KITP Conference on Emerging Concepts in Glass Physics

Activated Hopping, Dynamic Heterogeneity, and Nonlinear Rheology in Dense *Particle* Suspensions & Glasses

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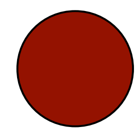
GOAL: Predictive Microscopic "Mean Field" **Theories @ Level of Forces**
NO *Fitting, Adjustable Parameters, Avoided Singularities*

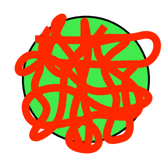
******THE BASICS***: Hard Sphere Colloids**



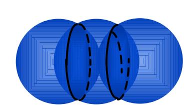
Erica Saltzman (***quiescent***)

Kang Chen, Vladimir Kobelev (***mechanically driven***)

* **Tunably Soft Repulsive Particles**: Jian Yang

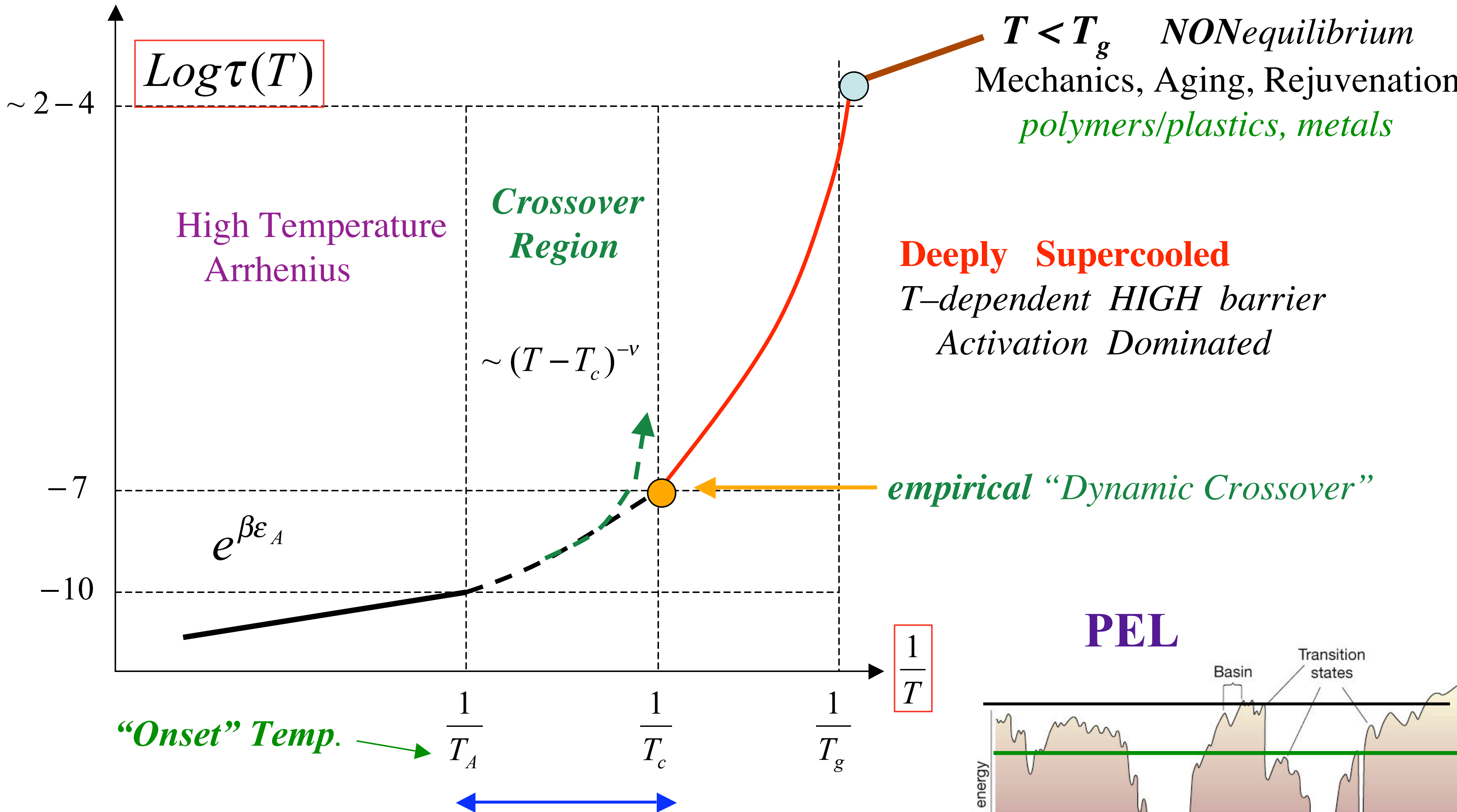


* **Molecular Colloids & Liquids**: Rui Zhang



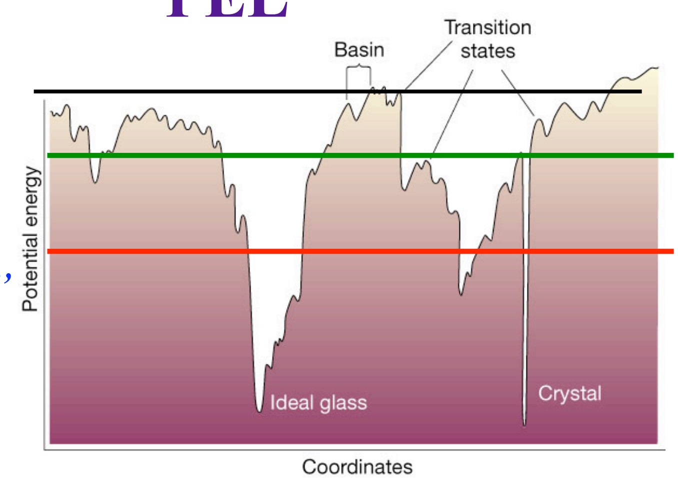
Coupled Translate-Rotate

Alpha Relaxation Map & Regimes



mode coupling effects + low barriers: "landscape influenced"

PEL

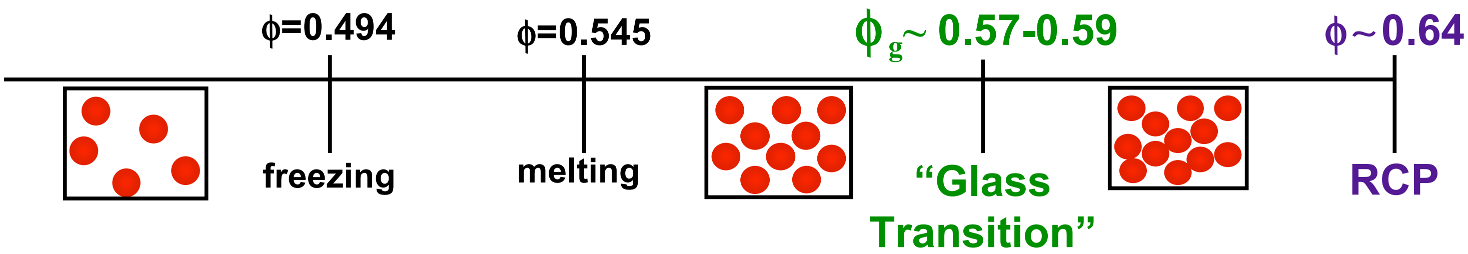


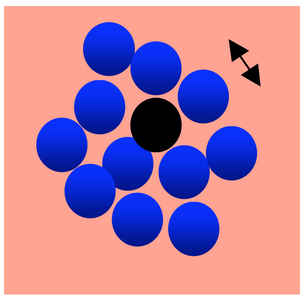
T^{-1} <---> ϕ

COLLOIDS: ϕ_A , ϕ_c , ϕ_g

HARD SPHERE Suspensions (and fluids)

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





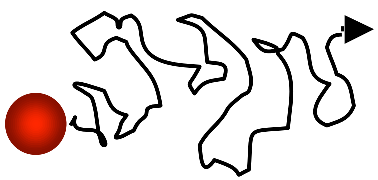
σ ~ 100 nm -2 μm

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

Kinetic "Vitrify": Relaxation Time > Expt time ~ 10,000 secs

σ~μm vs **nm** :"glassy" dynamics probed only over ~ 3-5 orders magnitude
…..***ala MD computer simulations***

CONFOCAL Microscopy & Simulations

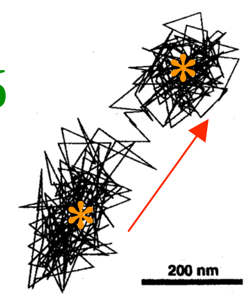


Collective, but Small Steps ~ **Gaussian**

"High" volume fraction

"Solid - Like"…intermittent hopping

$\phi = 0.56$

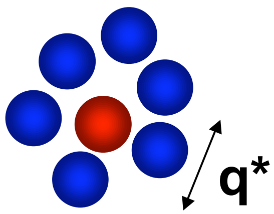


~σ/2

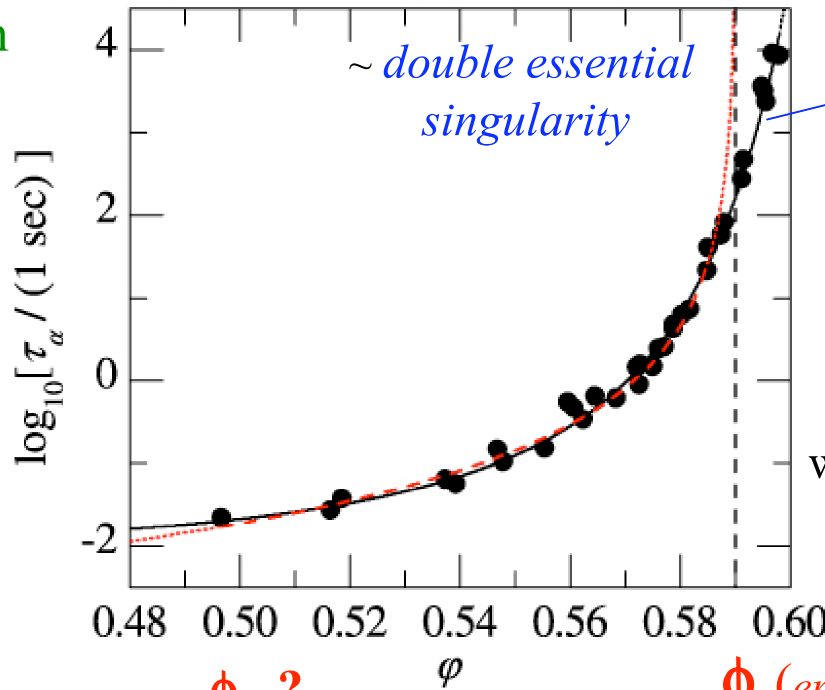
Weeks Weitz

Colloid Experiments & Computer Simulations

Incoherent
Alpha Relaxation



Cipelletti, Berthier, et al, PRL, 2009



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

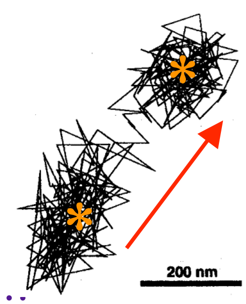
MCT ***fit*** **:** $\propto (\phi_C - \phi)^{-2.5}$

works over ~ 3-4 orders magnitude

ϕ_A ? ϕ_c (*empirically deduced*)

***In regime where can fit MCT, see strong NONgaussian effects** ("onset issue") **:**

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



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

Microscopic Theoretical Approach

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

BUT go beyond to treat **Activated Intermittent Dynamics**

@ ***Single Particle level***…especially relevant @ long times

…..*"theory of simulation or confocal microscopy particle trajectories"*

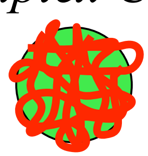
restores ergodicity, destroys "ideal" MCT glass transition

allows treatment of some space-time Dynamic Heterogeneity effects

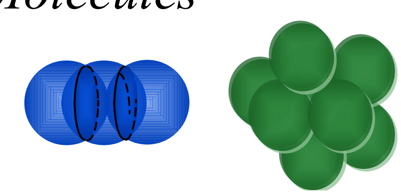
can generalize to NONlinear Viscoelasticity in fluid & "glass"

Relative simplicity: can go far beyond hard spheres *:*

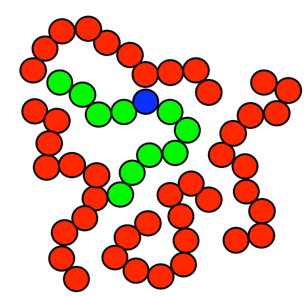
Complex Colloids



Molecules



Polymer Liquids & Glasses (**Mark Ediger**)



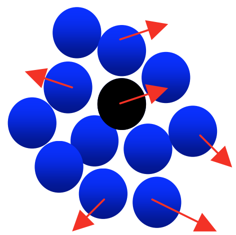
Saltzman & KSS
JCP, 2003

Nonlinear Langevin Eqn Theory

DERIVATION :
KSS, JCP, 2005

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

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



r(t) = *scalar* ***displacement of a particle*** *from initial position*

$\mathbf{D_s}$ *: dissipative, short time, "bare" process*

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

Physical Ideas & Technical Approx.

