



# ***Activated* Hopping, Dynamic Heterogeneity, and Mechanical Response in Glassy *Particle* Fluids and Suspensions**

**Ken Schweizer**

*Departments of Materials Science, Chemistry, and Chemical Engineering  
Frederick Seitz Materials Research Laboratory  
University of Illinois @ Urbana-Champaign*

## **Coworkers : 2003-present**

**Hard Spheres:** *Erica Saltzman*, Vladimir Kobelev, Daniel Sussman

**Soft Colloids:** *Jian Yang*

**Colloid-Polymer Gels:** Yeng-Long Chen, Vladimir Kobelev

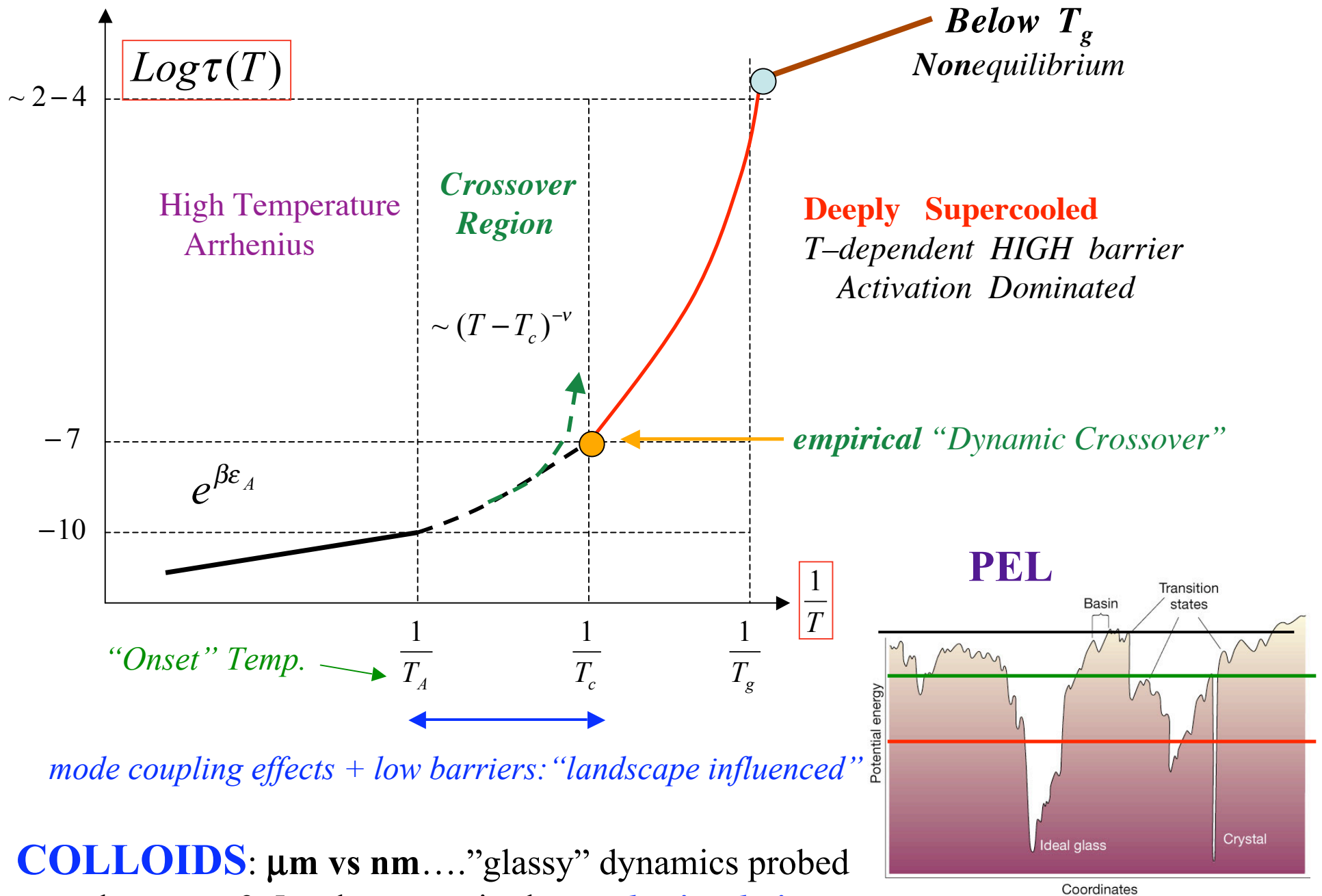
**Molecular Colloids & Liquids:** Mukta Tripathy, Galina Yatsenko, *Rui Zhang*

**Polymer Melts & Glasses:** Kang Chen, Erica Saltzman

## **Funding**

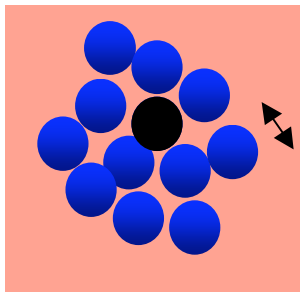
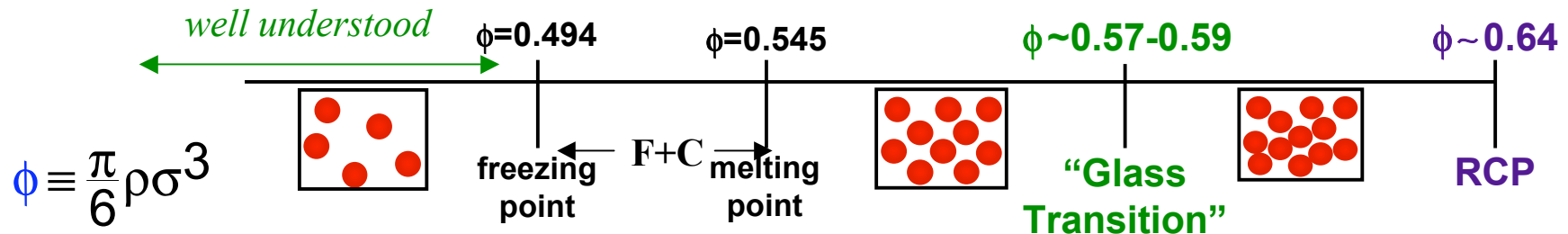
Rensselaer-Illinois NSF Nanoscience & Engineering Center  
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DOE-BES FS-MRL Soft Materials Cluster

# Alpha Relaxation Map & Regimes



**COLLOIDS:**  $\mu\text{m}$  vs  $\text{nm}$ ...."glassy" dynamics probed only over  $\sim 3$ -5 orders magnitude.....*ala simulations*

# “Athermal” HARD SPHERE Suspensions (and fluids)

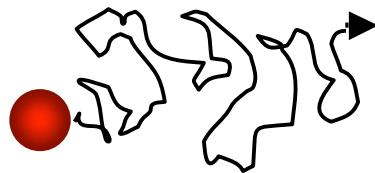


$\sigma \sim 100 \text{ nm} - 2 \mu\text{m}$

*Dilute Brownian time:  $\tau_0 = \sigma^2 / D_0 \sim 0.01-30 \text{ sec}$*

*Kinetically “Vitrify”: Relaxation Time > Expt time scale  $\sim 10,000 \text{ secs}$*

## CONFOCAL Microscopy & Simulations



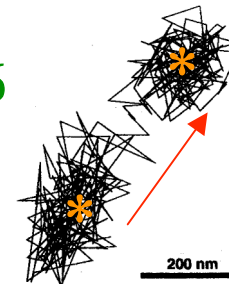
*“smooth, hydrodynamic like”  
Collective, small steps,  $\sim$ Gaussian*



*“High”  
volume  
fraction*

*“Solid - Like”...intermittent hopping*

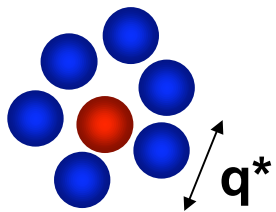
$\phi = 0.56$



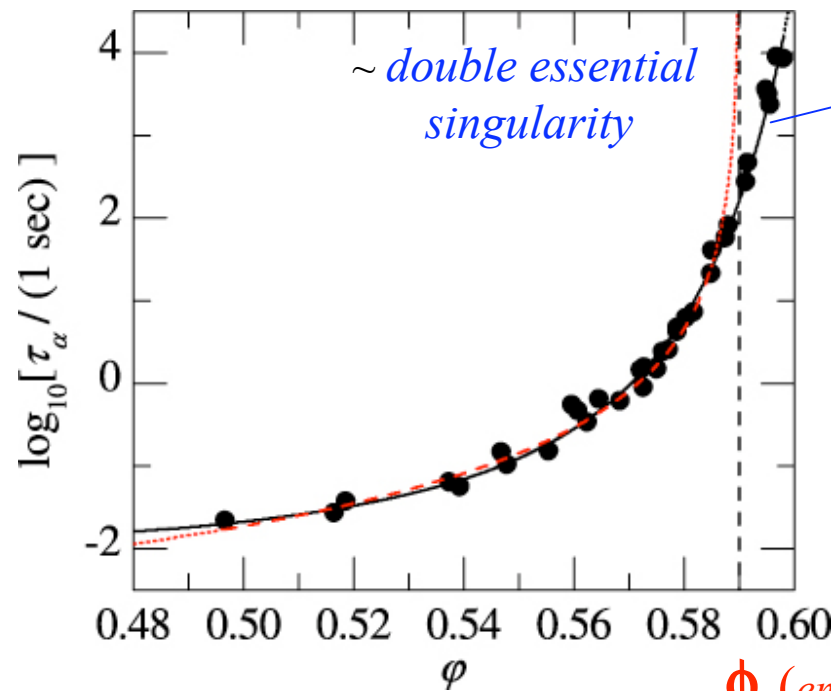
$\sim \sigma/2$  Weeks  
Weitz

# Colloid Experiments & Computer Simulations

## Alpha Relaxation



*Cipelletti, Berthier, et al, PRL, 2009*



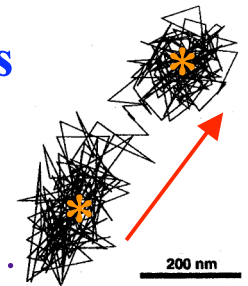
$$\propto \exp\left(\frac{B}{(\phi_{RCP} - \phi)^2}\right)$$

**MCT fit:**  $\propto (\phi_c - \phi)^{-2.5}$   
works over  $\sim 3$  order magnitude

$\phi_c$  (empirically deduced)

**\*But even in regime where can fit MCT, see large NONgaussian effects**

*Nongaussian parameter, Decoupling of diffusion & relaxation, Exponential tails in van Hove function, Growing dynamic length scale, .....*



**.....suggests large amplitude, intermittent activated processes important**

# GOAL: Predictive Microscopic Theory @ level of Forces

build on Ideal MCT: *retain Structure, Forces, Slow Dynamics connection*

*.... allows NONuniversal chemical/materials aspects to be addressed*

**BUT** go beyond to treat **Activated Intermittent Dynamics**  
at *Single Particle level* : “*theory of simulation or confocal microscopy trajectories*”

→ *restores long time ergodicity, destroys “ideal” MCT glass transition*

*allows treatment of some space-time Dynamic Heterogeneity effects*

*can generalize to NONlinear Viscoelasticity*

## Diverse Material Classes:

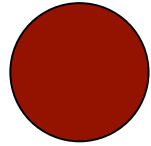
**Particle Suspensions** : hard/soft, sphere/nonspherical, glass/gel/Janus

Atomic & Molecular Liquids

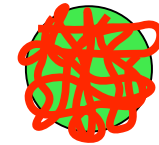
**Polymers** .....including nonequilibrium “plastics”

***Avoid Fitting & Adjustable Parameters....1<sup>st</sup> Principles***

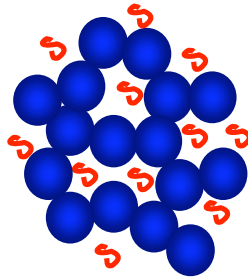
# DENSE Colloidal & Nanoparticle Brownian Suspensions



Hard **SPHERE**



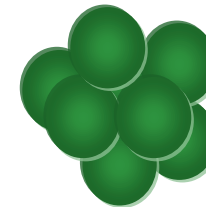
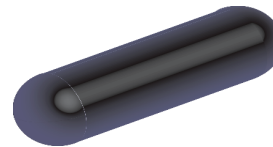
Sticky **GELS**



**Tunably SOFT** : many arm stars; microgels,....  
*metals ?*

**NONspherical**

*(molecular liquids)*



*Coupled  
Translate-Rotate*

## **TODAY :**

- I. **Hard Spheres** : *basic concepts, Mean & Fluctuation phenomena*
- II. **Soft Spheres** (microgels)....*role of highly variable soft repulsion*
- III. **Uniaxial hard particle**....*role of shape, rotation*
- IV. **Nonlinear Rheology of hard spheres** (*likely no time*)

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

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

 $\mathbf{r}(t) = \text{scalar displacement of a particle from initial position}$

$\mathbf{D}_s$  : dissipative, short time, "bare" process

Formally:

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

*Physical Ideas & Technical Approx.*

Solid State  
View

**CONTRACT** to lowest level,  $\mathbf{r}(t)$

\* Key "slow variable" : *density fluctuations* ...ala MCT

\* Average over local packings: dynamical caging constraints via  $\mathbf{S}(\mathbf{q})$

...Effective interparticle *pair force* :  $\vec{f}(r) = k_B T \vec{\nabla} C(r)$  ....from Structure (ala MCT)

