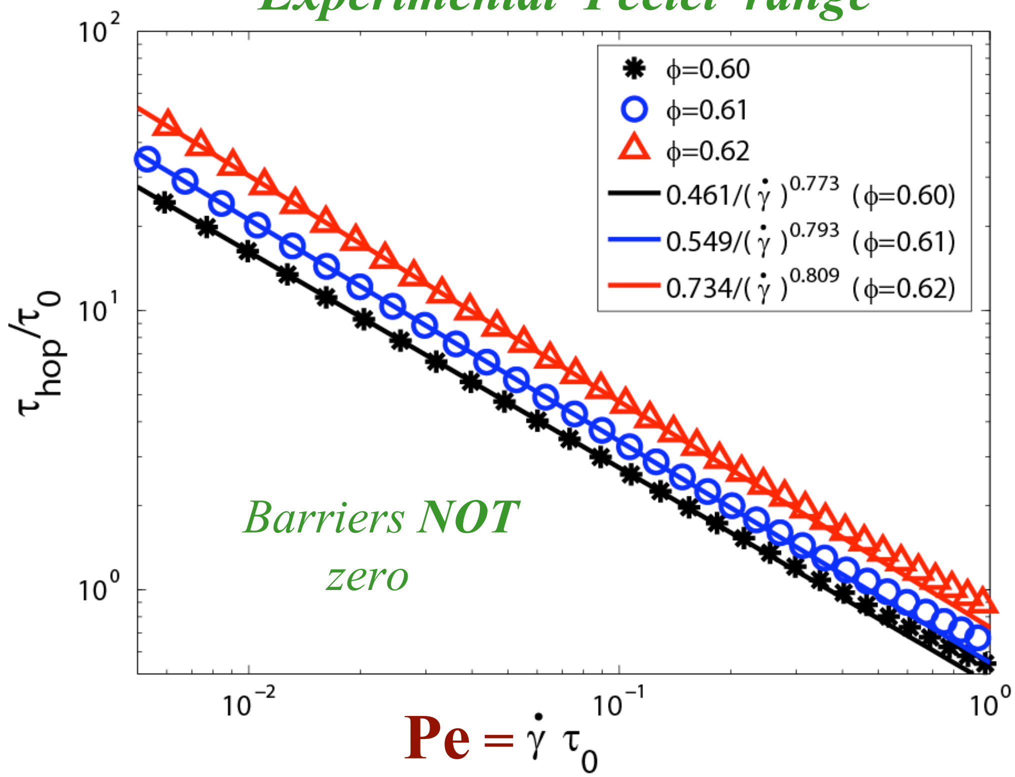
Quiescent differ by ~ **100**

…***BUT*** High Shear < **factor 2**

~ 1/(shear rate)$^{\mathbf{0.8}}$

~ EXPERIMENT

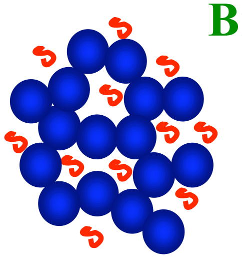
Experimental Peclet range

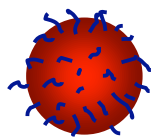


Ongoing & Future Directions : Fluids, Glasses, Gels

* **Glassy Colloid Nonlinear Mechanics** : Step-Strain, Creep + Recovery,….

* **Polymer-Colloid Depletion Gels**
Brushed Coated Thermal Gel Formers

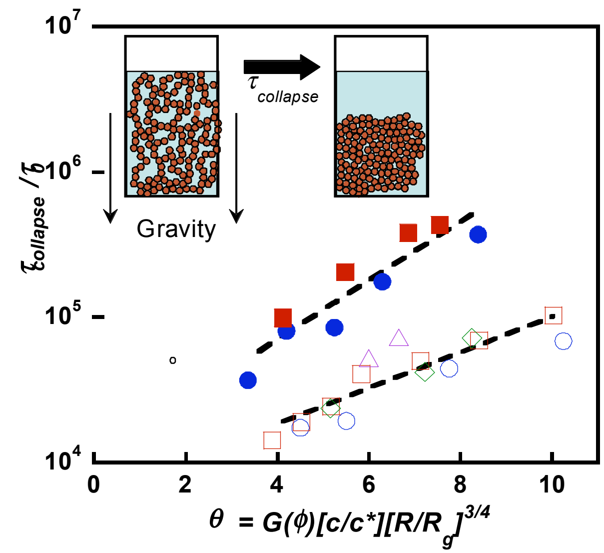




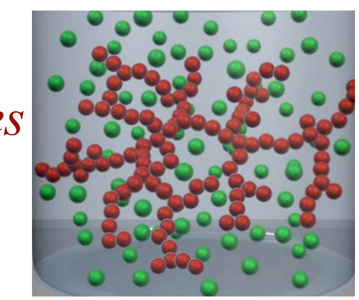
Hopping, Heterogeneity
Elasticity, Yielding

Transient Gel Collapse

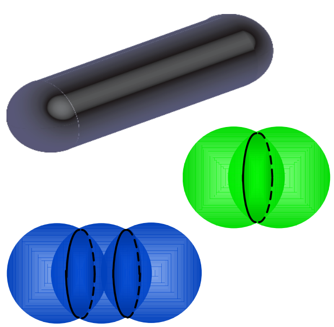
Zukoski, KSS, JPCM,2006



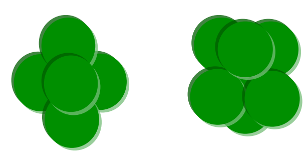
* **Biphasic** *Repulsive-Sticky Mixtures*

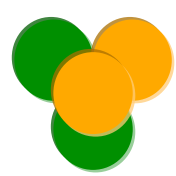


• ***Molecular Colloids***



"Pineoids"





"Patchy"

Polymer Melts and Glasses

Aging, Stress, Yield
Strain Harden,
Rejuvenate,…