Solid State View

CONTRACT to lowest level, **r(t)**

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

* **Average over local packings**: dynamical caging constraints via **S(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 **DDFT**

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

→ Nonlinear Langevin Eqn Theory *(General for Spheres)*

…force balance in overdamped regime

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

white noise

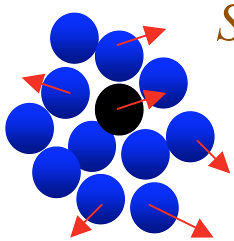
Instantaneous Force due to surroundings

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

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

compete

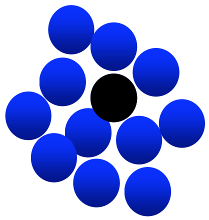
Favors :	**Delocalized *Liquid***	**Localized *Solid***



Structure ← ***Mean square Caging Force***

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

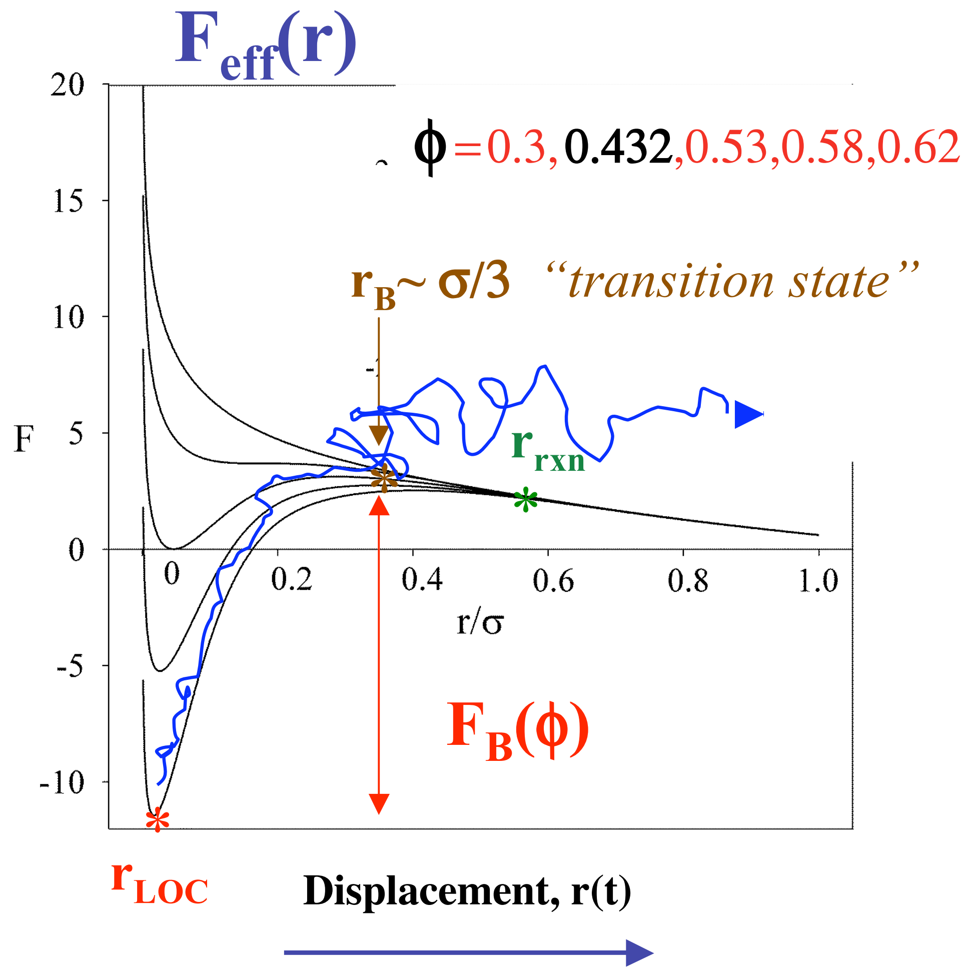
FULL Dynamics ~ *Sequence of independent,* ***locally complex, space-time*** *stochastic & heterogeneous "events"*



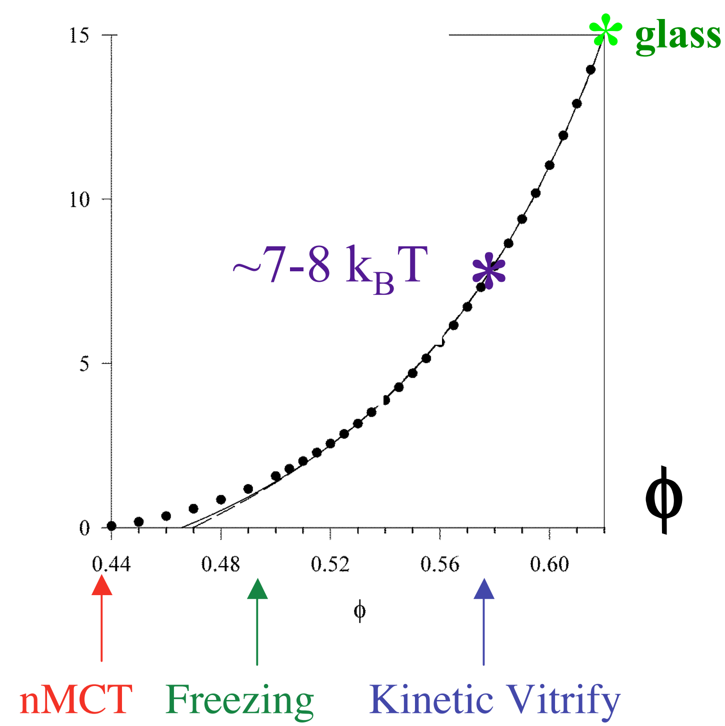
Dynamic Free Energy : Hard Spheres

simplified **MCT "ideal glass transition"** *(if NO hopping)* @ $\phi_C \sim 0.432$

= Dynamic Crossover



Entropic Barrier

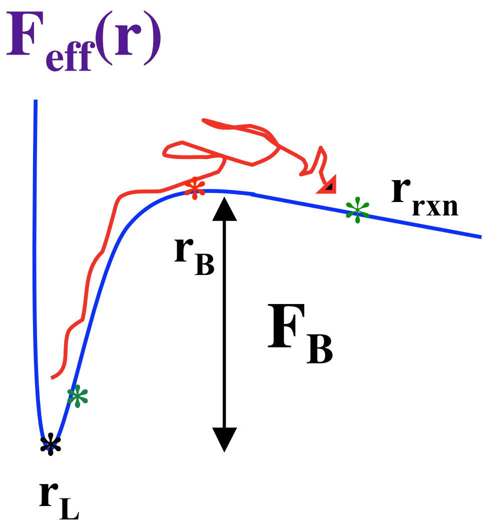


Reaction Point: Onset of **IRReversibility**

….negligible localizing ***force***

Analytic Analysis

KSS, JCP, 2007

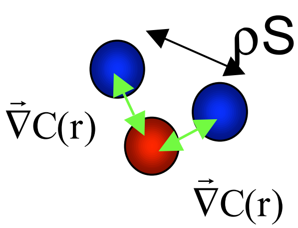


Kramers theory: *mean first passage time over barrier*

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

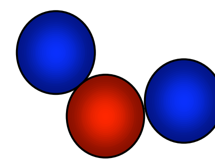
~ **mean** alpha time
@ cage q*

High Barrier Limit : (ultra-local) Real Space Picture



"mean square effective force"

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



Impulsive Collisions

"contacts"

"SOLID" only at RCP
Jamming

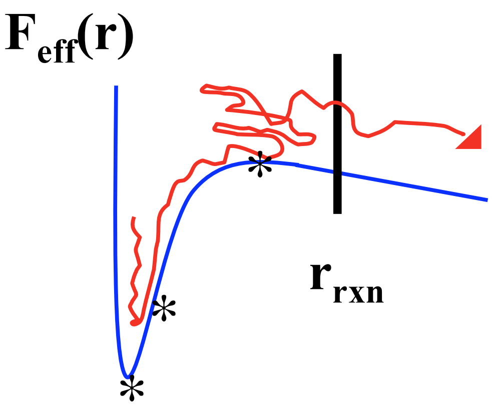
$$\boxed{F_B \propto \phi g^2(\sigma) \propto \left(\phi_{RCP} - \phi\right)^{-2} \to \infty}$$

Double Pole

Full Numerical Soln: Includes Dynamic Fluctuation Effects

JCP & PRE
2006 & 2008

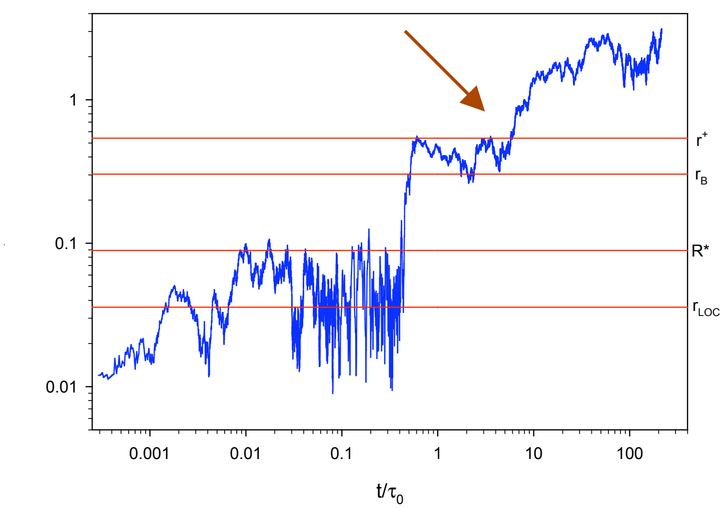
$$\zeta_s \frac{\partial r(t)}{\partial t} = -\frac{\partial}{\partial r} F_{eff}(r(t)) + \eta(t)$$



Noise-Driven Trajectory Fluctuations → ***Sole Origin of Heterogeneous Dynamics***

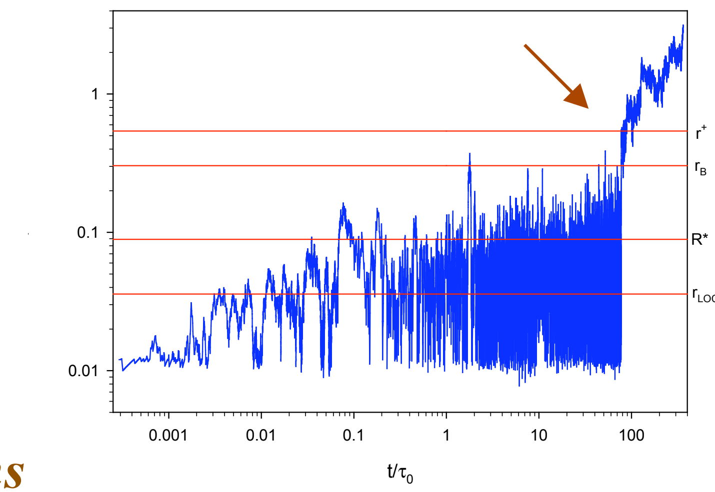
r(t)/σ trajectories

ϕ=0.55 ; Barrier ~ 5



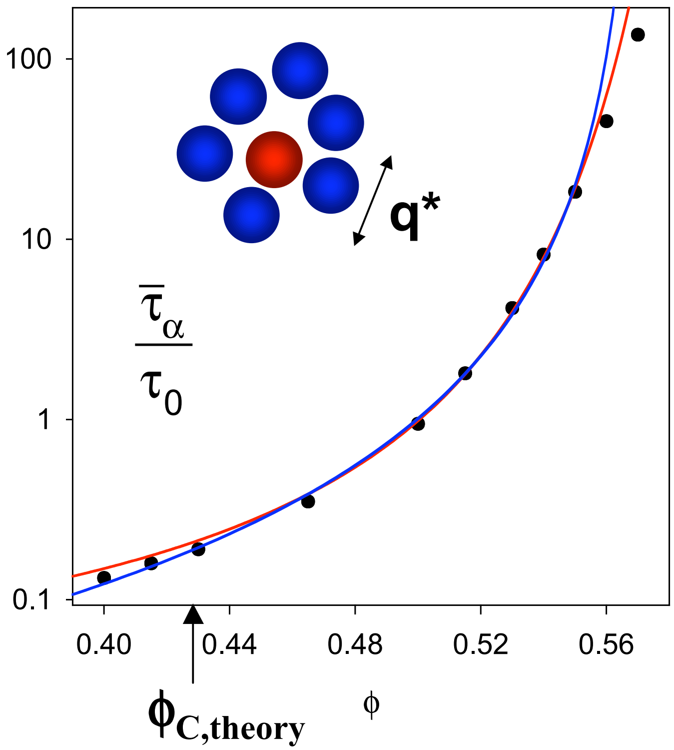
Reaction point
Barrier
Maximum force
Localization length

Re-crossings
"back-hops"
Large Fluctuations



Alpha (cage scale) **Relaxation**

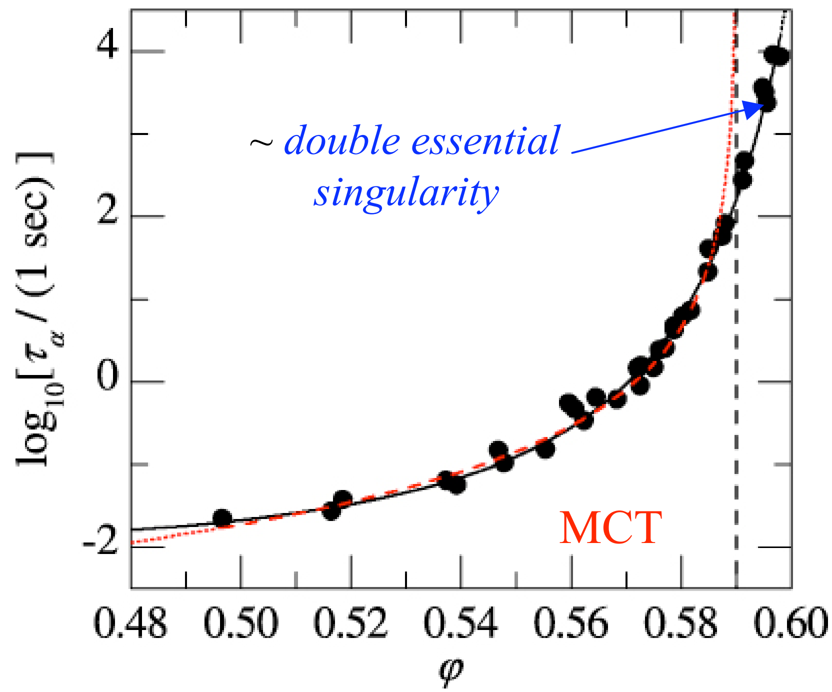
$F_s(q^*,t)$



$\sigma = 1\ \mu m$	
τ_α	ϕ
5x10⁴ s (14 hrs)	**0.57**
5 months *"glass"*	**0.61**

Cipelletti et al, PRL, 2009

extra 2 orders magnitude



Ideal MCT power law **fits** NLE THEORY & EXPT over ~**3 orders of magnitude…***then breaks down …..no critical singularity*

NLE prediction (2007) : $\tau^*/\tau_0 \propto \exp\left(F_B(\phi)\right) \underset{\substack{approach\\ RCP}}{\propto} \exp\left(B/(\phi_{RCP}-\phi)^2\right)$ *ala new expts*