\*\* Local Equilibrium Approx: *relate 1 and 2 body dynamics*

*Dynamic "closure"* ala Einstein solid or Vineyard

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

# → Nonlinear Langevin Eqn Theory

...force balance in overdamped regime

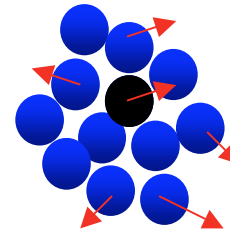
$$\zeta_s \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial r} F_{eff}(r(t)) + \eta(t)$$

*Instantaneous Force due to surroundings*

white noise

$$\langle \eta(t) \eta(0) \rangle = 2\zeta_s k_B T \delta(t)$$

$$r(t=0) = 0$$



**“Dynamic Free Energy”** = *Spatially-resolved, Time Local Displacement-Dependent “Field”*

$$\beta F_{eff}(r) = -3\ln(r) - \frac{1}{3} \int \frac{d\vec{q}}{(2\pi)^3} C^2(q) \rho S(q) e^{-q^2 r^2 (1+S^{-1}(q))/6} \equiv F_{ideal} + F_{cage}$$

*Structure*

↔  
*Mean square Caging Force*

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

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

*competition*



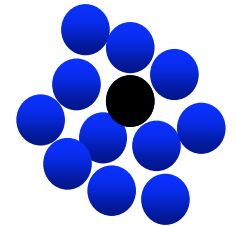
# Reduction to simplified Ideal MCT

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

\* **RECOVER** *Naïve MCT* Transition of Kirkpatrick-Wolynes **IF** :

*Dynamical Gaussian approximation for  $\langle r^2(t) \rangle$*

*Mean Localization Length*  $r_{LOC}^2 \equiv \langle r^2(t \rightarrow \infty) \rangle$

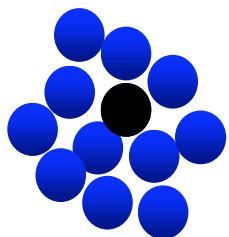


→  $\frac{1}{r_{LOC}^2} = \frac{1}{18\pi^2} \int_0^\infty dq q^2 q^2 C^2(q) \rho S(q) e^{-\frac{q^2 r_{LOC}^2}{6} (1+S^{-1}(q))}$  *Einstein solid Debye-Waller*

$\langle \vec{f}(0) \cdot \vec{f}(t \rightarrow \infty) \rangle$

*“uphill” thermally activated hopping NOT allowed* → **IDEAL GLASS** @  $\phi_c$   
T<sub>c</sub>

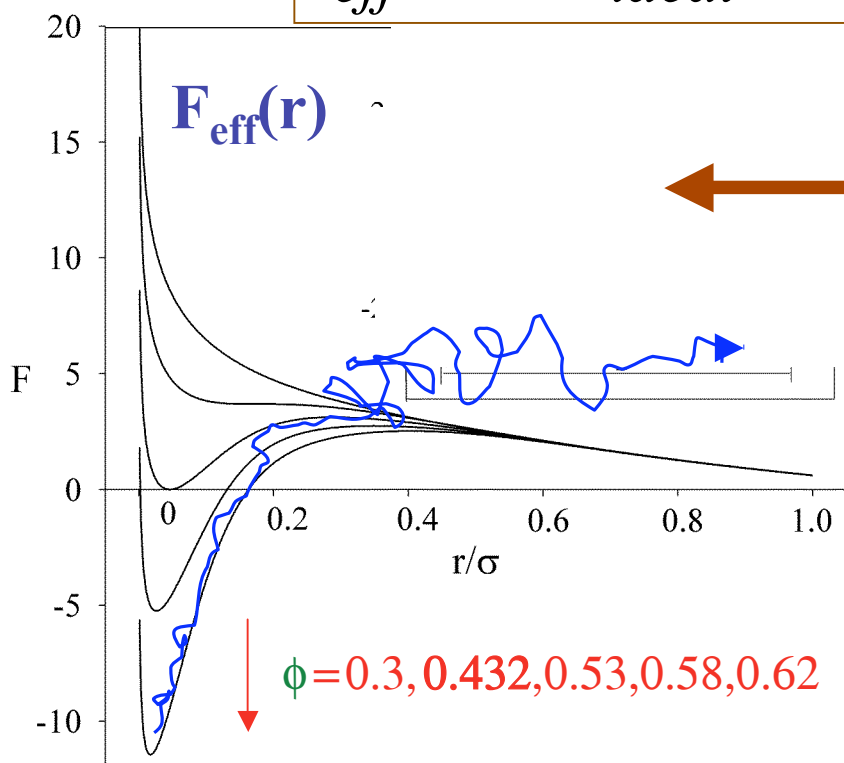
**Reality : MCT “transition” = Dynamical Crossover**



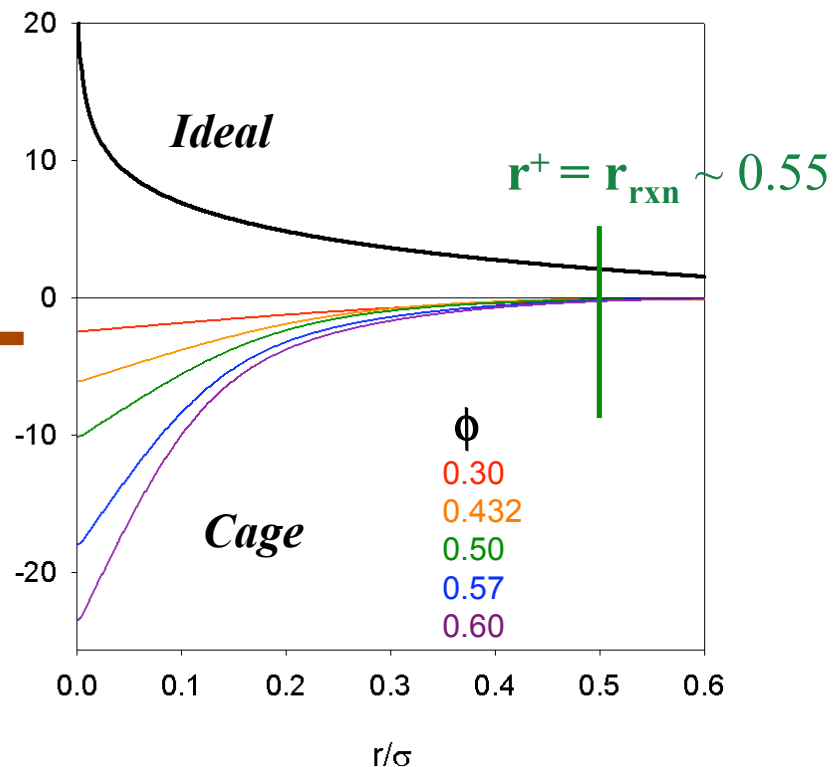
# I. Dynamic Free Energy: Hard Spheres

\* Naïve MCT “ideal glass transition” at  $\phi_C \sim 0.432$

$$F_{eff}(r) = F_{ideal} + F_{cage}$$



Displacement,  $r(t)$



**Reaction Pt:** Cage Escape, Onset of IRReversibility ....negligible localizing *force*

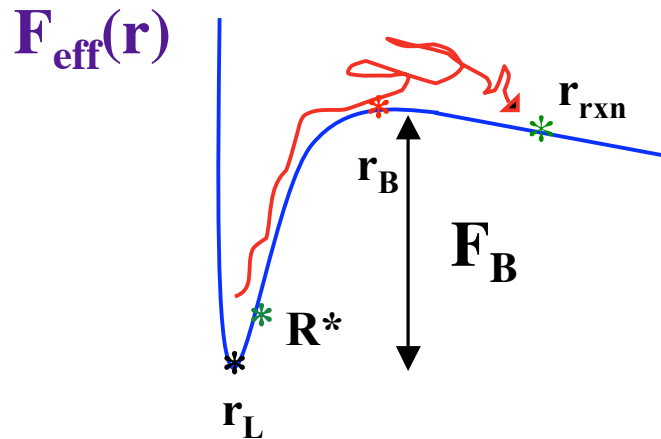
$$\zeta_{tot} = \zeta_s + \zeta_{HOP} \quad ; \quad D_{HOP} = r^{+2} \langle \tau_{rxn}^{-1} \rangle / 6 \equiv k_B T \zeta_{HOP}^{-1}$$

# Source of Rich Physics : Many Relevant Energy and Length Scales

as  $\phi$  increases :

$$r_L \sim 0.18 \rightarrow 0.03 \quad R^* \text{ decrease}$$

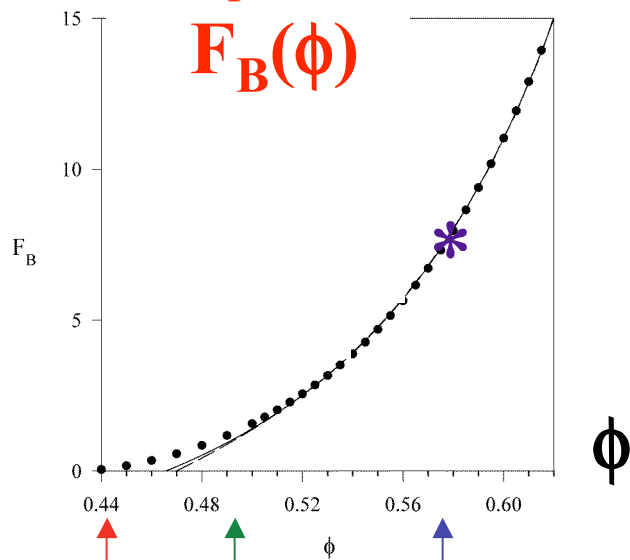
$$r_B \sim 0.25 \rightarrow 0.35 \quad \text{ala "interstitial"} \quad r_{rxn} \sim 0.55$$



Localization well & Barrier curvatures  
 Entropic barrier height  
 Maximum restoring force,  $f^*$

ALL  
 increase

Entropic Barrier



NMCT    Freezing    Kinetic Vitrify

**ANALYTICS** : Kramers, Green-Kubo

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

Shear Modulus, Diffusion constant, .....

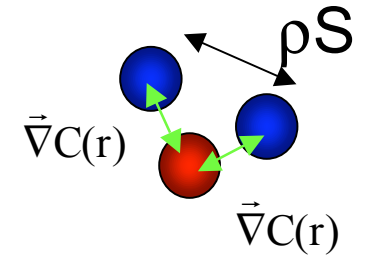
# Limiting Analytic Analysis : Real Space Picture & “Universality”

KSS, JCP, 2007

Caging Force

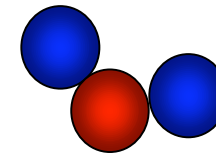
*Fourier-resolved mean square force*

$$-\frac{\partial F_{\text{eff,cage}}(r)}{\partial r} \propto -r \int_0^\infty \frac{d\vec{k}}{(2\pi)^3} [\mathbf{kC(k)}] \rho S(k) [\mathbf{kC(k)}] e^{-\frac{k^2 r^2}{6}(1+S^{-1}(k))}$$



**Single**  
“coupling constant”  
controls **entire**  $F_{\text{eff}}$ !

$$V_\infty \equiv \phi g^2(\sigma) \propto F_B$$

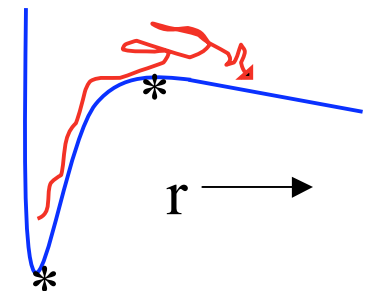


“contacts”

→ Predicts connections between slow dynamics on different time & length scales : e.g., late  $\beta$  / early  $\alpha$  vs. final  $\alpha$

e.g.,

$$G_{\text{glass}} \propto \phi \frac{k_B T}{\sigma r_{loc}^2} \quad F_B \propto \frac{\sigma}{r_{loc}}$$



“SOLID” only at RCP  
**Jamming**

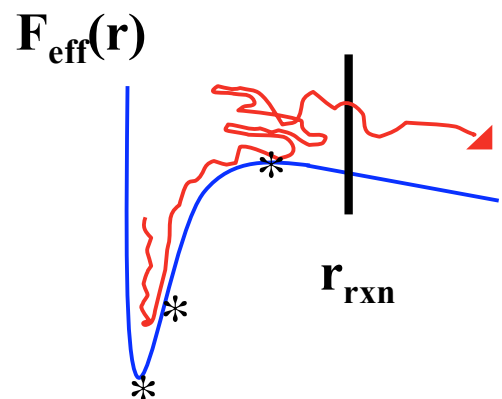
$$F_B \propto \phi g^2(\sigma) \propto (\phi_{RCP} - \phi)^{-2} \rightarrow \infty$$

Double Pole

# Full Numerical Soln: Includes Dynamic Fluctuation Effects

*JCP & PRE  
2006 & 2008*

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

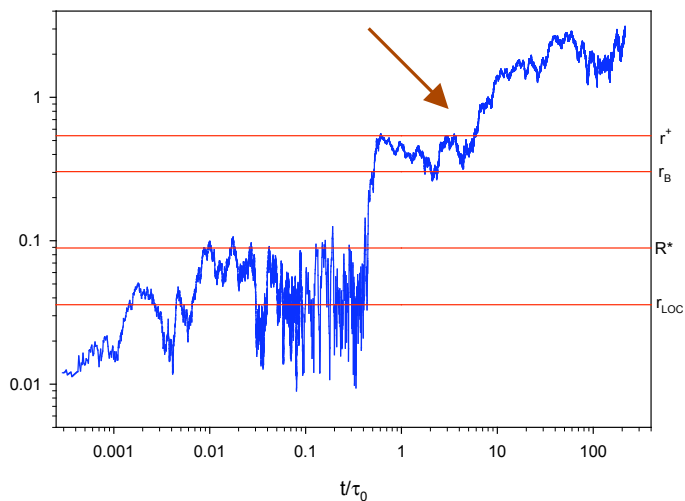


*Noise-Driven  
Trajectory Fluctuations*

*Heterogeneous  
Dynamics*

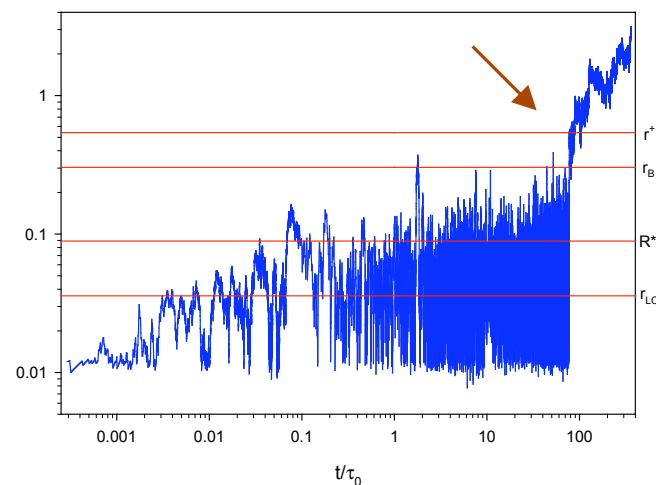
*r(t)/σ trajectories*

$\phi=0.55$  ; Barrier  $\sim 5$



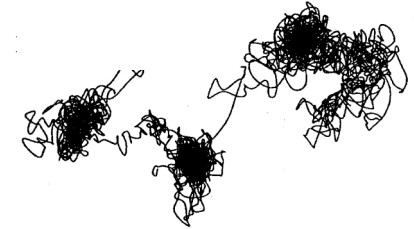
**Reaction point**  
Barrier  
Maximum force  
Localization length

*Re-crossings  
“back-hops”  
Large Fluctuations*



# Limitations & Possible Caveats

## \* *Full Dynamics ~ Sequence of Independent “local events”*



evidence for weak space-time correlation of **rare** “hops” :

Joerg Rottler simulations: EPL, 2009; PRL, 2010

successes of simple CTRW,...

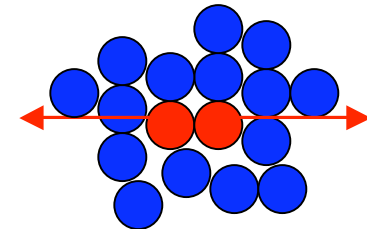
## \* *Single Particle vs. Cage vs. Stress Relaxation time ?*

evidence closely correlated from simulation:

Yamamoto-Onuki; Rottler ;.....

and experiment

Daniel Sussman & KSS

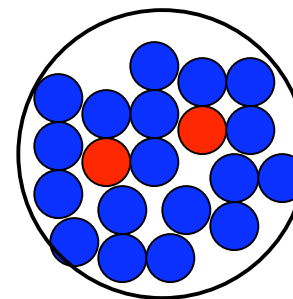


## \* *Single particle Dynamic Heterogeneity vs. Many particle space-time ?*

expect connected if hopping controlled

We do find explicit connections

e.g.  $\chi_4(t)$



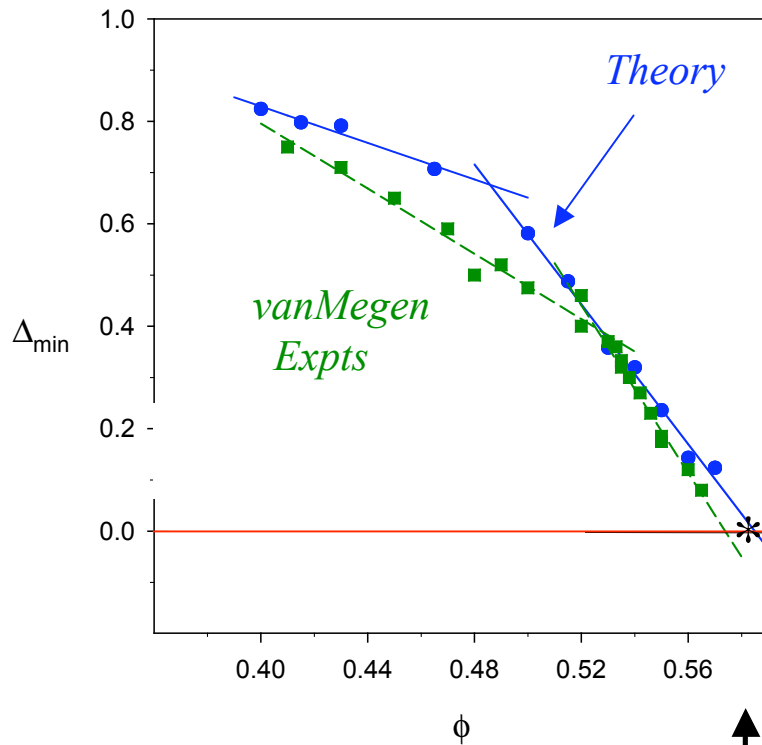
Dasgupta & Sastry  
Szamel  
many others

*dynamic length scale*  
 $\xi$

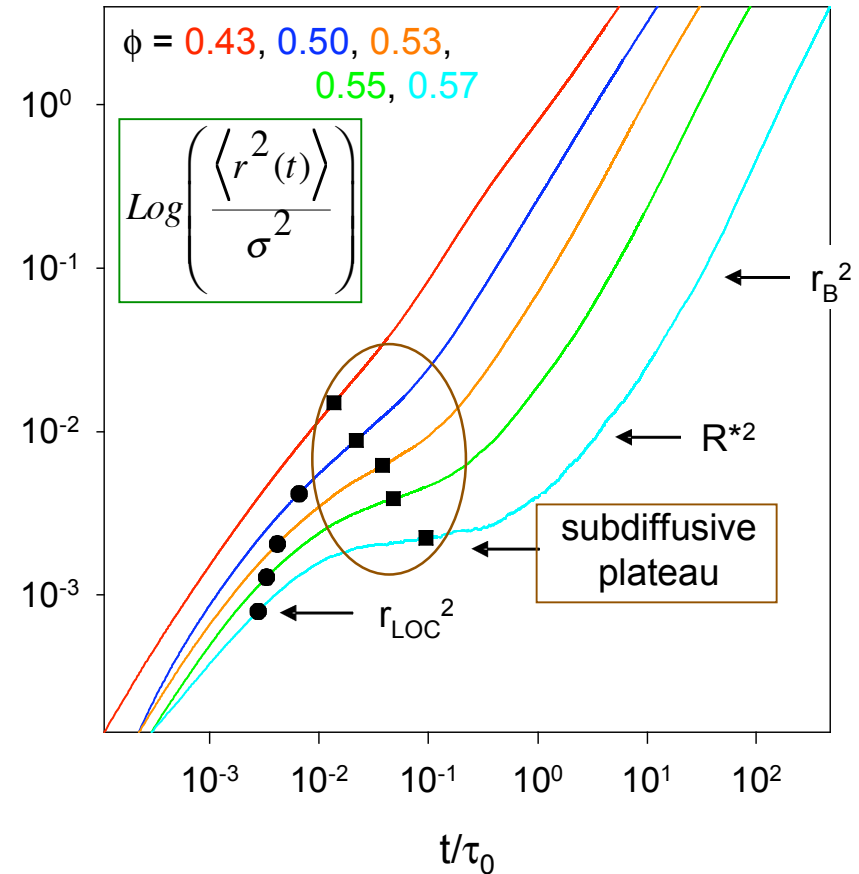
# Mean Square Displacement & Anomalous Diffusion

Maximum  
non-Fickian

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



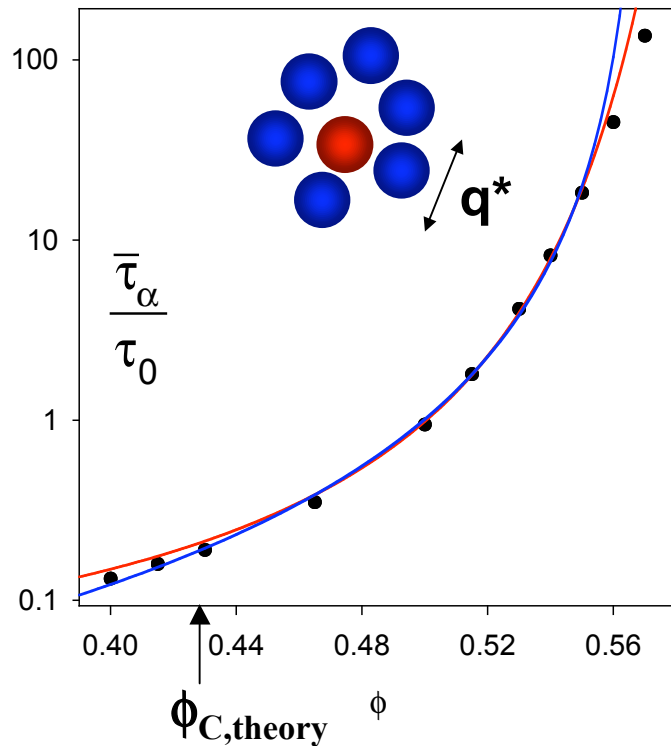
2<sup>nd</sup> moment



Extrapolate:  $\phi_c \sim 0.58$  ~ Experimental result based on fits to MCT

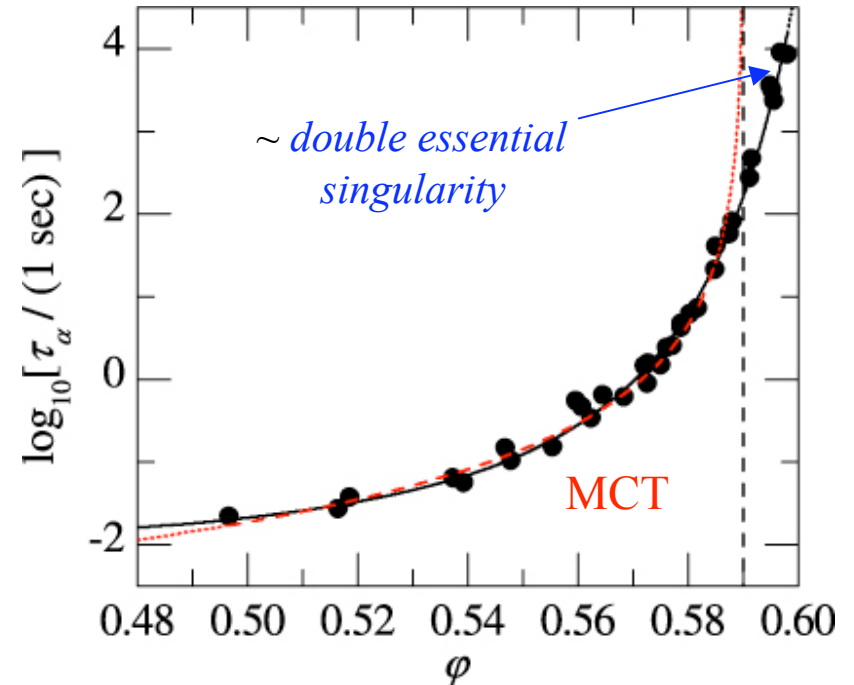
# Alpha (cage scale) Relaxation

$F_s(q^*, t)$



$\sigma = 1 \mu\text{m}$	
$\tau_\alpha$	$\phi$
$5 \times 10^4 \text{ s}$ (14 hrs)	0.57
5 months "glass"	0.61

*Cipelletti et al, PRL, 2009*  
*extra 2 orders magnitude*



**MCT critical power law** fits the **NLE THEORY & EXPT** over  $\sim 3$  orders of magnitude..... then breaks down (no singularity)

NLE Prediction  
(JCP, 2007)