QUESTION : Dynamic Fluctuation consequences of Hopping ?…..Many

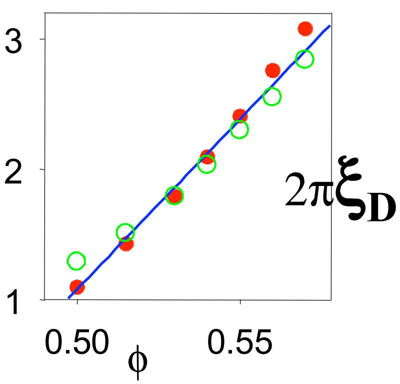
Growing Dynamical Length Scale

$$F_s(q,t) = \exp\left(-t/\tau(q)\right) \underset{Expt;Sims}{\neq} \quad Fickian \approx MCT$$

qσ=2.6~ q*/3 --> 2q*~14

***IF* Activated, we find :**

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



$D(q) \approx \; D\left(q\xi_D\right)^{-2}, \quad q\xi_D >> 1$

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

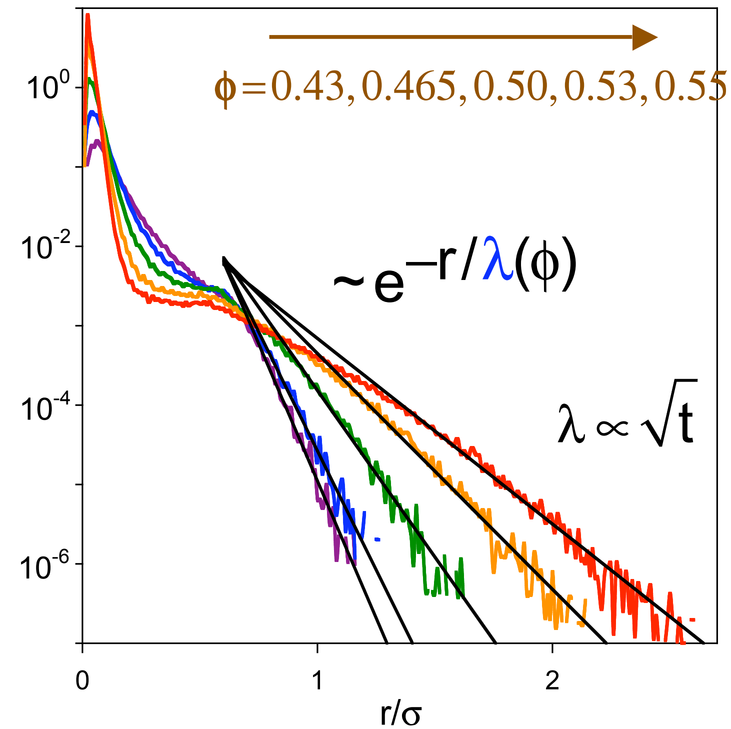
$$\boxed{\xi_D(\phi)}$$

Growing Length Scale for
Recovery of Fickian diffusion

Mobility Bifurcation

Real Space Van Hove @ alpha time

Log $\mathbf{G_s(r, t{=}\tau_\alpha)}$



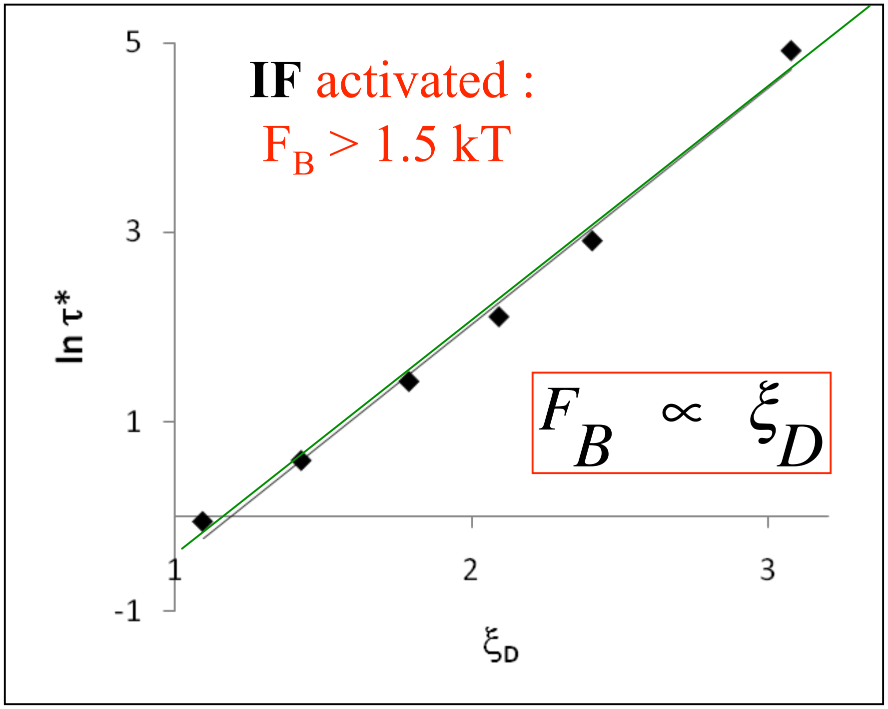
Exponential tail…. *"fast hoppers"*

$$\boxed{\lambda \simeq \xi_D / 2}$$

Jump Length ~ [0.07-0.24]σ

Consistent with simulations [Berthier, Kob, Szamel,…] & Expt [Ediger, Weitz/Weeks,..]

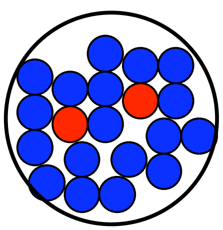
Connection of Alpha Time and Growing Length Scale



Slow ***logarithmic*** growth

$$2\pi \frac{\xi_D}{\sigma} \simeq 1.1 + 0.44 \ln\left(\frac{\tau_\alpha}{\tau_0}\right)$$

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



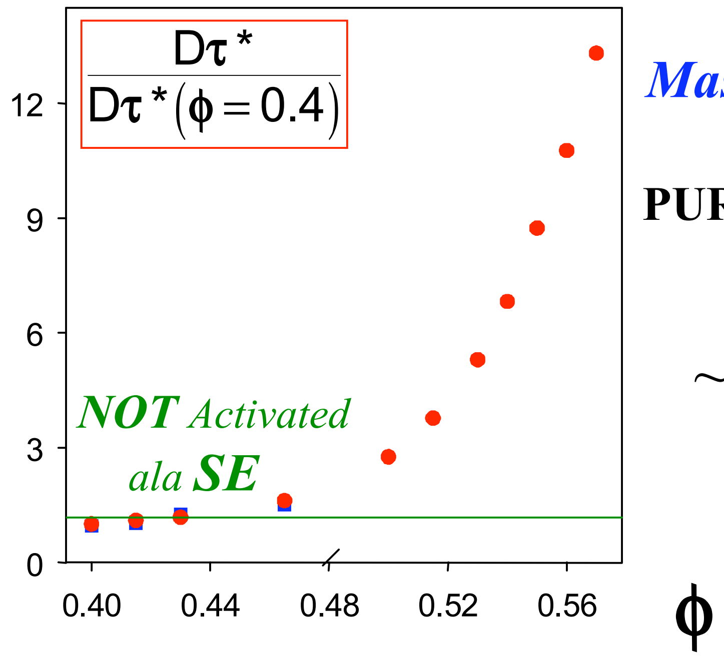
expect connected if dynamics rare hopping controlled….several evidences

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

Dasgupta-Sastry simulations (2009 PNAS): $\boxed{\ln(\tau_4) \propto F_B \propto (\xi_4)^{0.7}}$

"Decoupling" of Self-Diffusion & Alpha Relaxation

aka Stokes-Einstein breakdown

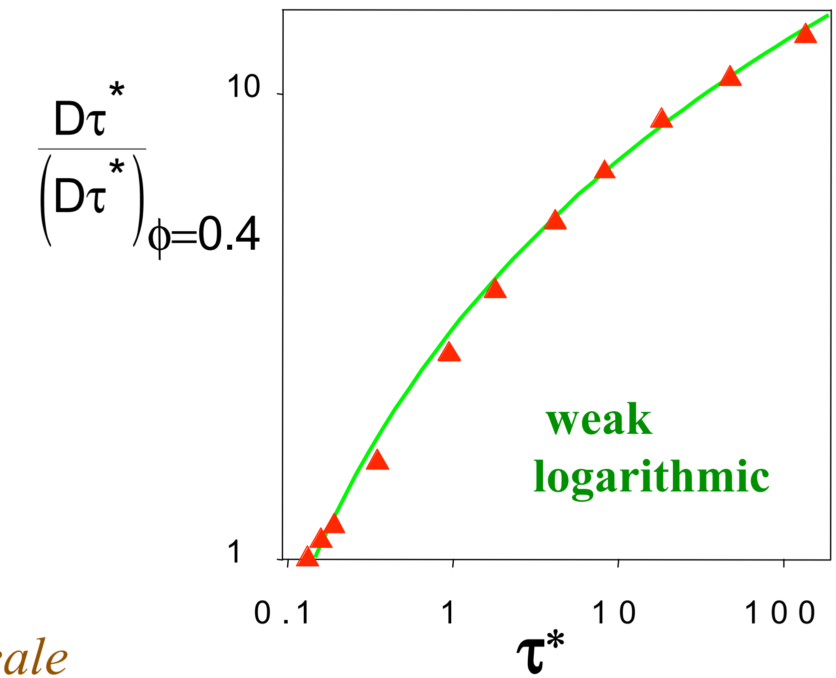


Mass Transport ENHANCED @ fixed relaxation time

PURE Dynamic Effect….and **NOT** change of KWW exponent

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

Kumar; Truskett
PD-Hard Sphere SIMS



"Decoupling length"

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

……reflects Mobility = function of length scale

Relevant to Thermal Molecular Liquids ?

Simple ***Hard Sphere "Mapping"***

$$\frac{\tau_\alpha(T_g)}{\tau_0} = \frac{\tau_\alpha(T_g)}{\tau_\alpha(T_{c,\mathrm{expt}})} \bullet \frac{\tau_\alpha(T_{c,\mathrm{expt}})}{\tau_0}$$

T$_g$ @ 100 s

(Novikov-Sokolov) $\sim 10^{8\text{-}10}$ $\qquad \sim 150$ from HS theory @ $\phi_{c,\mathrm{expt}}=0.58$

***NON-Fickian crossover length**

$$2\pi\frac{\xi_D}{\sigma} \simeq 1.1 + 0.44\ln\left(\frac{\tau_\alpha}{\tau_0}\right)$$

$$\xi_D \simeq 2\sigma \simeq 2\,nm\,(TNB)$$

~ Ediger expt (2009)

*** Decoupling Ratio**

$$R \equiv \frac{D\tau_\alpha}{(D\tau_\alpha)_0} \simeq \left[1.6 + 0.44\ln\left(\frac{\tau_\alpha}{\tau_0}\right)\right]^2 \approx 4\pi^2\left(\frac{\xi_D}{\sigma}\right)^2$$

~ 150 @ T$_g$

Ediger expts: ~ 100 for OTP, TNB

Nonlinear Viscoelasticity: *Stress Perspective*

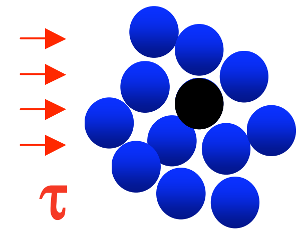
Motivating Idea: *External Deformation Reduces Barriers to Flow*

* ***Eyring*** *(1936)*
Frenkel (crystals)

"Tilted Landscape" idea

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

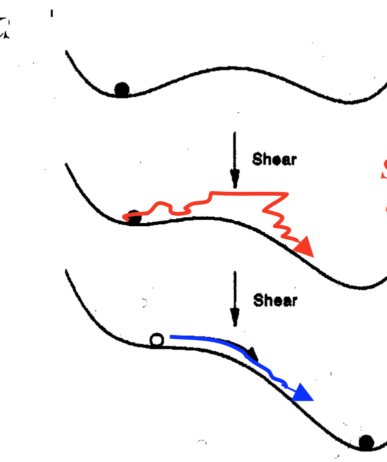
Mechanical Work



** **Potential Energy Landscape simulations…** Dan Lack*

stress reduces and ultimately destroy barriers

Deformation



stress-assisted "thermal hop"

* **Macroscopic Rheology** ⟷ **Alpha Process**

Simulation Support *: Yamamoto-Onuki-Reichman*
Riggleman-dePablo ; Joerg Rottler……

Irreversible
"Absolute Yield"
aka
T=0 Quasi-Static
Granular limit

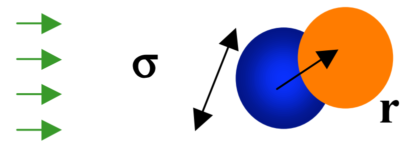
* *Structure & Dynamics ~ **Isotropic** on CAGE scale*

Incorporation of Stress in NLE Theory

Kobelev+KSS
PRE 2005

External force on particle

τ = Applied Stress

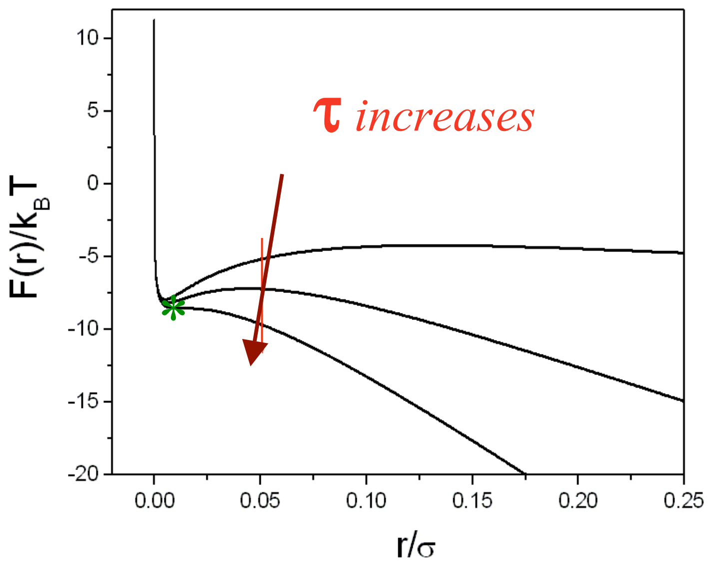


Mechanical Work

*ala Eyring @ "**instantaneous** dynamical variable" level*

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

Stress "tilts landscape"



STRESS : ***Reduces Modulus & Barrier***

$$F_B(\tau) \cong F_B(0)\left[1-(\tau/\tau_{y,abs})\right]^{5/2}$$

Accelerates Relaxation

"Absolute YIELD" → Barrier destroyed

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

(transient) Glassy Modulus

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

0^{th} Order Generalized Maxwell Constitutive Eqn

Kang Chen+KSS
EPL, 2007
Macromolecules
& JCP, 2008

Nonlinear Boltzmann

$$\boxed{\tau(t) = \int_0^t dt' \; G(t-t'; stress)\dot{\gamma}(t')}$$

Minimal PHYSICS: Elastic Modulus and α–Time coupled to Stress *via* $\mathbf{F_{eff}(r)}$

$$\frac{\partial}{\partial t'} G(t';\tau(t')) = -\frac{1}{\tau_\alpha(\tau(t'))} G(t';\tau(t')) \Rightarrow G(t-t'; stress) = G'(\tau(t'))\exp\left(-\int_{t'}^{t} dt'' \tau_\alpha^{-1}\left[\tau(t'')\right]\right)$$

NONlinear & Self-Consistent Constitutive Eqn *"effective time"*

** **Constant STRAIN RATE**

$$\gamma = \dot{\gamma} t$$

$$\boxed{\tau(\gamma) = \int_0^\gamma d\gamma' G'(\gamma') e^{-\int_{\gamma'}^{\gamma} \frac{d\gamma''}{\dot{\gamma}\tau_\alpha(\gamma'')}}}$$