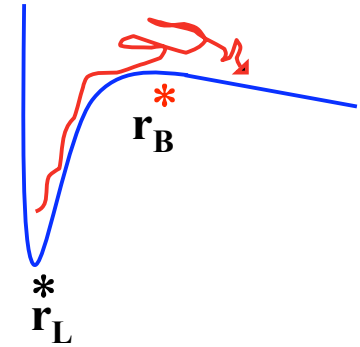
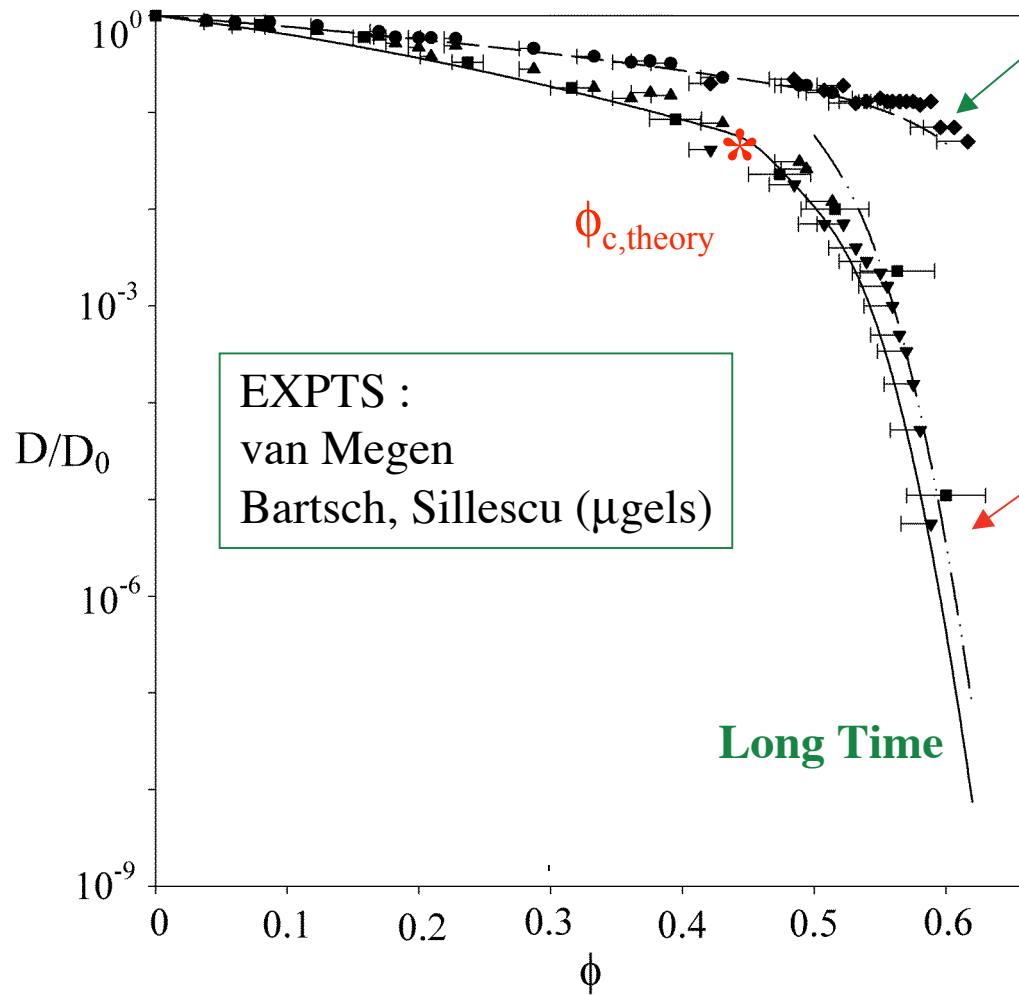
$$\tau^* / \tau_0 \propto e^{F_B(\phi)} \underset{\text{approach RCP}}{\propto} \exp\left(\frac{B}{(\phi_{RCP} - \phi)^2}\right)$$

*ala new expts*



# Self-Diffusion Constant

NLE theory + Green-Kubo +... (JCP, 2003)



$$D_{HOP} \equiv \frac{(r_B - r_L)^2}{6\bar{\tau}_{hop}}$$

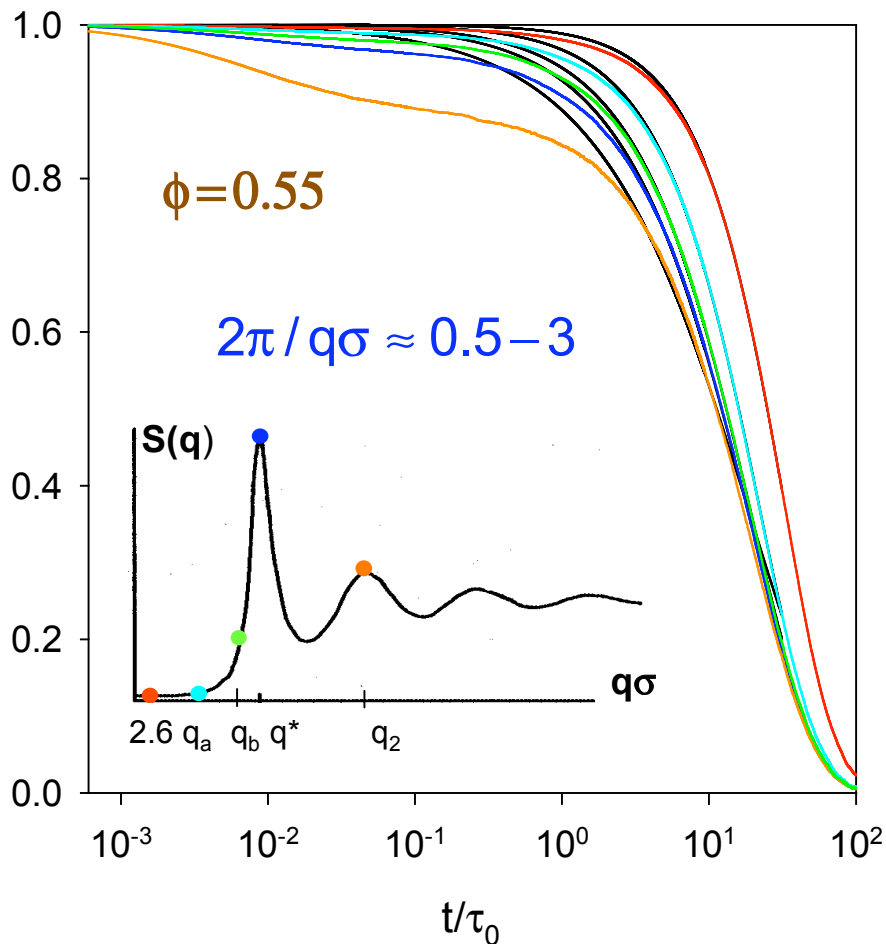
**NO divergences below RCP**

**Barriers important for  $\phi > 0.5$**

*Fluctuation consequences ?*

# NONgaussian Spatial $\alpha$ -Relaxation: *a signature of hopping*

$$F_S(q,t) = \langle \exp[i\vec{q} \cdot \vec{r}(t)] \rangle = \text{F.T.} \langle \delta(r-r_1(t)) \rangle$$



**q-dependent relaxation :**

Grossly NONgaussian

$$F_S(q,t) \neq \exp(-q^2Dt)$$

**WHY ?**

*Intermittent Hopping ?*

*Growing NonFickian length scale ?*

# Growing Dynamical Length Scale

$$F_s(q,t) \equiv \exp(-D(q)q^2t) \\ \equiv \exp(-t/\tau(q))$$

**Define:**  $R(q) \equiv q^2 D \tau(q) \rightarrow 1$ , Gaussian  $\approx$  MCT

*IF activated, Numerics described by:*

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

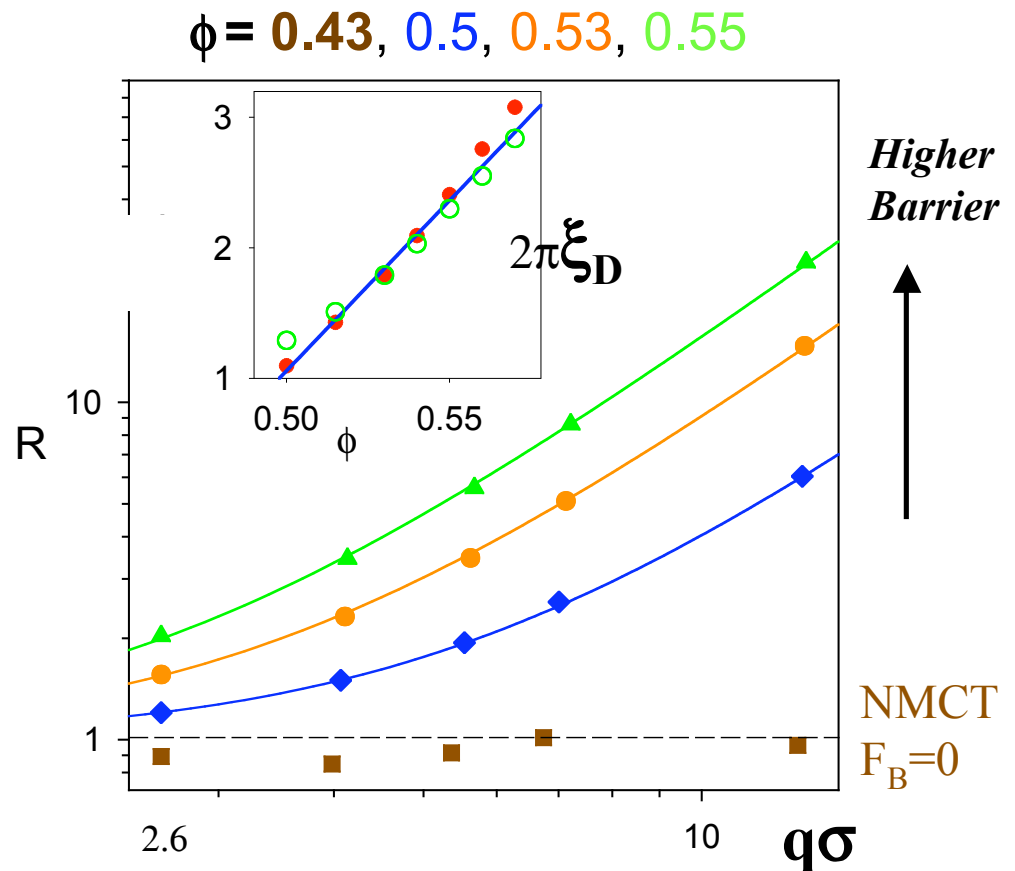
$$D(q) \approx D (q\xi_D)^{-2}, \quad q\xi_D \gg 1$$

$\tau(q) \approx q$ -independent



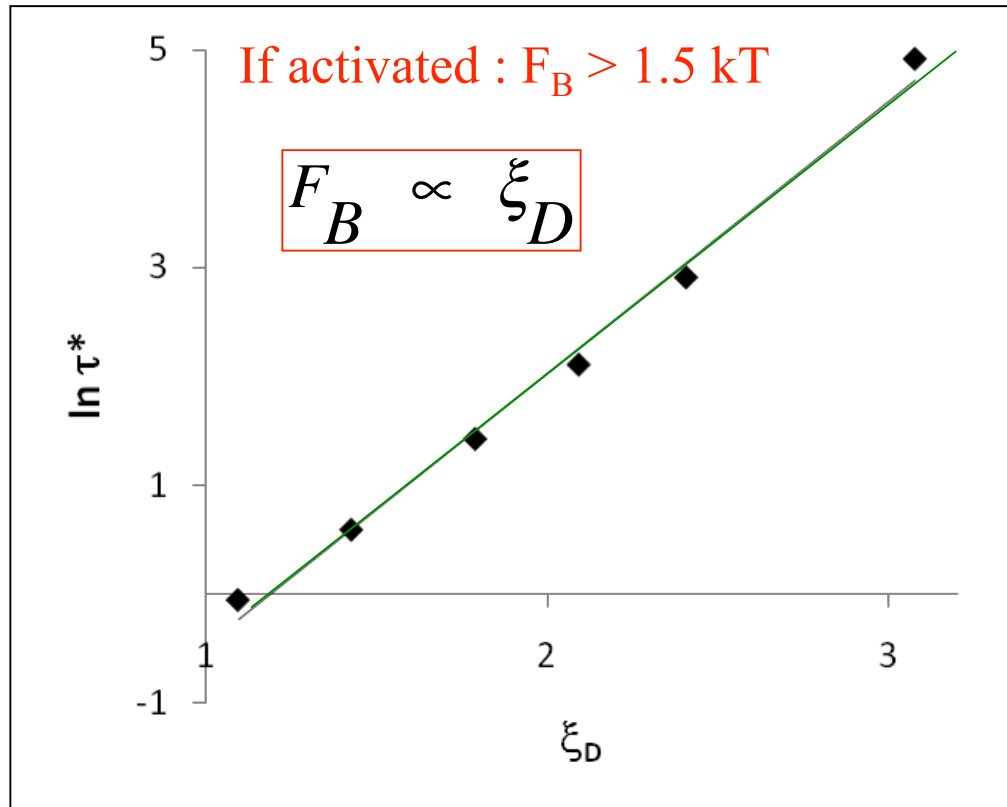
*Growing length scale for recovery of Fickian diffusion*

$$\xi_D(\phi)$$



*Consistent with BLJM Simulations (Szamel ; Berthier)*

# Connection of Alpha Time and Growing Length Scale



Very different scaling than :

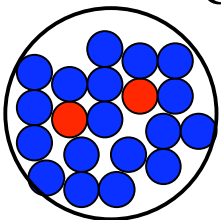
Naive Adams-Gibbs

Inhomogenous-MCT

other thermo-based theories

Close to Dasgupta-Sastry BLJM simulations:  
(PNAS, 2009)

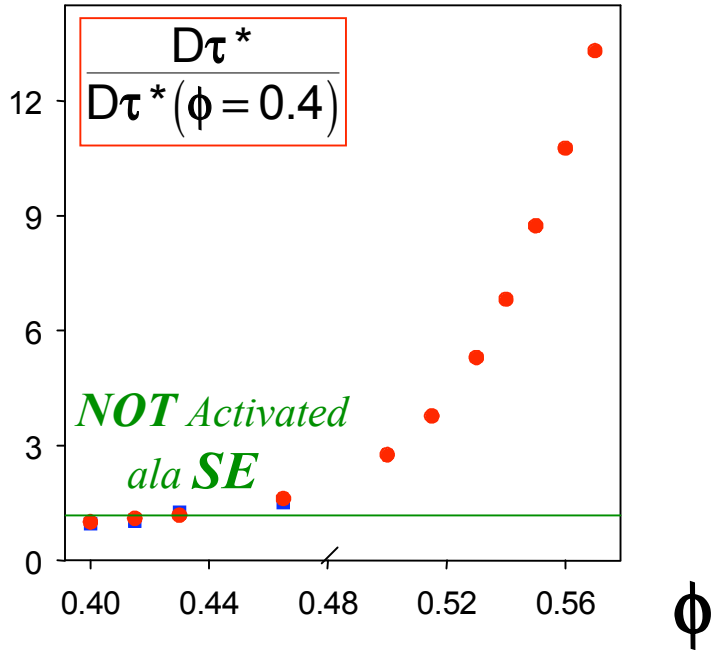
$$\ln(\tau_4) \propto (\xi_4)^{0.7}$$



*4-point “susceptibility”  $\chi_4(t)$ : time scale & dynamic correlation length*

# “Decoupling” of Self-Diffusion & Alpha Relaxation

...failure of Stokes-Einstein behavior



*Mass Transport ENHANCED  
@ fixed “relaxation time”*

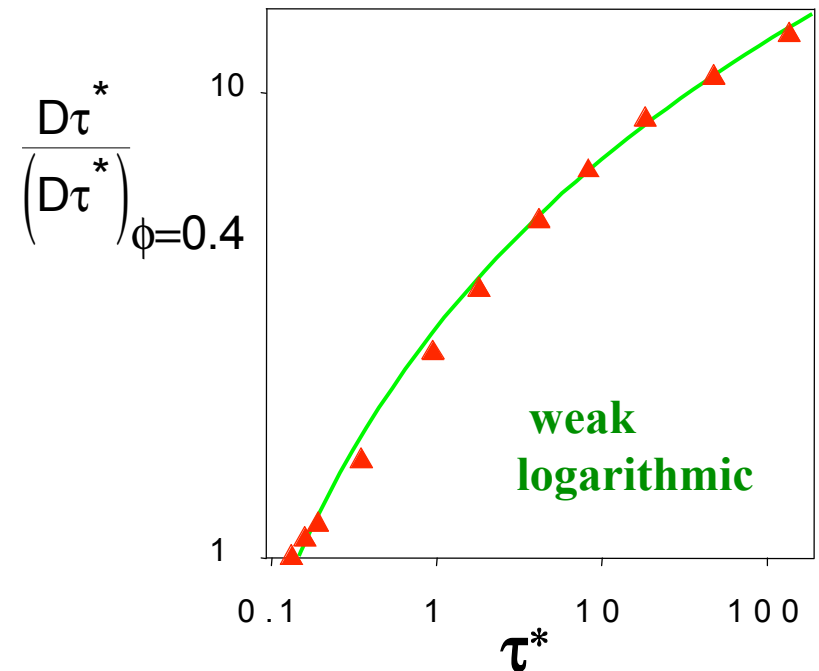
$$\sim \frac{D\tau^*}{(D\tau^*)_0} \approx 10 - 20 ; \phi = 0.58 - 0.59$$

*Sanat Kumar; Tom Truskett  
PD-Hard Sphere SIMS*

*“Decoupling length”*

$$L_d \equiv \sqrt{D\tau^*} \propto \xi_D \propto \ln(\tau^*)$$

↑  
**WHY?**



# Mobility Bifurcation and Exponential Tails

PRE, 2008

Real Space Van Hove

$$G_S(r,t) = \langle \delta(r-r_1(t)) \rangle$$

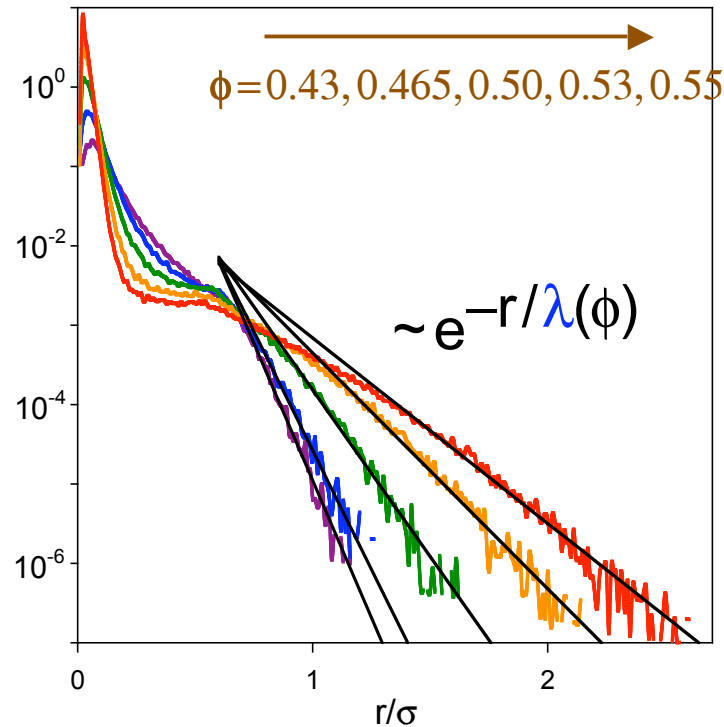
@  $\alpha$ -time :  $\text{Log } G_S(r, t=\tau_\alpha)$

$\lambda$  = "Jump Length"  
grows with  $\phi$

directly correlated with

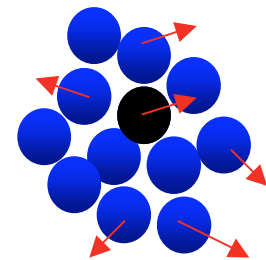
**Fickian Crossover**  
and  
**Decoupling lengths**

$$L_d \equiv \sqrt{D\tau^*} \propto \lambda \propto \xi_D$$



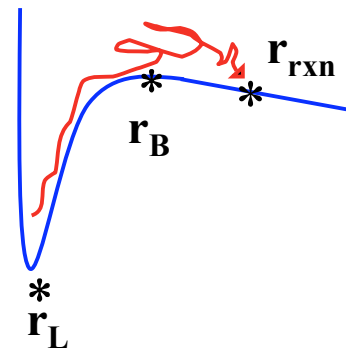
**Exponential tail**

"fast hoppers"



$$\lambda \propto \sqrt{t}$$

in  $\alpha$ -regime



**Mobility = function of length scale**

**Relaxation more local process**

(barrier,  $r_B$ , slow) **than**

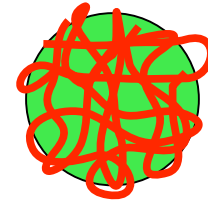
**Diffusion** (reaction pt,  $r_{rxn}$ , faster)

...akin to "facilitation" ? (Chandler, Garrahan)

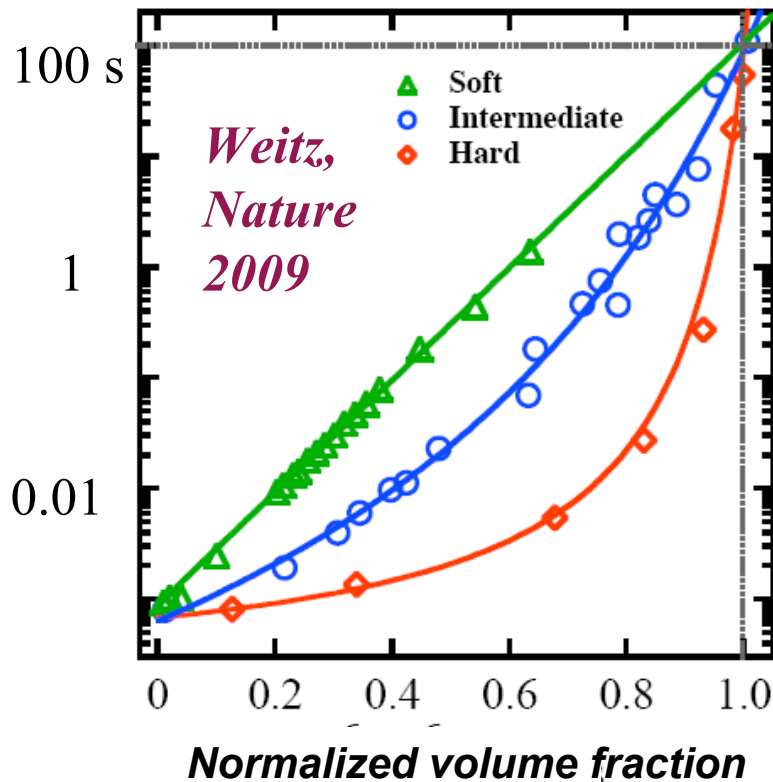
## II. Soft Repulsive Spheres ~ MICROGELS...important materials !

Vary Single Particle Stiffness (*crosslinks*) ...interparticle repulsion strength

→ Massive Change in Dynamic Fragility



Relax Time ( $\phi$ ) from DLS



“glass”

*finite range*  
Hertzian Contact Model :

$$V(r) = \frac{4}{15} E^* \sigma^3 \left(1 - \frac{r}{\sigma}\right)^{5/2}, r \leq \sigma$$

$$= 0, r > \sigma$$

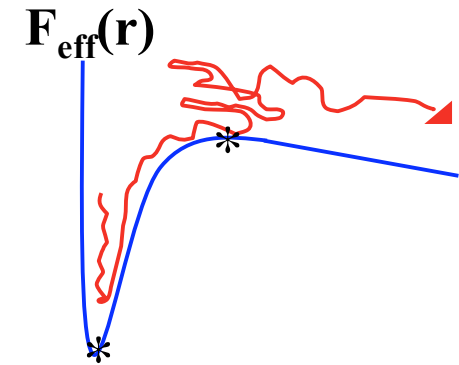
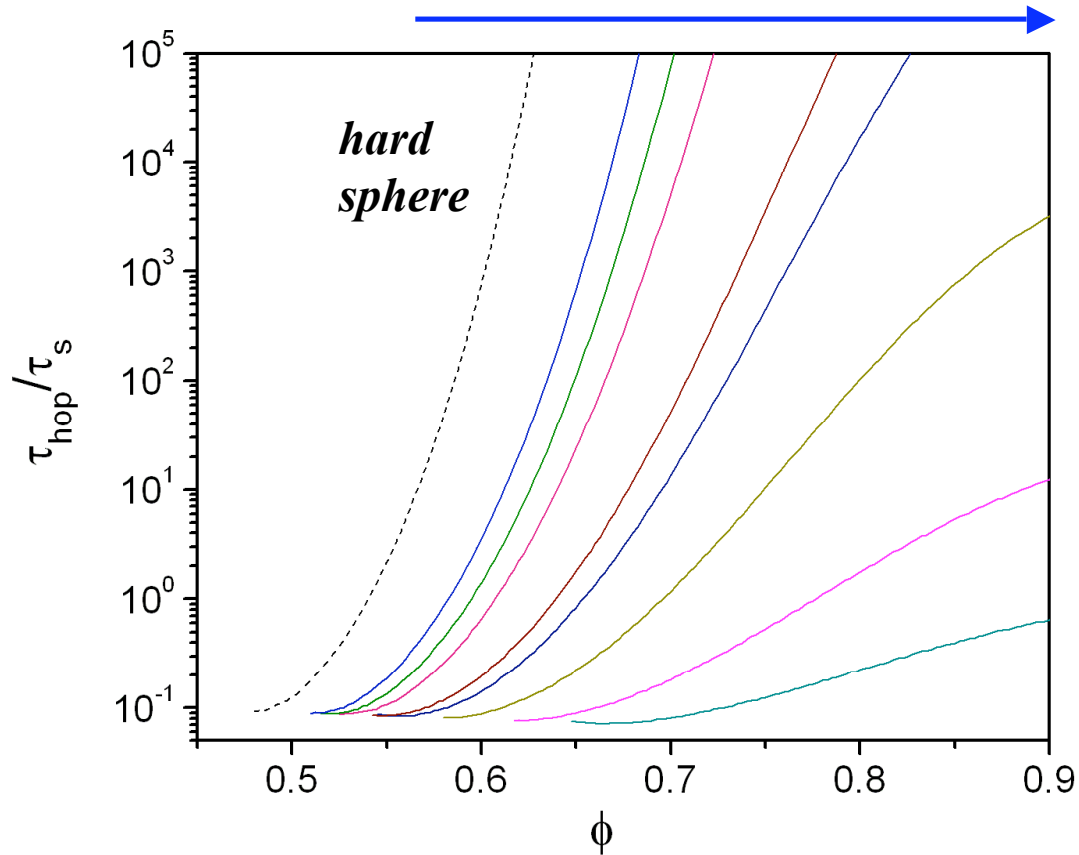
*Packing Complexity*  
as function of  $\phi$  and  $E^*$

$$g(r)$$

# NLE Theory: Activated Kramers Time

Yang & KSS  
submitted

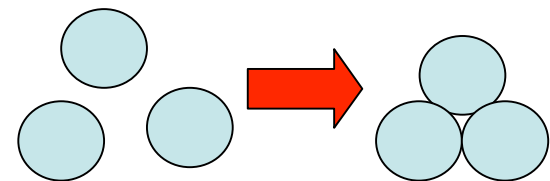
Fix  $E^* = \text{infinity}, (5,3,2,1)10^4, (8,5,3,2) 10^3$