** **STEADY STATE SHEAR**

$$\boxed{\tau = \eta(\tau)\dot{\gamma}} \qquad \eta(\tau) = \eta_\infty + G'(\tau)\tau_\alpha(\tau)$$

* **STEP STRAIN**

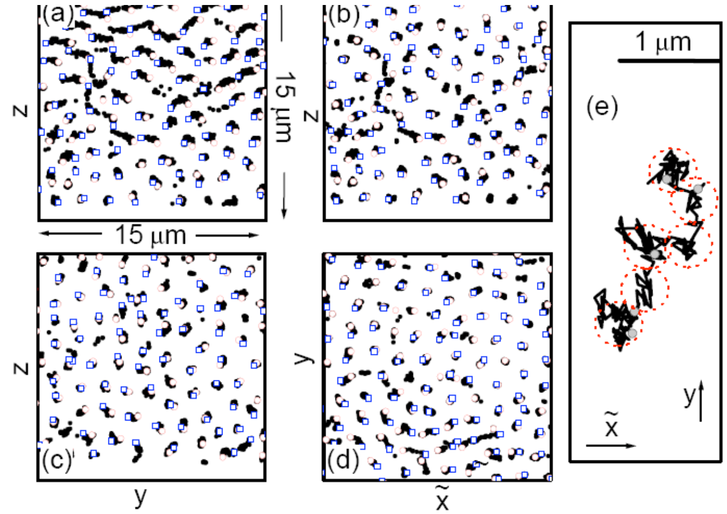
$$\boxed{\tau(t) = G(t)\gamma} \xrightarrow[\text{quasi-static}]{} \tau = G'(\tau)\gamma$$

* **CREEP** $\gamma(t)$ @ *fixed stress*

SELF-Motion Under Steady Shear

Besseling, Weeks, Poon, PRL, 2007

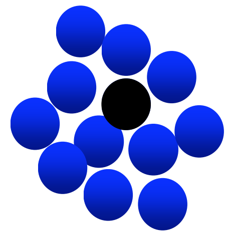
***Confocal :** direct microscopic probe of theory*

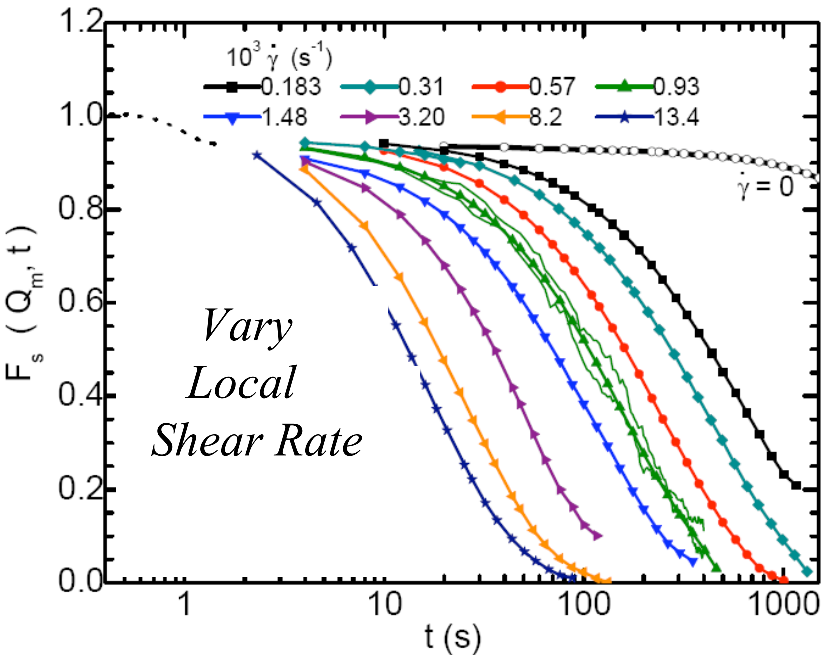


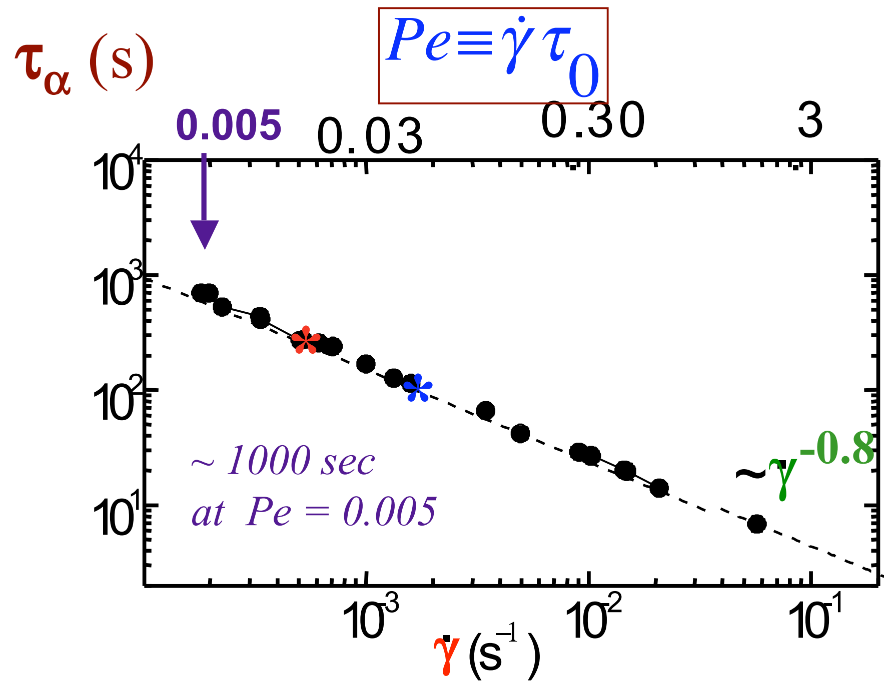
~ Isotropic Intermittent Motion

$F_s(q^*,t)$

$\phi = 0.62$
$\sigma \sim 2\mu m$
$\tau_0 \sim 30$ s







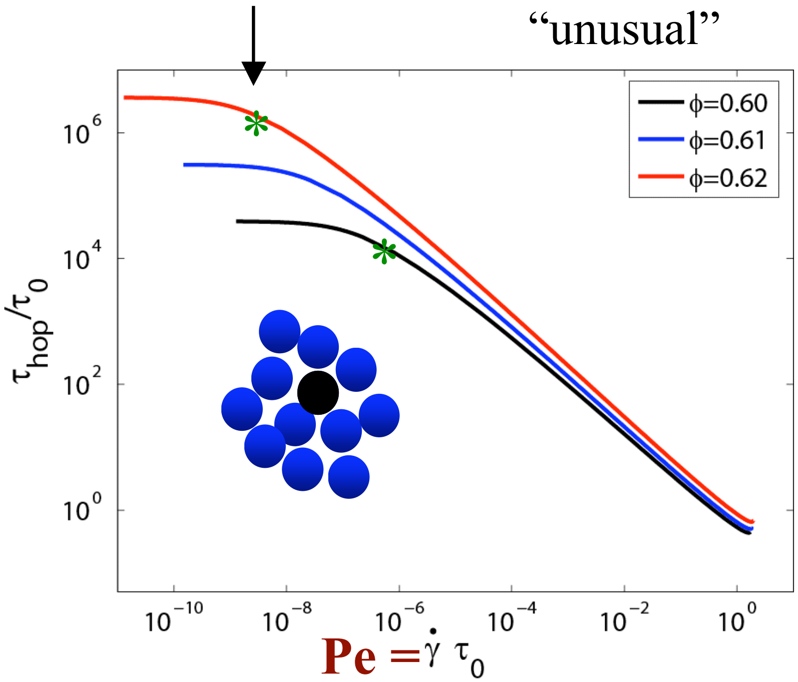
Exponential Relaxation

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

Steady State Predictions

Saltzman, Yatsenko, KSS, JPCM, 2007

$\tilde{Pe}_c \equiv \dot{\gamma}\,\tau_{\alpha}(0) \approx 0.01 << 1$



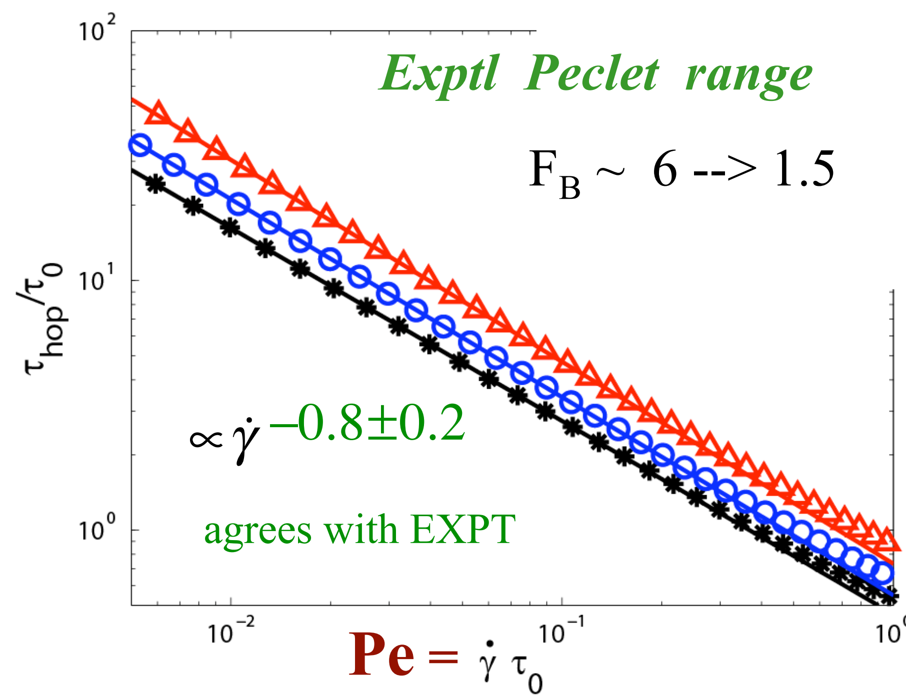
ϕ=0.62 --> F_B = Barrier ~ 15 kT

NB: **E_f(STZ) ~ 16-18 kT (***Schall, Weitz, Spaepen***)**

→ **τ_α~ 60 million secs ~ 2 Years**

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

"shear thins" by ~5 orders of magnitude !



Entropic Barriers NOT Zero

per Intermittent Hopping seen in confocal

$$\tau_\alpha \propto \dot{\gamma}^{-\Delta(\phi)}, \quad \Delta \sim 0.7-0.9$$
$$\textit{for } \phi = 0.57 \rightarrow 0.635$$

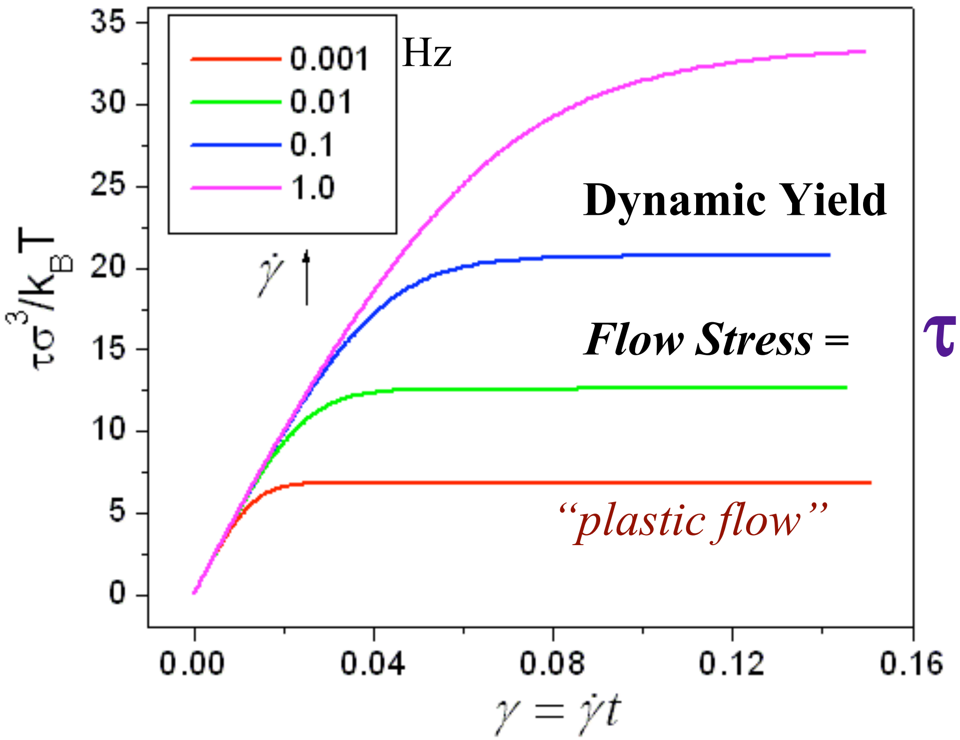
same story for D, Viscosity

Constant *Strain Rate* Deformation

$$\gamma = \dot{\gamma} t$$

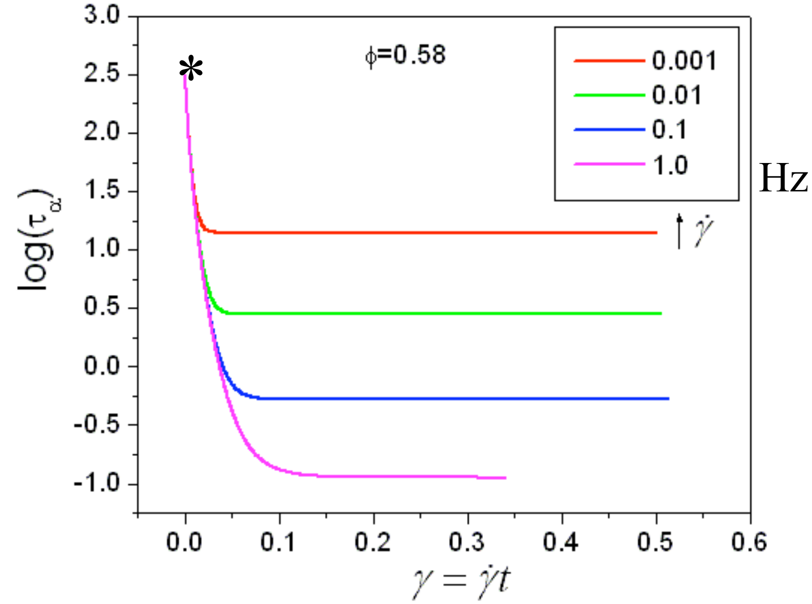
$\tau_0 = 0.5$ s

$\phi = 0.58$



τ_y

Deformation Accelerates Relaxation



ala mechanically-induced "De-vitrification"

Steady State:

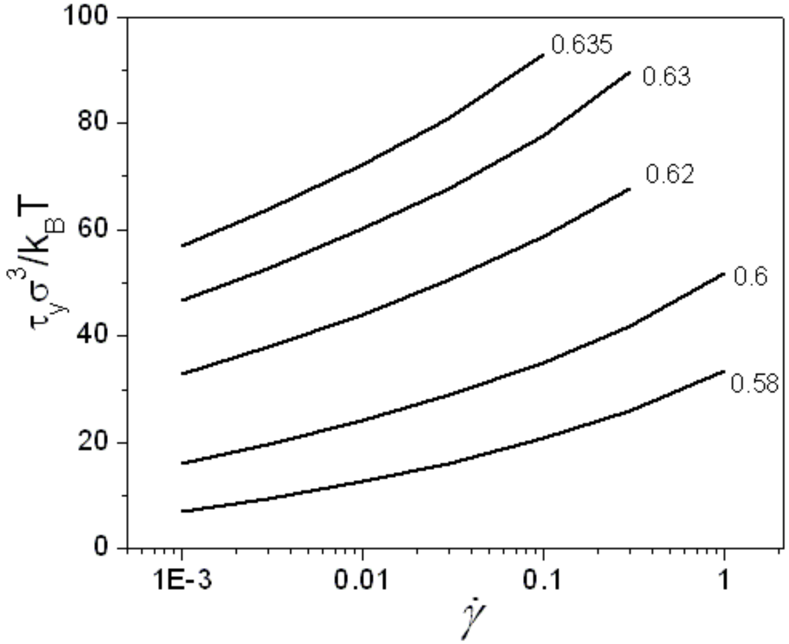
$$\boxed{\left(\dot{\gamma}\,\tau_\alpha\right)_{yield} \approx 0.025 - 0.1}$$

increases with strain rate and ϕ

ϕ=0.58–0.635
strain rate = 0.001-1 Hz

Flow Stress : Effect of Strain Rate & Volume Fraction

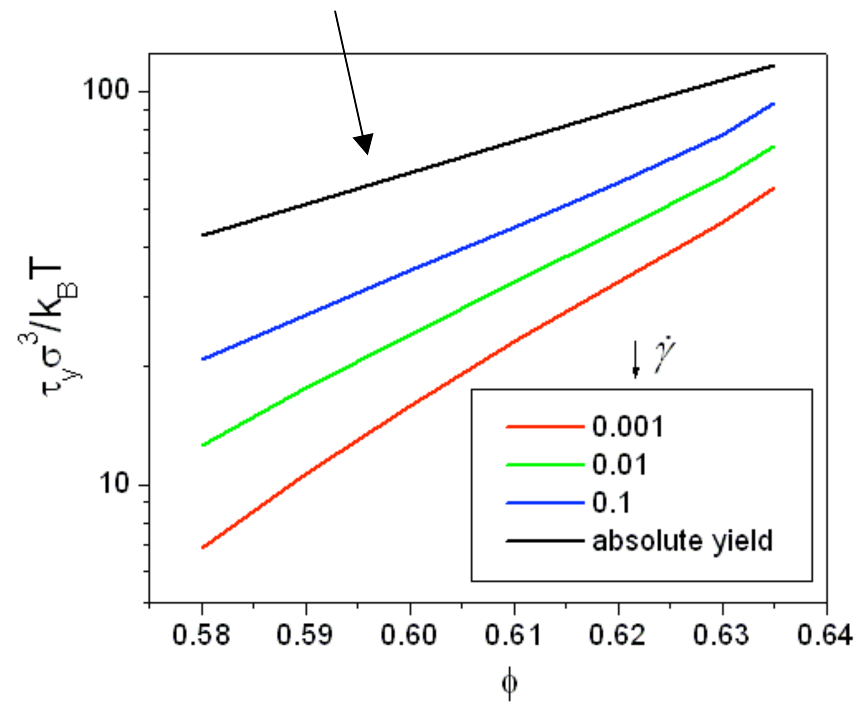
$\phi = 0.58 - 0.635$



***Roughly logarithmic** in strain rate*

"Quasi-static" = NO hopping

"absolute yield"



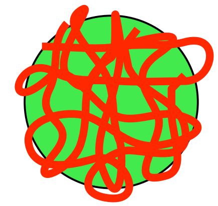
~ Exponential Dependence

Stronger as strain rate decreases….

effect of thermally activated hopping

Soft Repulsive Spheres ~ MICROGELS…important materials !

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



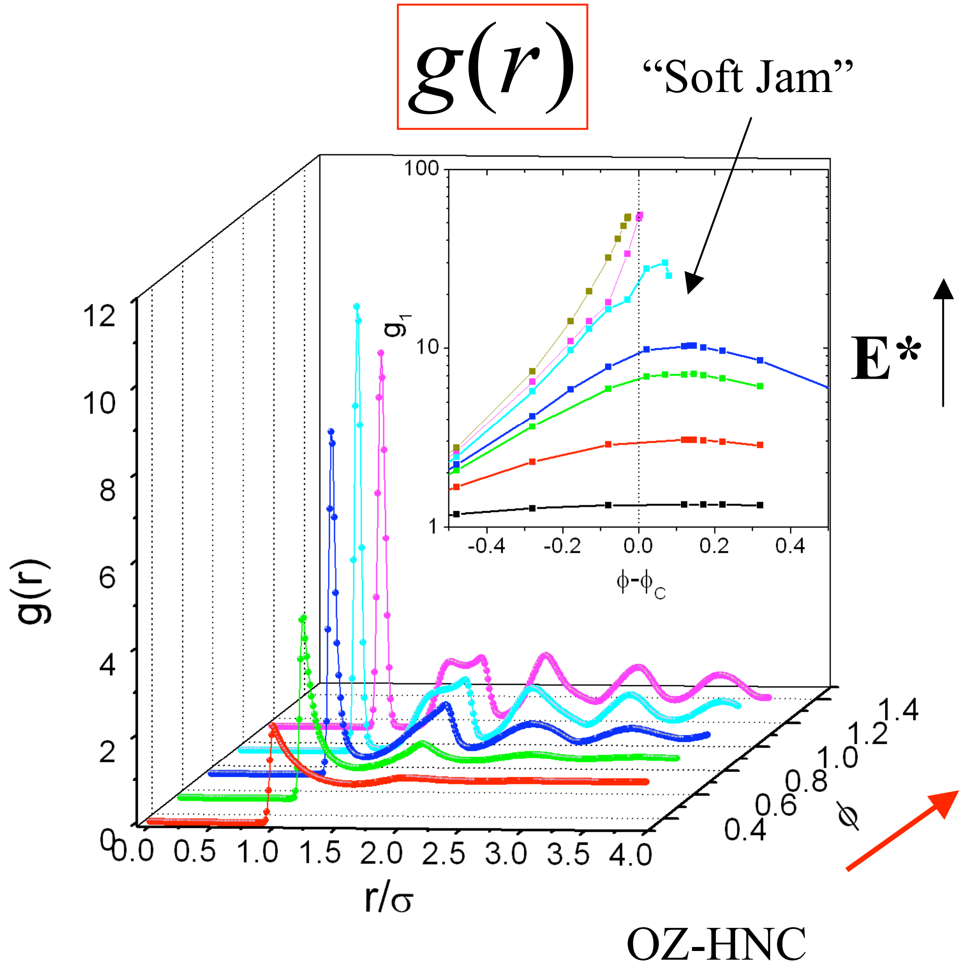
→ **Expect Big Change in Glassy Dynamics**

finite range **Hertzian Contact** *model* :

$$V(r) = \frac{4}{15} E^{*} \sigma^{3} \left(1 - \frac{r}{\sigma}\right)^{5/2}, r \leq \sigma$$
$$= \quad 0 \quad , \quad r > \sigma$$

Packing Complexity
as function of **φ and E***

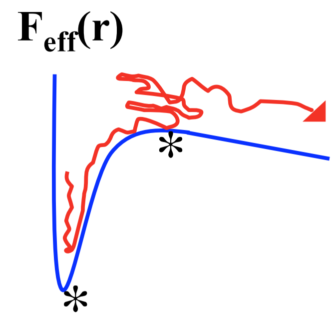
ala Yodh, Liu et al, Nature 2009
Expts and Simulations

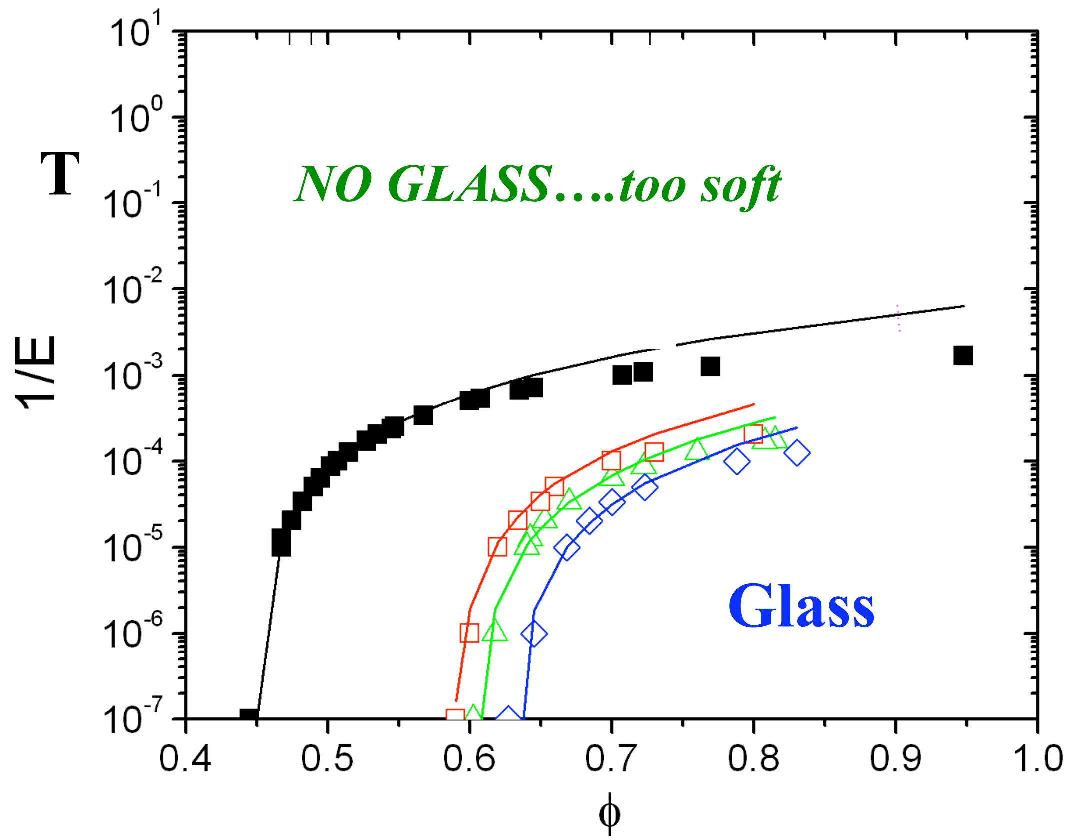


Dynamic Phase Diagram

Yang & KSS submitted

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





Ideal MCT (crossover)

Kinetic vitrify

$$\tau_\alpha(\phi_g, E_g)/\tau_0 \equiv 10^x$$

x=2,3,5

ALL Parabolic

$$\boxed{E_g^{-1} \propto T_g \propto \left(\phi - \phi_g\right)^2}$$

Hard Sphere potential:

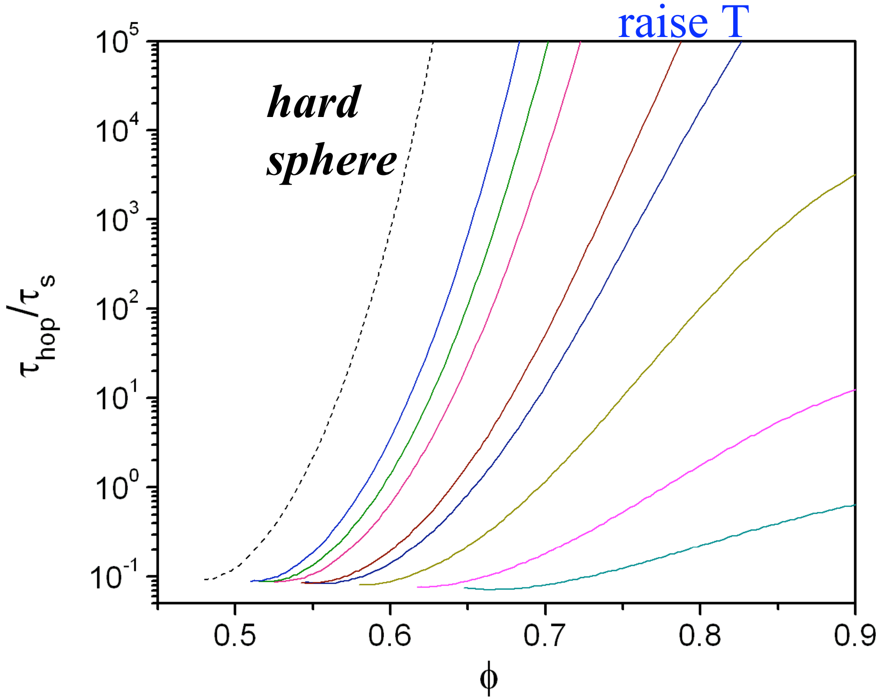
$$E \rightarrow \infty, \quad T \rightarrow 0$$

ala simulations of Berthier-Witten: EPL+PRE, 2009

Relaxation Time : ϕ & T-dependences

Fix **E***= infinity,(5,3,2,1)10^4,(8,5,3,2) 10^3

raise T

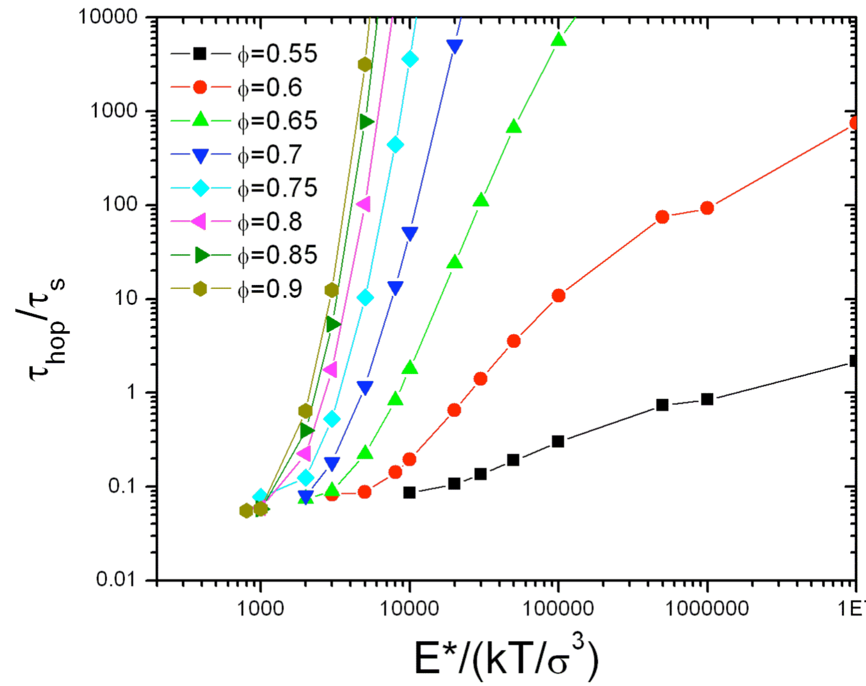


NONexponential Growth

Less "Fragile" as *Single Particle* Softens

ala Mattson, Weitz, et al, Nature 2009

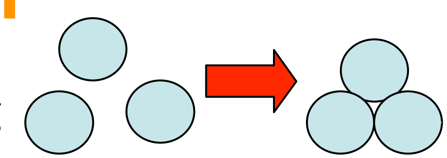
Fix ϕ and "Cool"