**NON**exponential Growth  
non-Arrhenius

**More "Fragile" as  
Single Particle Stiffens**

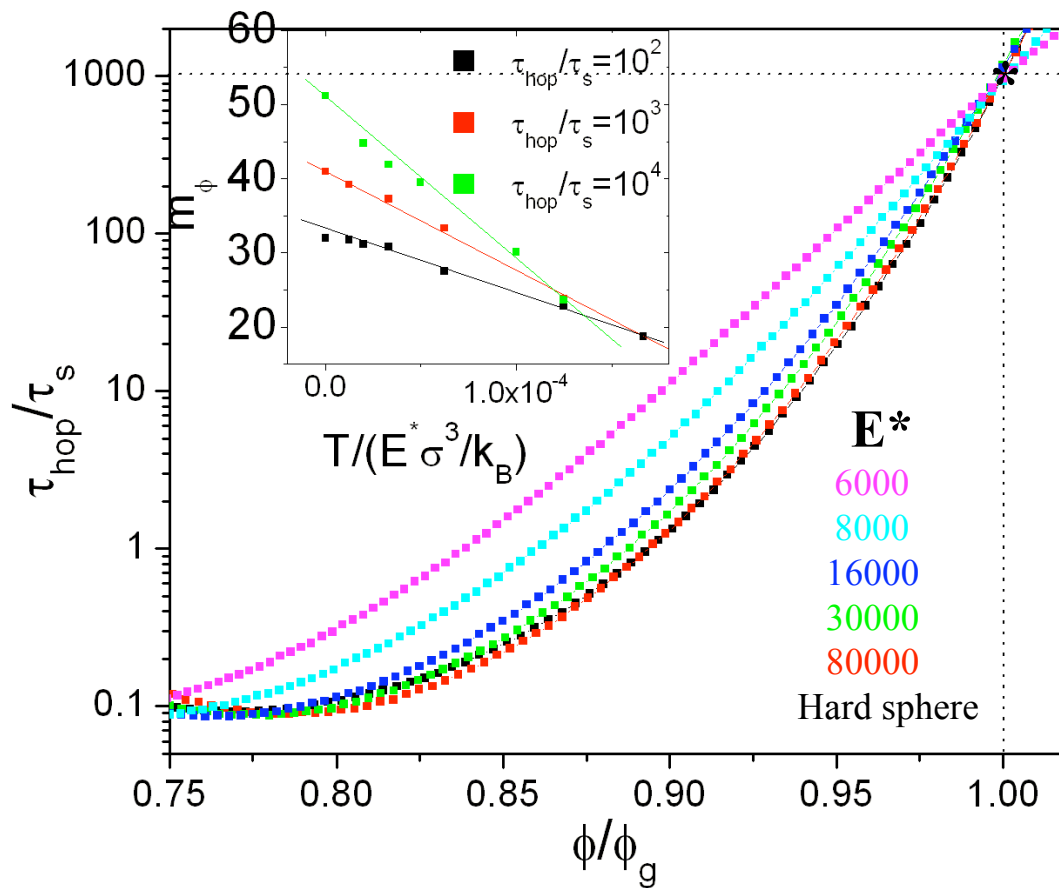
"Bends over" as "soft jamming" approached  
due to qualitative change of packing





# Dynamic Fragility: Tunable via Particle Softness

*Angell Fragility Plot based on Kinetic Glass Criterion*



$$m_\phi \equiv \left. \frac{\partial}{\partial(\phi / \phi_g)} (\log \tau_{hop}) \right|_{\phi_g}$$

varies by factor  $\sim 3 - 4$

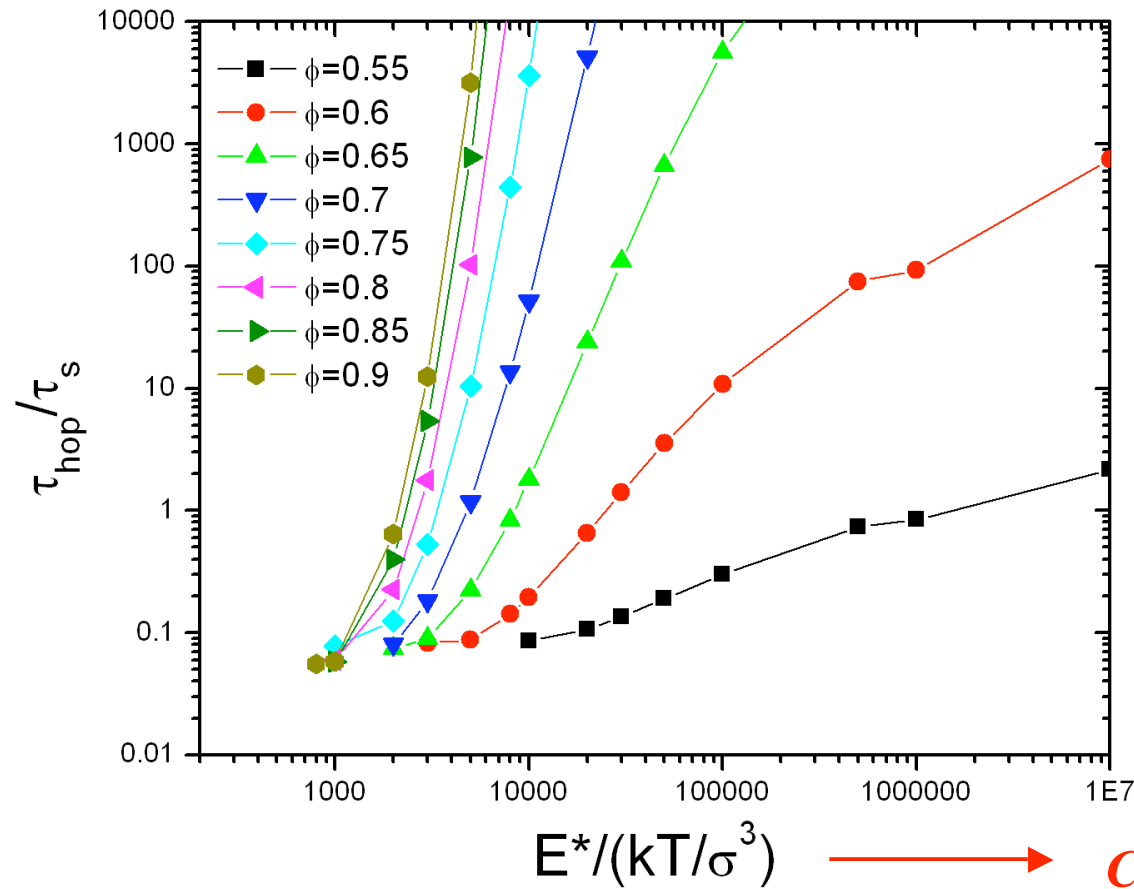
*Decreases*  
**LOGARITHMICALLY**  
*as Particle softens*



**“Soft Particles Make  
STRONG GLASSES”**  
~ Arrhenius

*ala Weitz et al, Nature, 2009*

# “Thermal Fragility” at Fixed Volume Fraction



“Two  $\phi$ -Regimes”

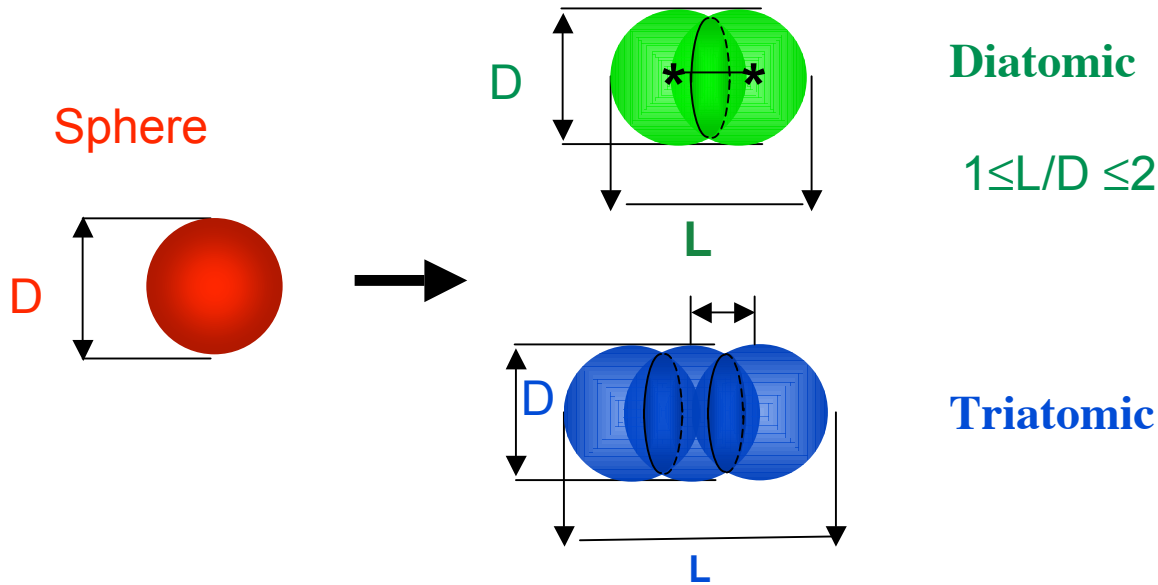
*ala Simulations with  
harmonic repulsions*

**Berthier & Witten**  
*EPL; PRE, 2009*

**MASSIVELY Enhanced Thermal Fragility as Volume Fraction grows**

*PHYSICS: below vs. above HS “jamming” per Berthier-Witten scaling argument*

# BEYOND SPHERES : Hard *Uniaxial* Particles



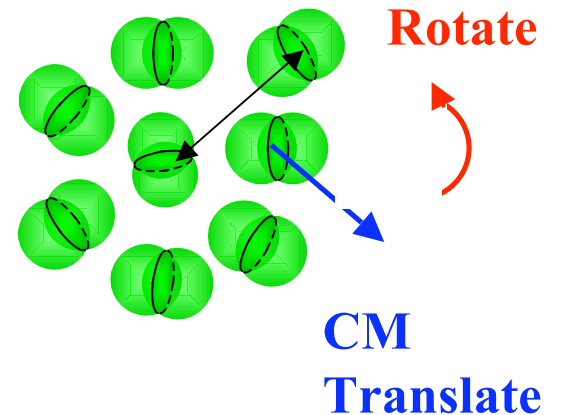
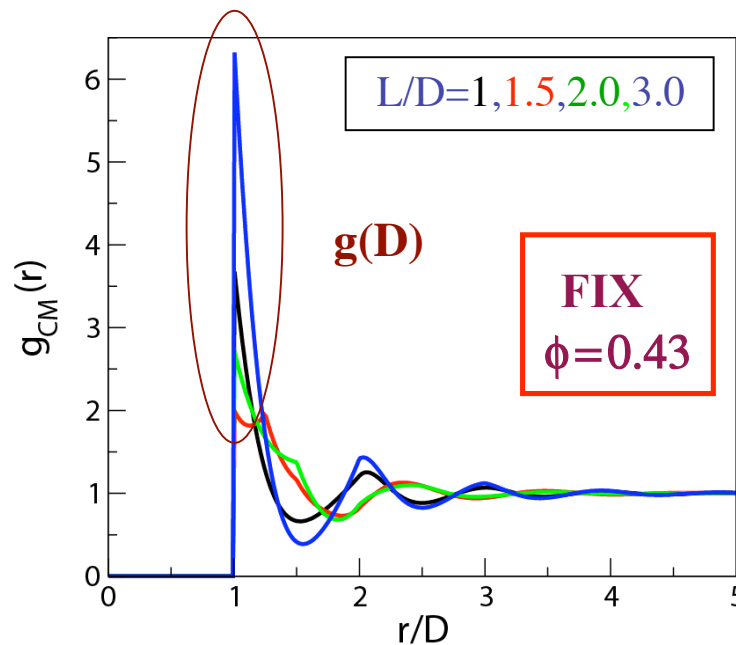
**“Molecular Colloids”**

*A frontier of particle science  
and engineering*

*Site-Site Hard Core  
Repulsions*

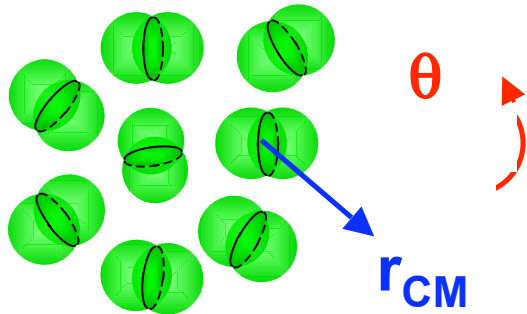
*NON-monotonic  
local order  
as vary  
ASPECT RATIO  
L/D*

*incommensurate  
Packing Frustration*



# COUPLED Translation-Rotation Dynamics

Zhang & KS  
PRE 2009



*Cumulative angular rotation*

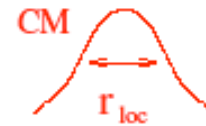
$$|\vec{\theta}(t)| = \left| \int_0^t dt' \vec{\omega}(t') \right|$$

*Center-of-Mass displacement*

**Naïve MCT**

*CM Force & Torque*

Time correlations



**Vibrate**



**Librate**

*2 coupled self-consistent localization eqns*

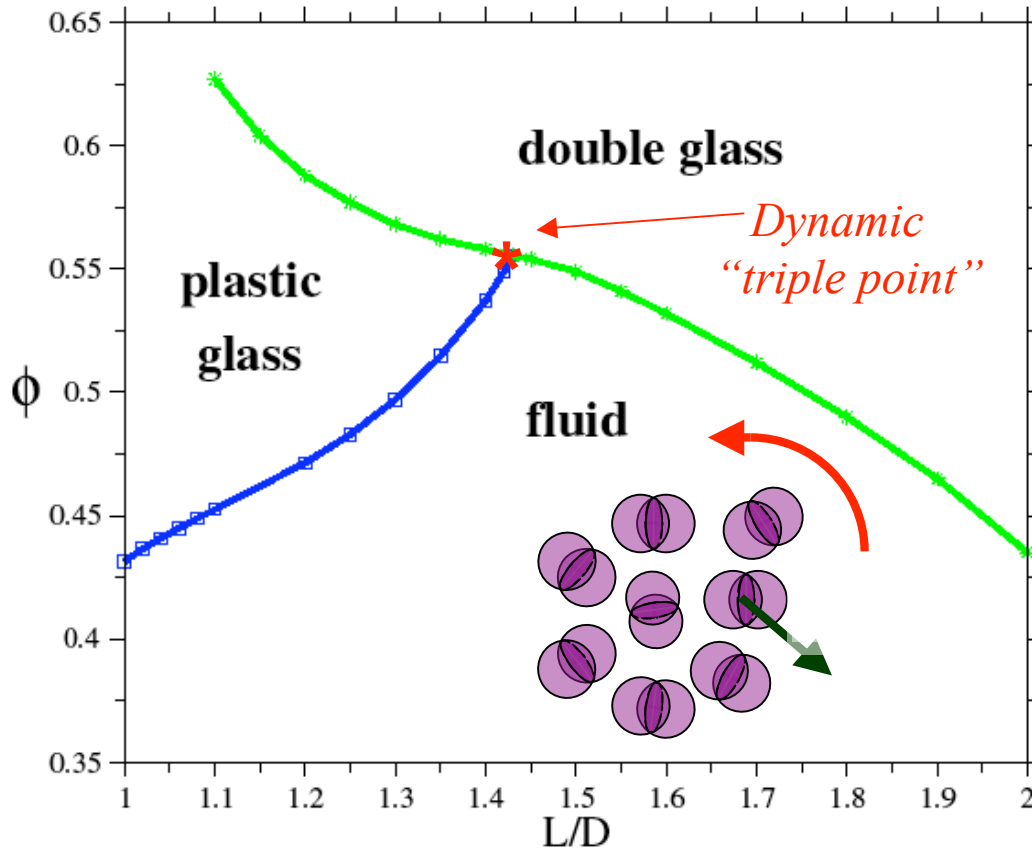
## NLE Activated Dynamics Theory

*Dynamic Free Energy*  
**SURFACE**

$$-\zeta_T \frac{d}{dt} r_{CM} - \frac{\partial}{\partial r_{CM}} F_{eff}(r_{CM}, \theta) + \delta f_T = 0$$

$$-\zeta_R \frac{d}{dt} \theta - \frac{\partial}{\partial \theta} F_{eff}(r_{CM}, \theta) + \delta T_R = 0$$