"Two ϕ–Regimes"

Greatly Enhanced Thermal Fragility as Volume Fraction grows

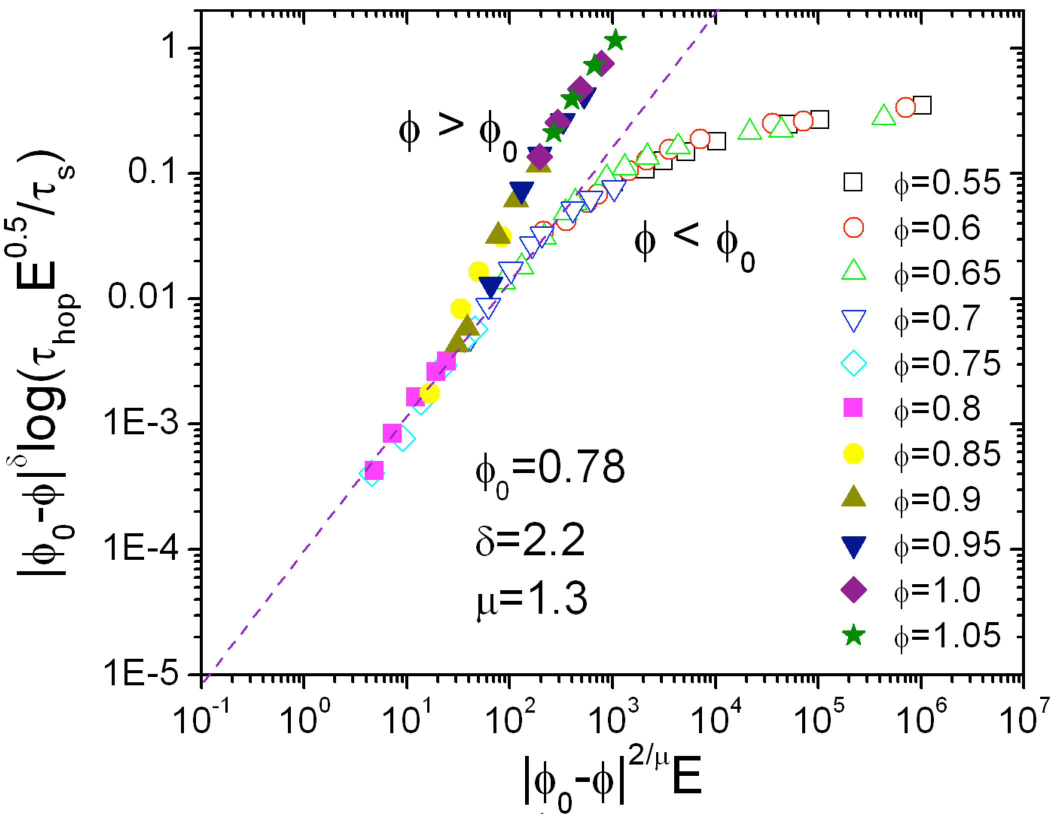
qualitative change of packing



Universal "2-Branch" Collapse *per Berthier-Witten Arguments*

$$\tau_\alpha(\varphi, T) \sim \exp\left[\frac{A}{|\varphi_0 - \varphi|^\delta} F_\pm\left(\frac{|\varphi_0 - \varphi|^{2/\mu}}{T}\right)\right],$$

Describes Simulations



Hard sphere RCP

Activated Hopping Theory also Collapses !

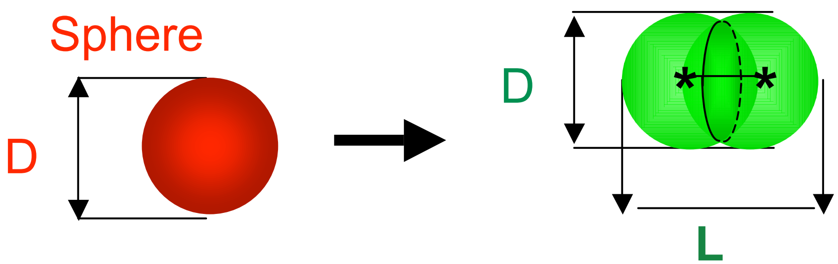
N.B.
Andrea Liu talk:

Use P, not ϕ

...1 master curve

μ, δ SAME as in simulation (*has theory motivation*)

BEYOND SPHERES : Hard *Uniaxial* Particles



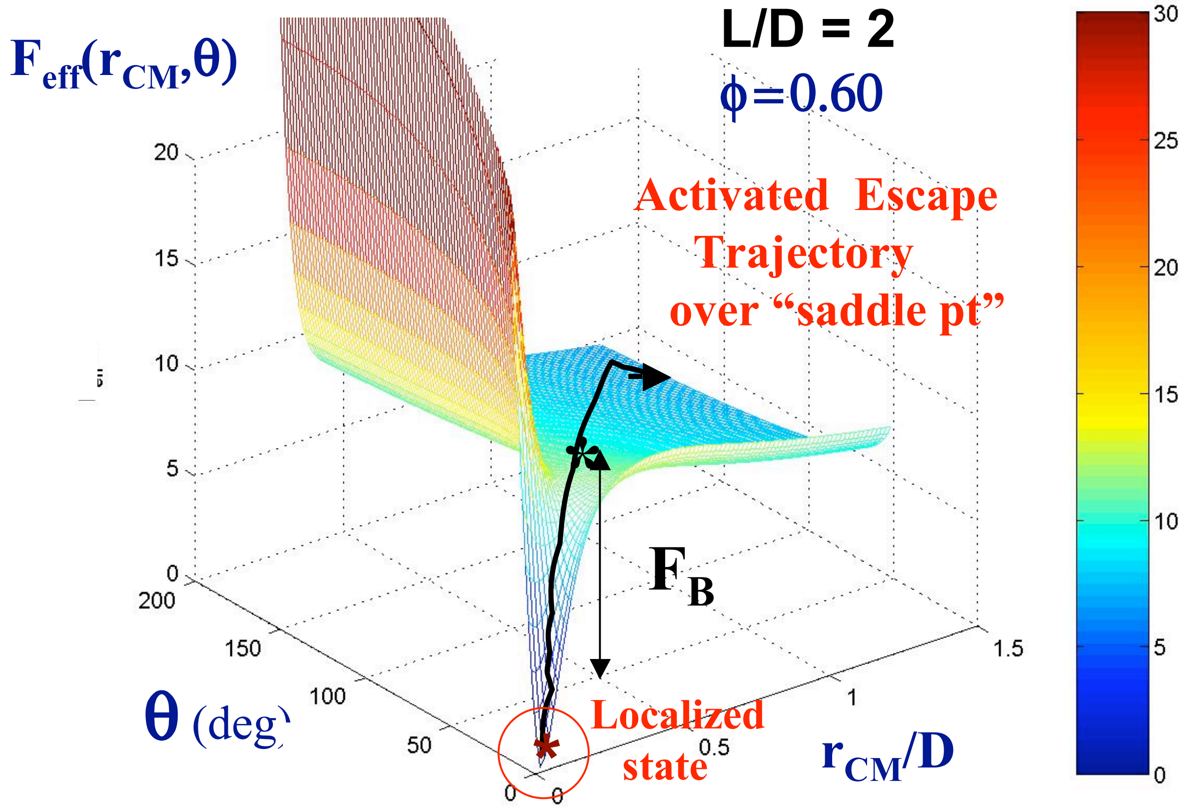
Diatomic

$1 \leq L/D \leq 2$

"Molecular Colloids"

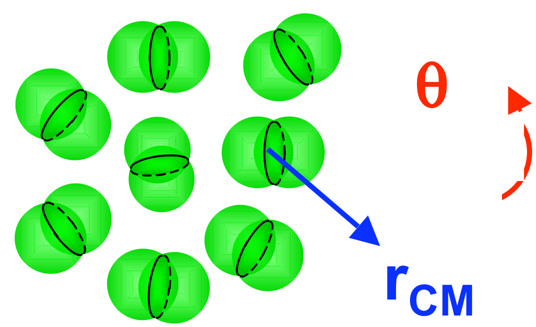
A frontier of particle science and engineering

Dynamical Free Energy Surface



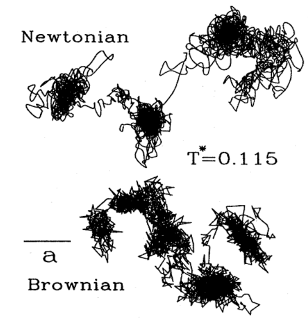
COUPLED Translation & Rotation

forces and torques



Mechanistic picture ala chemical reaction

Summary



Microscopic theory of ACTIVATED dynamics @ SINGLE particle level

...NO singularities at T > 0 or below RCP

Allows integrated understanding of :

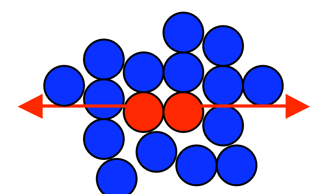
* **Mean Dynamics** : *NONuniversal aspects*: kinetic arrest map, fragility, shear modulus,…
relevant to materials science & engineering

* **Nongaussian Fluctuation or Dynamic Heterogeneity effects** :
Nongaussian parameters, Decoupling, Exponential tails & Mobility bifurcation,
NonFickian crossover, $\tau(q)$, Growing length scale,…..

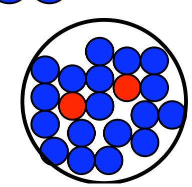
* **Nonlinear Rheology** : strain softening, shear thinning, dynamic yielding,flow curves,…

* **Generalizable**: Soft Colloids; Nonspherical Molecular Colloids & Liquids; Gels;
Patchy Particles; ***Polymer Melts & Glasses*** (JPCM,2009; ARCP, August, 2010)

FRONTIERS : space-time correlated: **2 & beyond** particle dynamics



Role of “Harris disorder” ? **Rheology** : *role of anisotropy, heterogeneity ?*

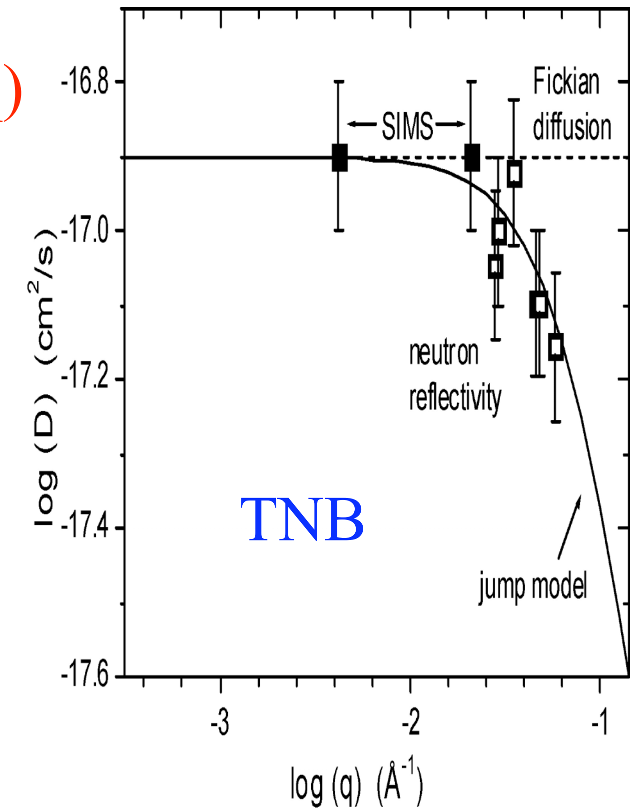


Below T_g: combined treatment of physical aging, rejuvenation, hardening…..

EXTRAS

Stephen F. Swallen; Katherine Traynor; Robert J. McMahon; **M.D.Ediger**;
Published in: Thomas E. Mates; *J. Phys. Chem. B* **2009,** 113, 4600-4608.

D(q)



Diffusion coefficient as a function of wavevector q at 342 K. SIMS data are shown as solid squares. Previously reported neutron reflectivity data are shown as open squares.Solid line is calculated with the jump diffusion model, with **ξ = 14 Å**, and log(D(q = 0)/cm2 s−1) = −16.9. The dashed line is extrapolation of SIMS data to high q, assuming the Fickian model.

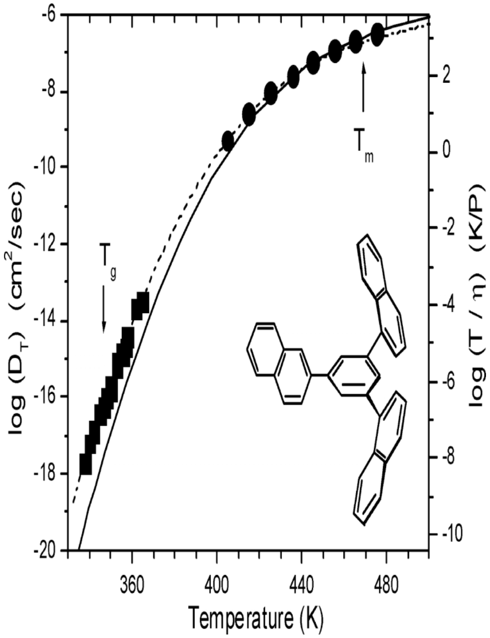
Extrapolate fit to NLE theory numerical results :

jump length: **ξ ~2σ** ~ 2 nm for TNB (~ 1.4 nm for OTP) @ Tg

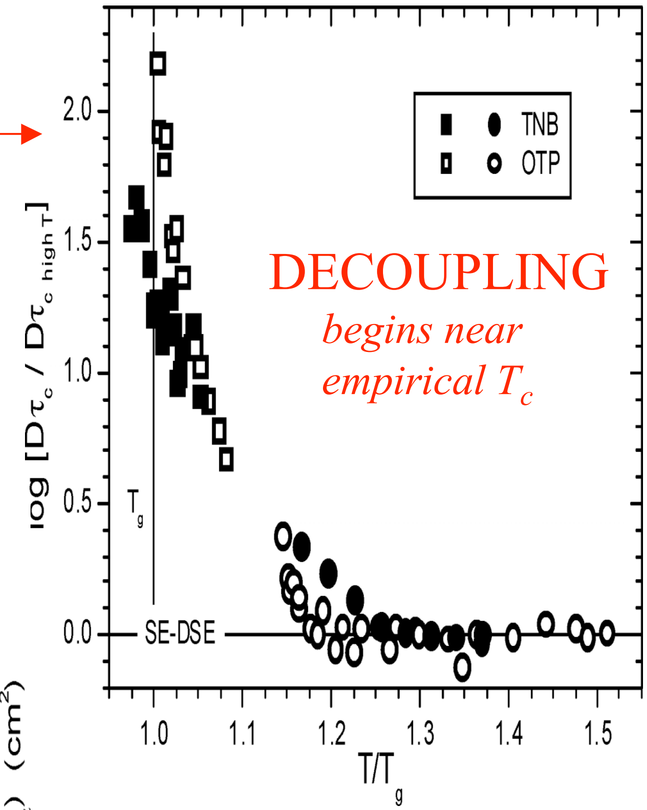
Mean Square jump length = sqrt(6) ξ ~ 3.4 nm (EXPT)….*ala 4-d NMR ?*

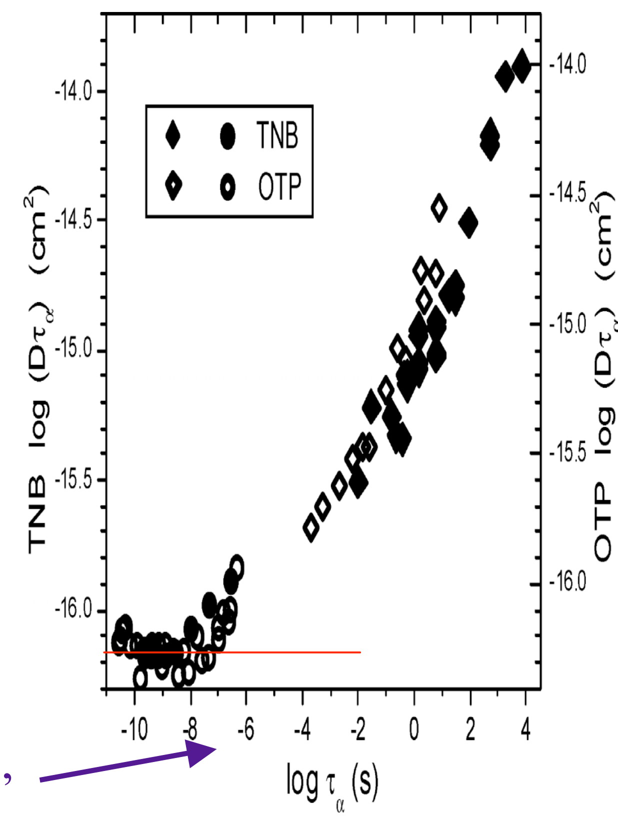
theory ~ 3.4 nm for OTP

----- 1/viscosity^0.87



~100 →

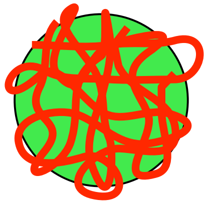




Sokolov
crossover
“magic time”

Decoupling factor NOT
Power Law in τ_α

Microgels : Soft Repulsive Spheres

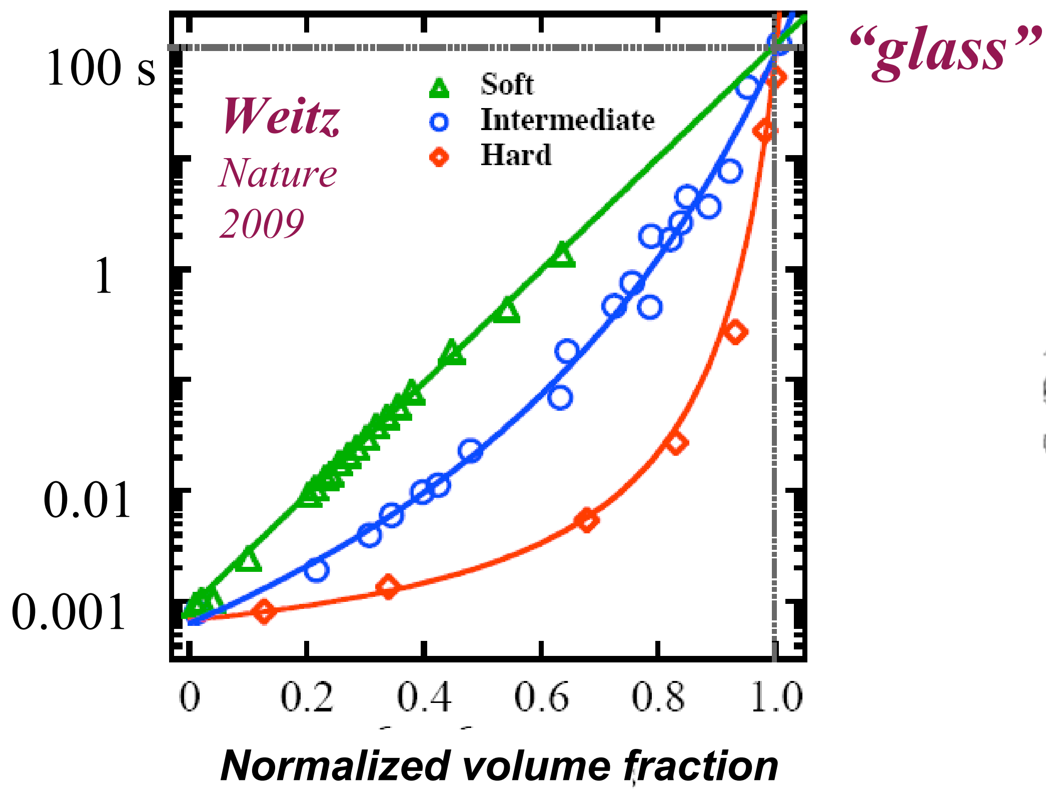


Hertzian Contact Model :

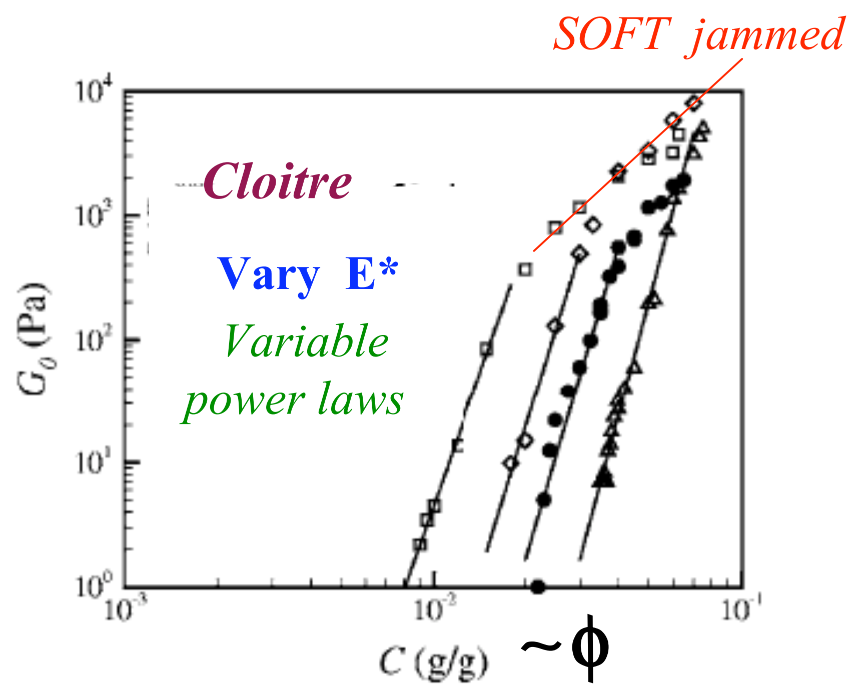
$$V(r) = \frac{4}{15} E^{*} \sigma^{3} \left(1 - \frac{r}{\sigma}\right)^{5/2} \quad , r \le \sigma$$

Vary Single Particle Stiffness, **E***, (*crosslinks*)
Massive change in Dynamic Fragility

Relax Time (ϕ) from DLS

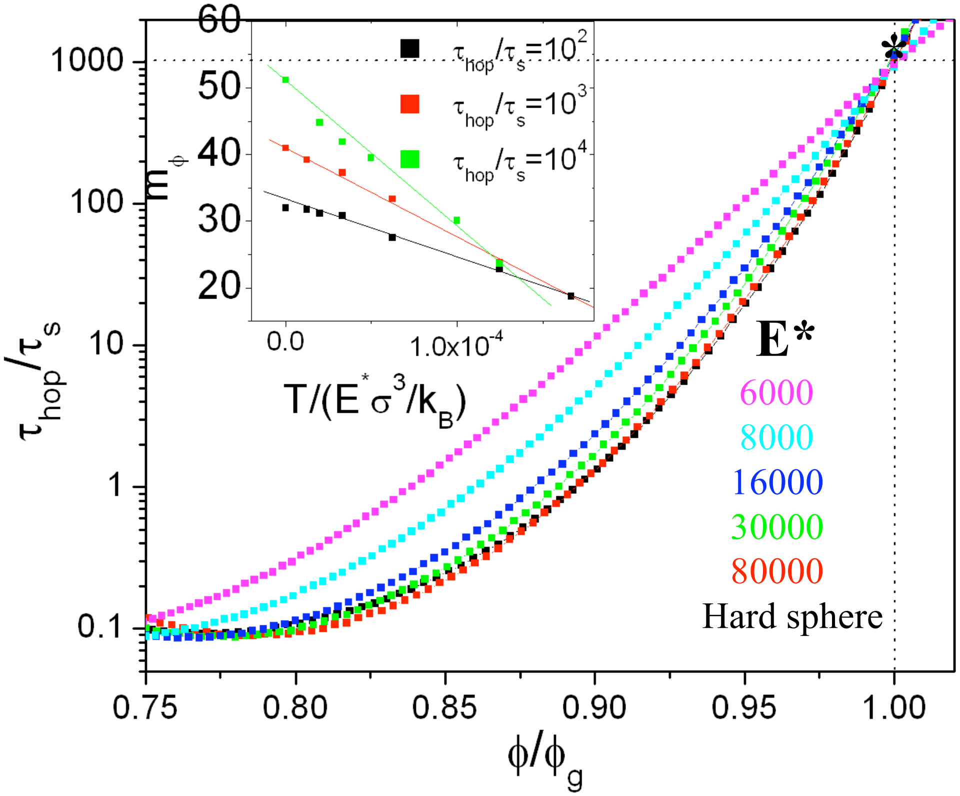


Glassy Shear Modulus



Tunable Dynamic Fragility via Particle Softness

Fragility Plot based on ***Kinetic Glass Criterion***

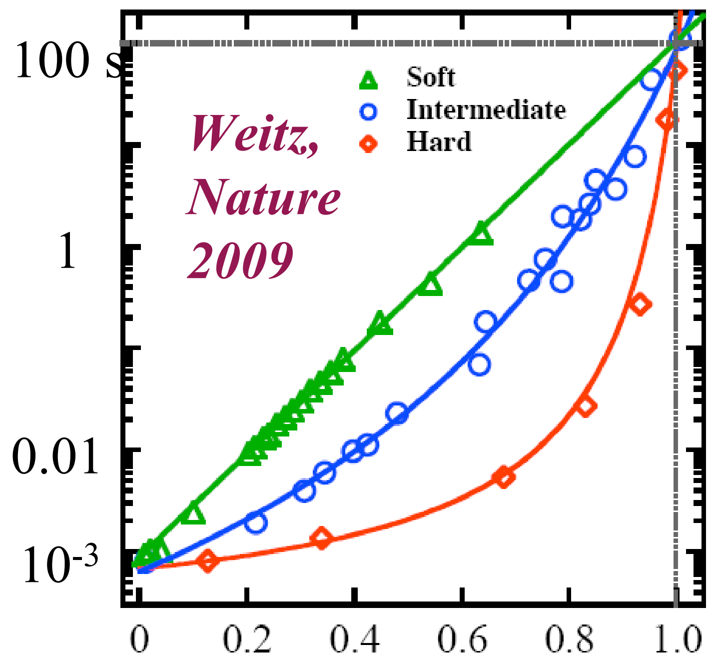


$$m_\phi \equiv \frac{\partial}{\partial(\phi/\phi_g)}(\log \tau_{hop})\,|_{\phi_g}$$

varies by factor ~ 3 - 4

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

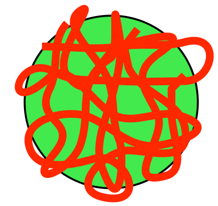
Relax Time (φ) from DLS



Normalized volume fraction

"Soft Particles Make STRONG GLASSES"

Glassy Shear Modulus



Cloitre & Bonnecaze, JOR, 2006

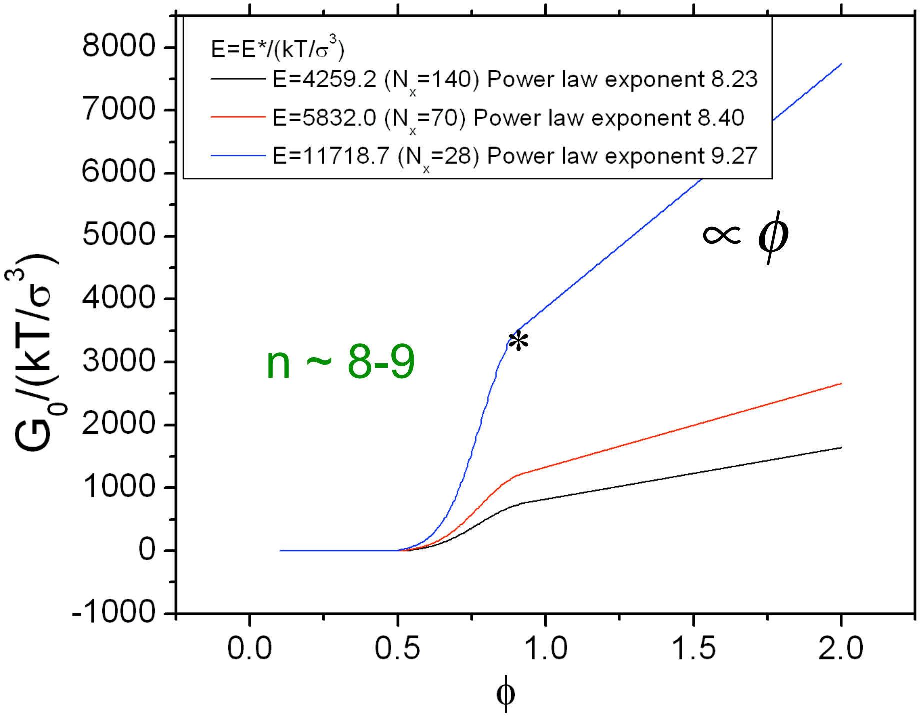
Vary crosslink density R ~ 100-200 nm, E* ~ 300-3000 Pa