# Dynamic Crossover Diagram (*naive MCT “ideal glass”*)



**3 dynamical states**

**Fluid**

**Plastic Glass**  
*...CM localized, Rotation Ergodic*

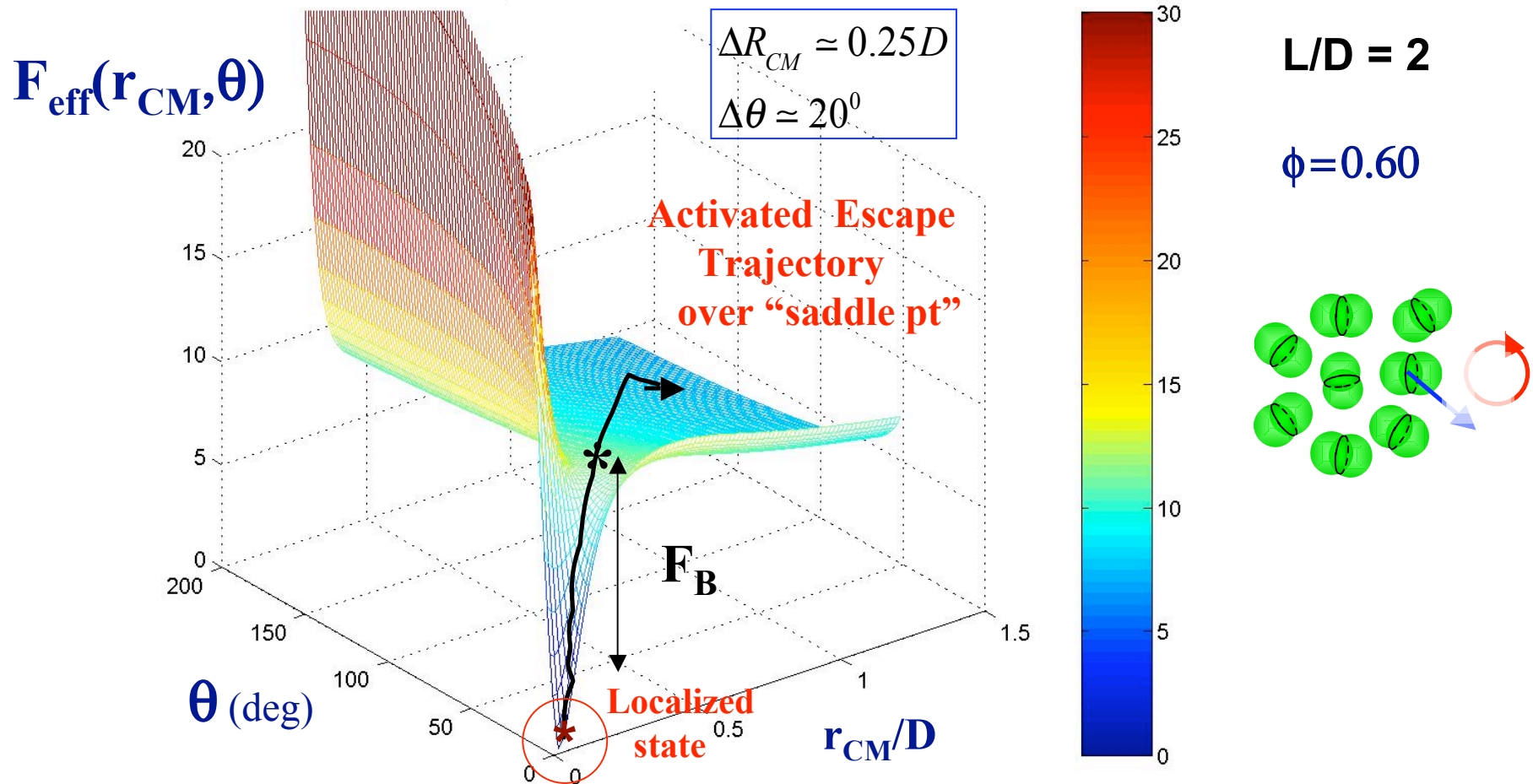
**Fully Arrested “Double Glass”**

Qualitatively ala Full site-site MCT  
 (Chong & Gotze, PRE, 2002)

“Most Difficult to Vitrify” state....*analogous to granular jamming !*

Physical Mechanism: “packing frustration”....*weakest short range caging order*

# Dynamical Free Energy Surface *(double glass regime)*



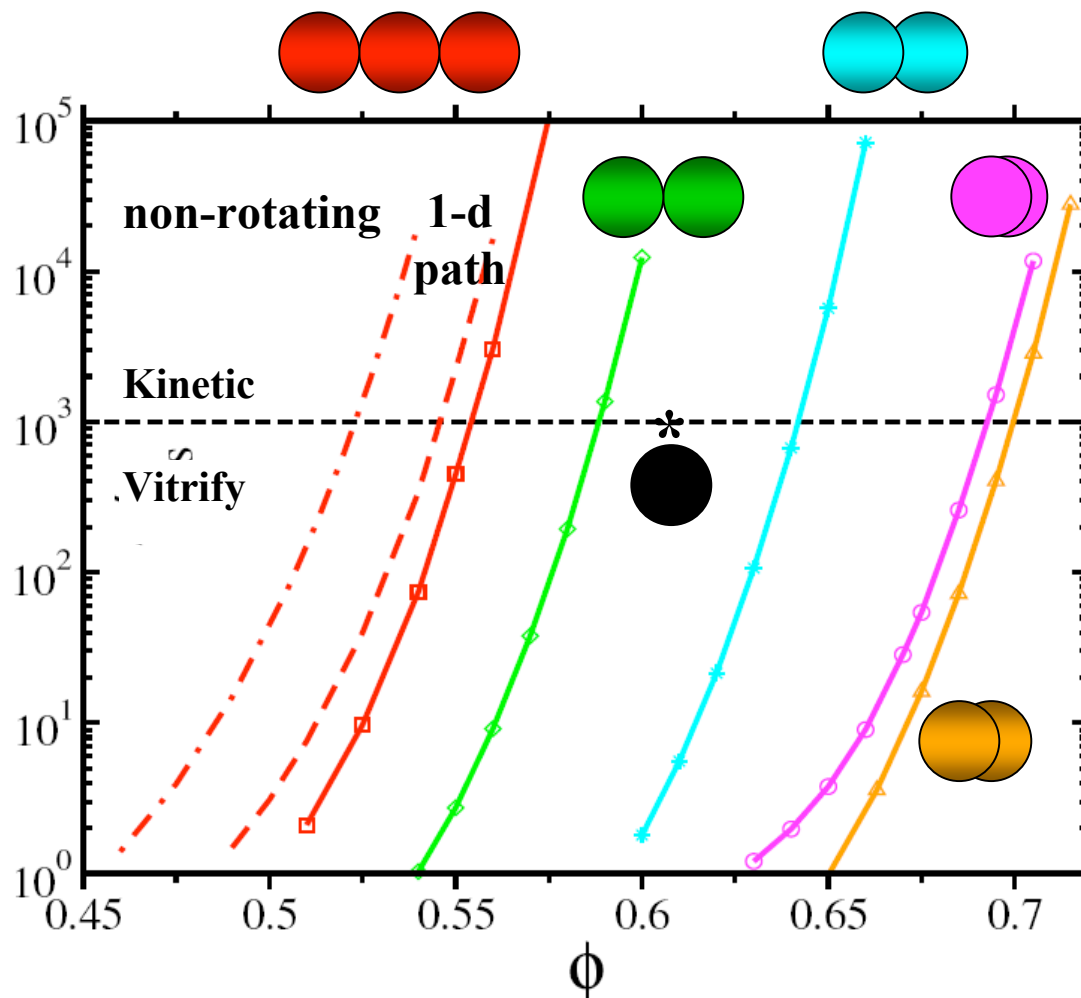
*Cooperative Translate-Rotate Activated Path.....barrier varies with "eigenvector" depends mainly on particle shape*

*Mechanistic picture of Alpha Relaxation ala chemical reaction*

# Relaxation Rate: Multi-Dimensional Kramers-Langer Theory

$$\frac{\tau}{\tau_s} = \frac{2\pi}{\lambda^+} \left( \frac{|\det \mathbf{K}_B|}{\det \mathbf{K}_o} \right)^{1/2} \exp(F_{B,SP})$$

Saddle Trajectory + local fluctuations



- Supra-Arrhenius Growth
  - NON-monotonic
  - Less rotation @ saddle
- L/D ↑

L/D	$\phi_g$
1	0.60
1.25	0.693
1.43	0.700
1.8	0.642
2	0.588
3	0.554

*Connection between ideal MCT and activated NLE*

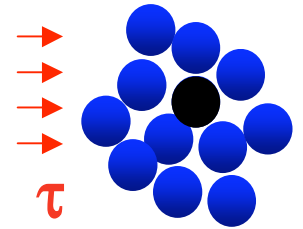
# Nonlinear Viscoelasticity: Simple Stress Perspective

## Classic Idea: External Deformation Reduces Barriers to Flow

- \* **Eyring (1936)** *Arrhenius viscoplastic flow*
- Frenkel (crystals)*

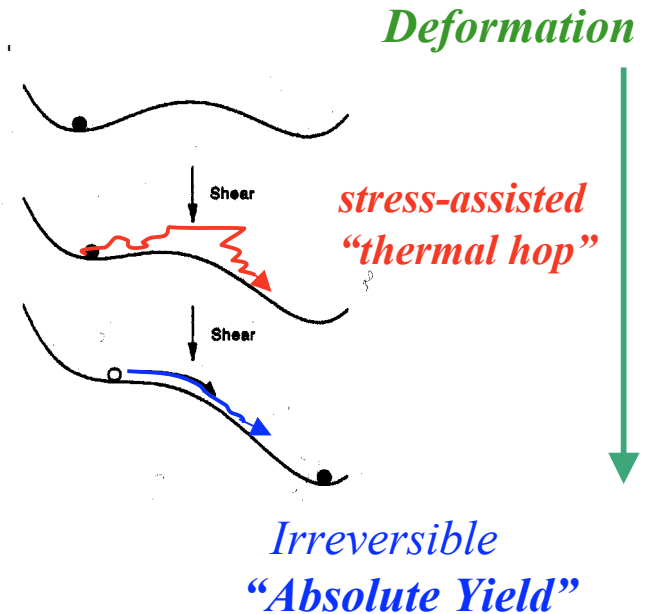
*Mechanical Work*

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



- \* *Potential Energy Landscape simulations... Dan Lack*

*stress reduces and ultimately destroy barriers*



- \* **Macroscopic Rheology** ↔ **cage scale physics**

*Microrheology concept*



**Simulation Support** : Yamamoto ; dePablo ; Rottler ; .....



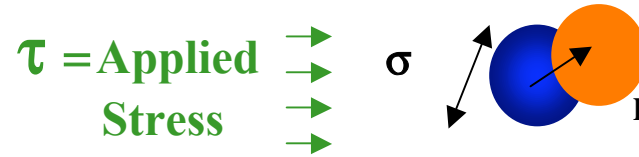
- \* *Dynamics ~ Isotropic on CAGE scale*



# Incorporation of Stress in NLE Theory

Kobelev+KSS  
PRE 2005

*External force on particle*



*Mechanical Work*

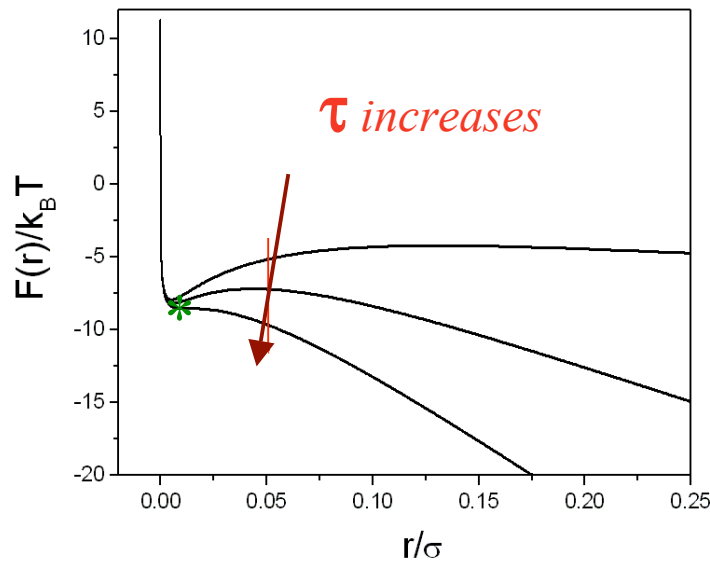
*ala Eyring @ “instantaneous dynamical variable” level*

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

**STRESS** : *Reduces Modulus*  
*Accelerates Relaxation*

“Absolute YIELD” → Barrier destroyed

“tilted landscape”



$$\frac{\bar{\tau}_{hop}}{\tau_0} = \frac{2\pi g(\sigma)}{\sqrt{K_0(\tau) K_B(\tau)}} e^{F_B(\tau)}$$

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

**Viscosity, Flow Curve, Shear Thinning,...**

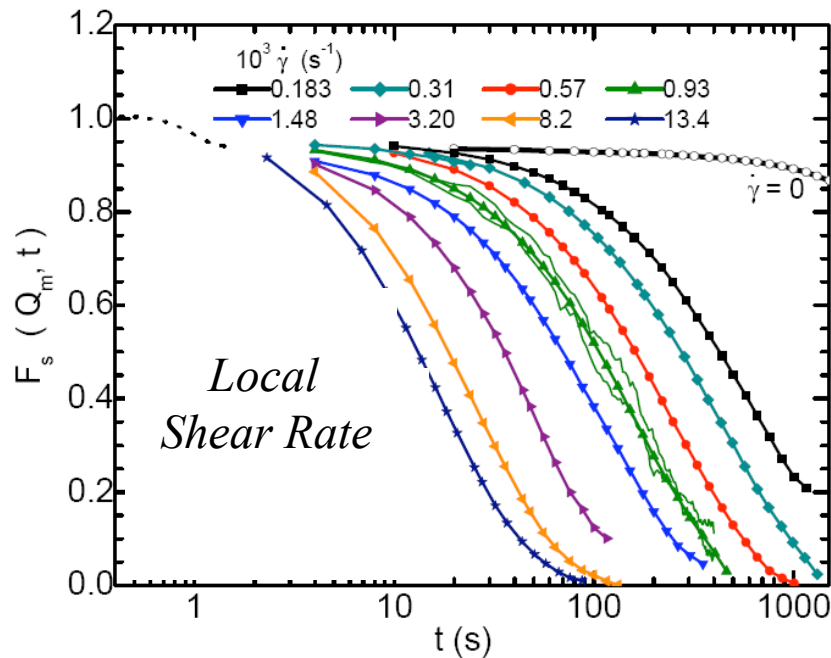
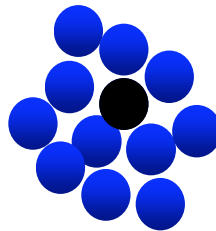
Constitutive eqn: Chen + KSS, Macromolecules, 2008

# SELF-Motion Under Shear

Besseling, Weeks, Poon, PRL, 2007

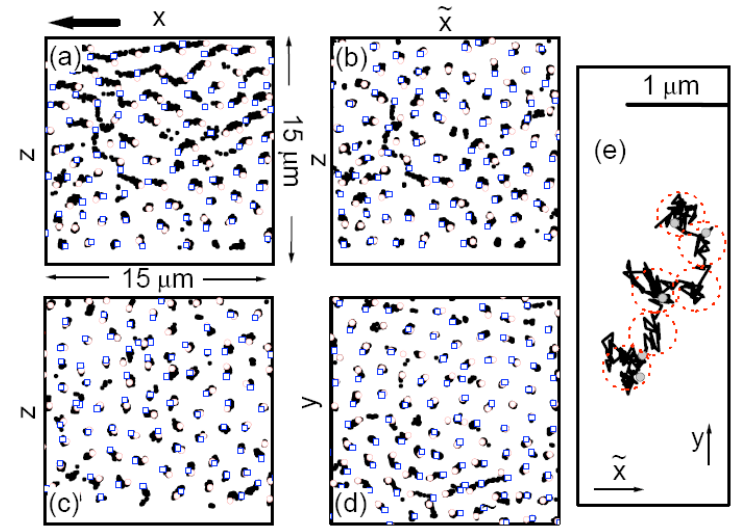
*Confocal* : direct microscopic probe of theory

$$F_s(\mathbf{q}^*, t) \quad \phi = 0.62$$

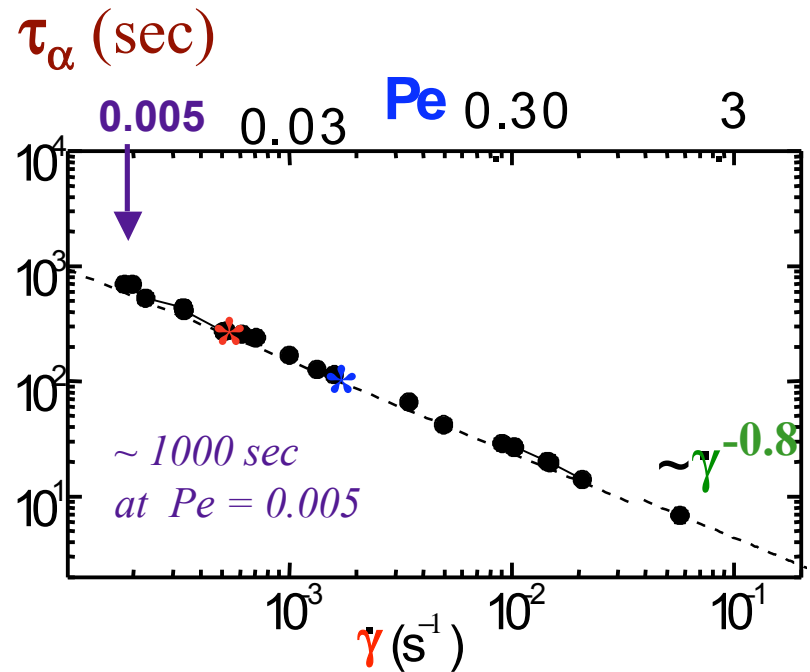


Exponential Relaxation

$$\tau_\alpha \sim 1/(\text{shear rate})^{0.8}$$



~ Isotropic Hopping Motion



# Steady State NLE Theory Predictions

PRE, 2005  
JPCM, 2008

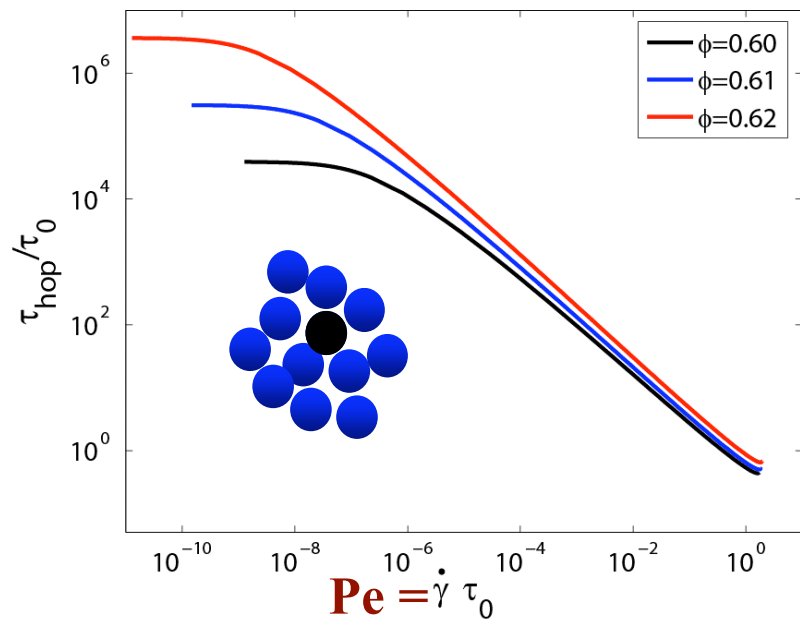
$$\tau = \eta(\tau) \dot{\gamma} = G'(\tau) \tau_{\alpha}(\tau) \dot{\gamma}$$

*Hopping*

$\tau_0 \sim 30$  secs  $\rightarrow$   $\tau_{\alpha} \sim 60$  million secs  
 $\phi = 0.62$   $\sim 2$  Years

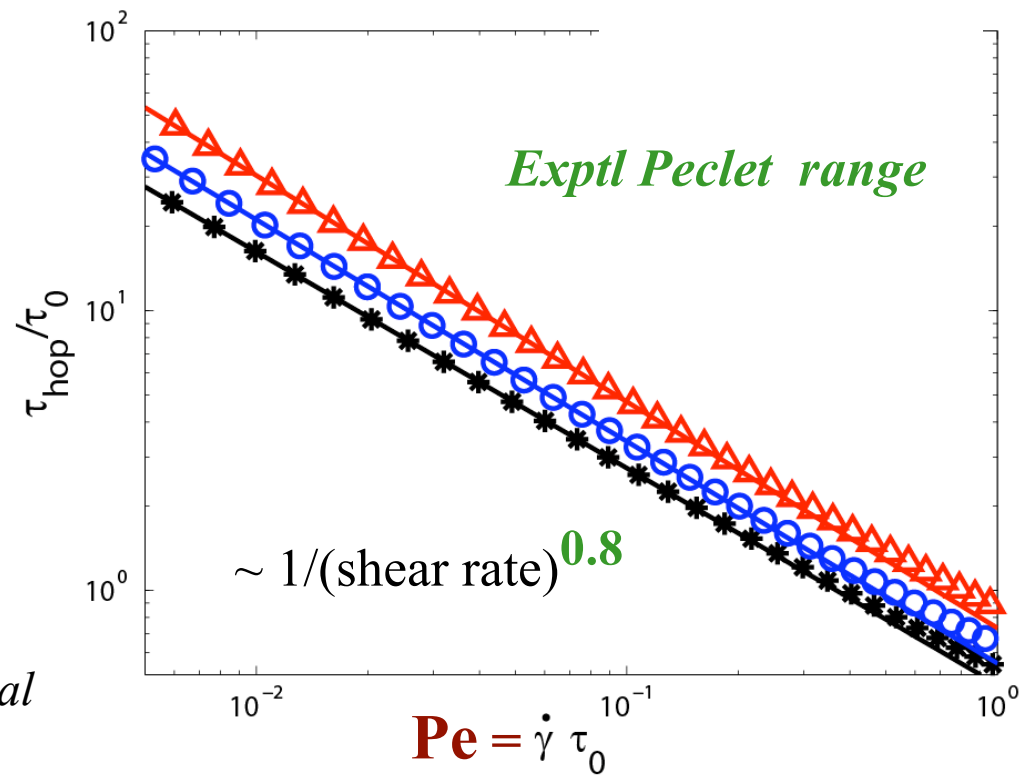
AT lowest  $Pe = 0.005$  : 900 secs  $\sim$  EXPT

“shear thins” by  $\sim 5$  orders of magnitude !



agrees with EXPT

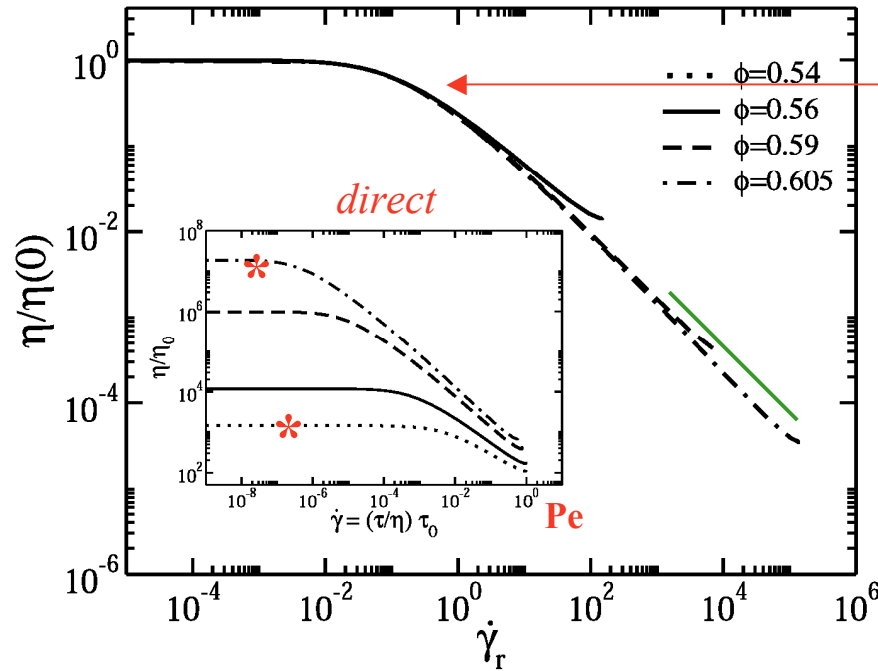
*Entropic Barriers NOT Zero*  
*per Intermittent Hopping seen in confocal*



# Viscosity Thinning & Flow Curves

$\phi$   
0.54  
0.56  
0.59  
0.605

$\eta/\eta_s$   
 $10^3-10^7$



$\dot{\gamma}_{r,crit} \approx 0.3-0.4 \sim \text{Expts}$

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

“stress relaxation time”

Near collapse

**FLOW CURVES**

*No rigorous plateau (hopping)*

**Apparent power law regime**

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

exponents  $\sim 0.1 - 0.3$