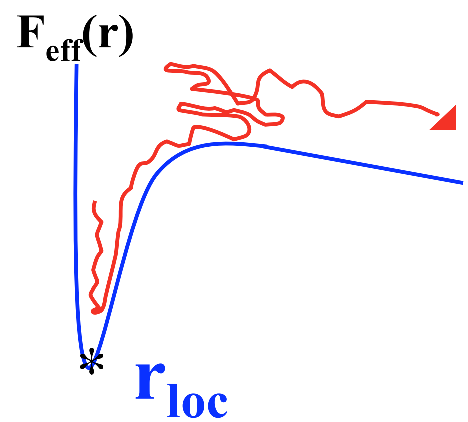
Power law: $\boxed{G_0 \sim \phi^n}$ **n ~ 7** then much weaker….~ **linear**

$\boxed{E^* \propto N_x^{-1}}$

$N_x = 28,70,140$

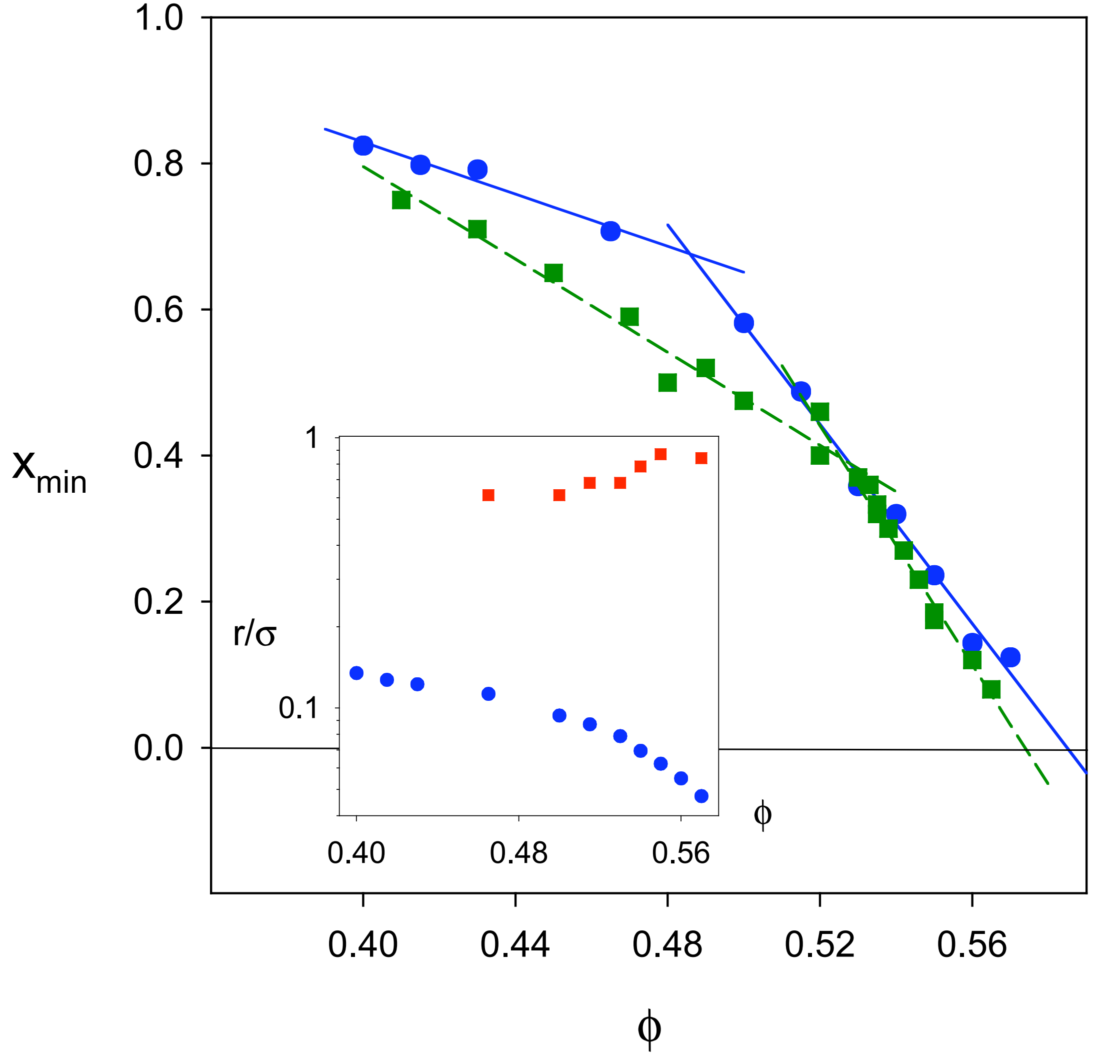
THEORY





Minimum NO-Fickian Exponent of MSD(t)

JCP,2006
JPCM,2008



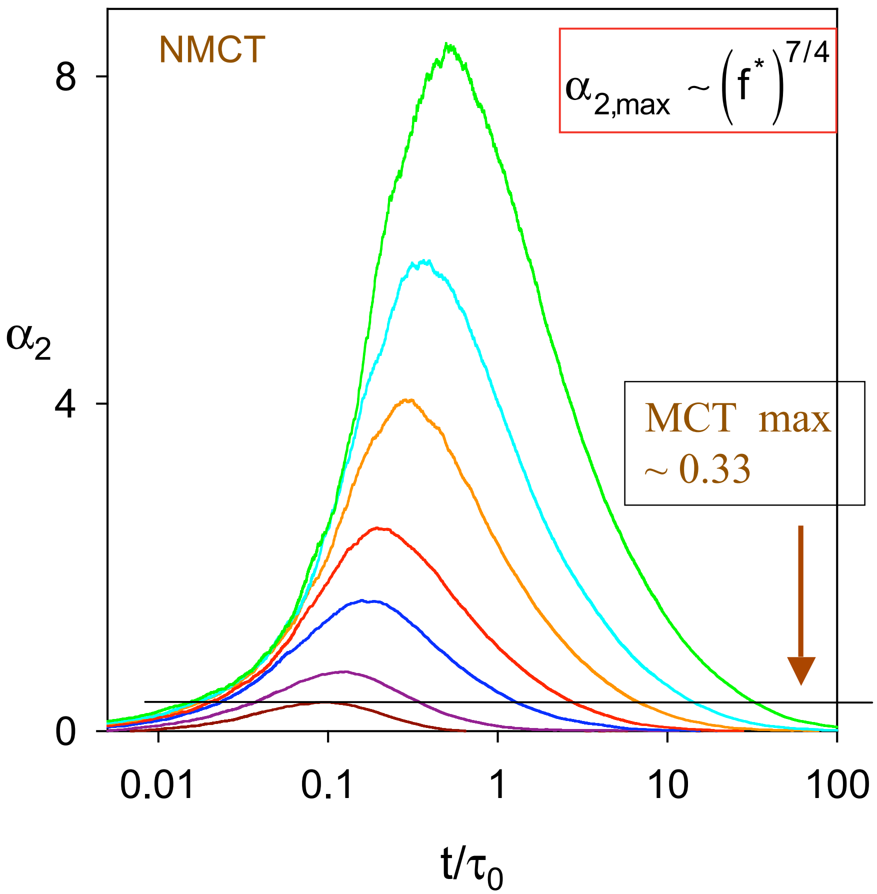
Theory

Experiment

Nongaussian Parameters : Classic and Alternate

Weights **Short** Times (α/β crossover)

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

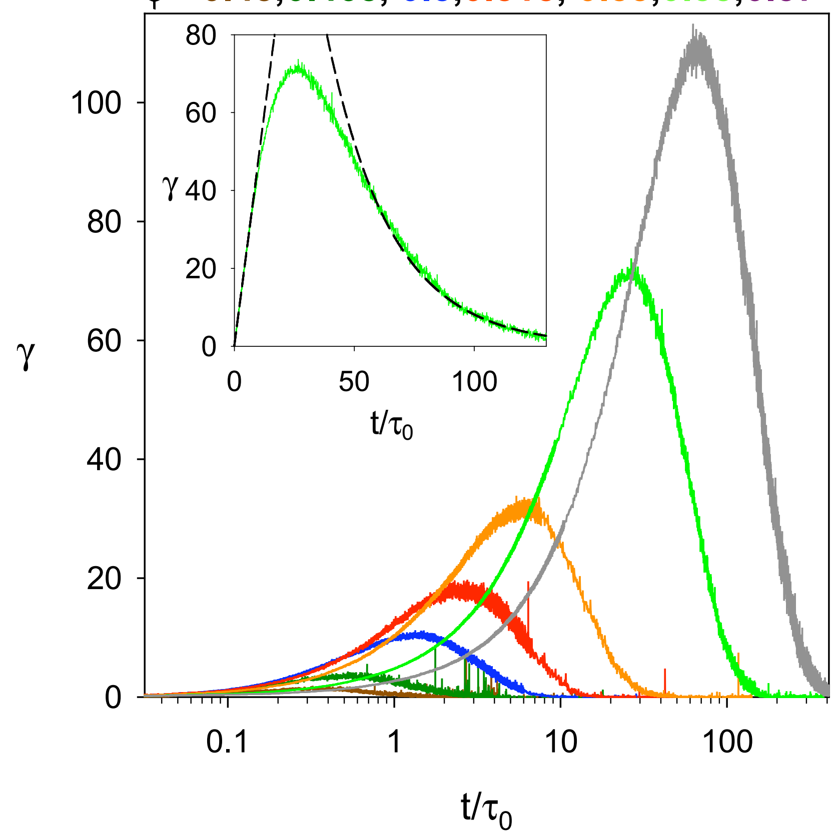


$$\gamma(t) = \frac{1}{3}\left\langle r(t)^2 \right\rangle \left\langle \frac{1}{r(t)^2} \right\rangle - 1$$

Flenner and Szamel, PRE 2005

Quantifies Heterogeniety of ***LONG*** *Time Alpha Process*

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



ala Colloid confocal expts, PD-HS and BLJM simulations

"LOOKS LIKE" $\chi_4(t)$

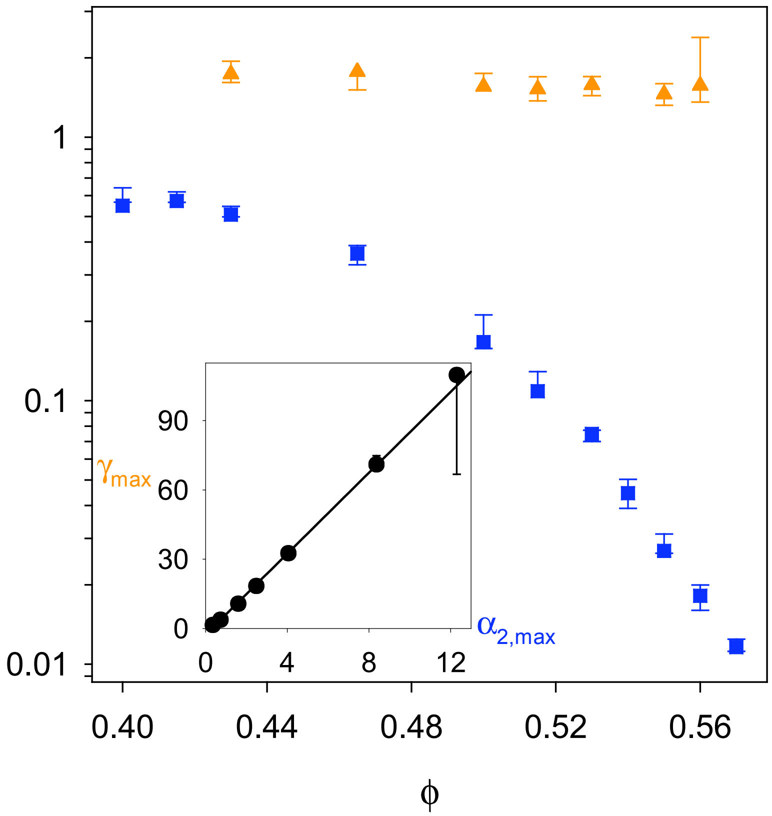
NONGaussian Parameters: Time Scales & Amplitudes

***NGP** and **Alternate** NGP*
Maximum Times

$\boxed{\dfrac{\tau_i}{\tau^*}}$

a-NGP

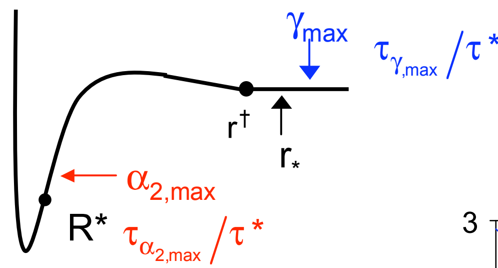
- Timescale tracks τ^* vs. $\alpha_{2,max}$ time
- Amplitude LARGER than NGP
- Different Shape : *sharp long time cutoff*



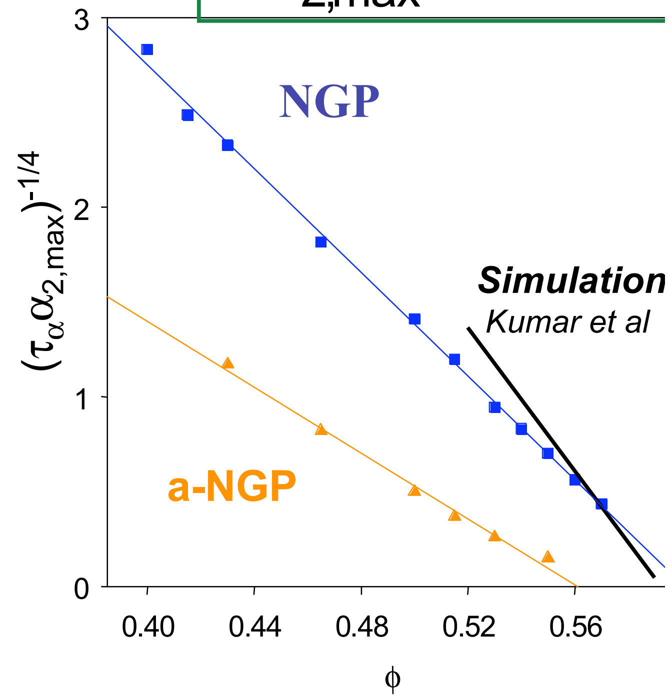
MSD at MAXIMUM

NGP : 0.3 --> 0.07 ~ R*….*SHRINKS*

a-NGP : ~ 0.4 --> 1 *GROWS*



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



$$\gamma_{max} \sim 9\alpha_{2,max} - 3$$

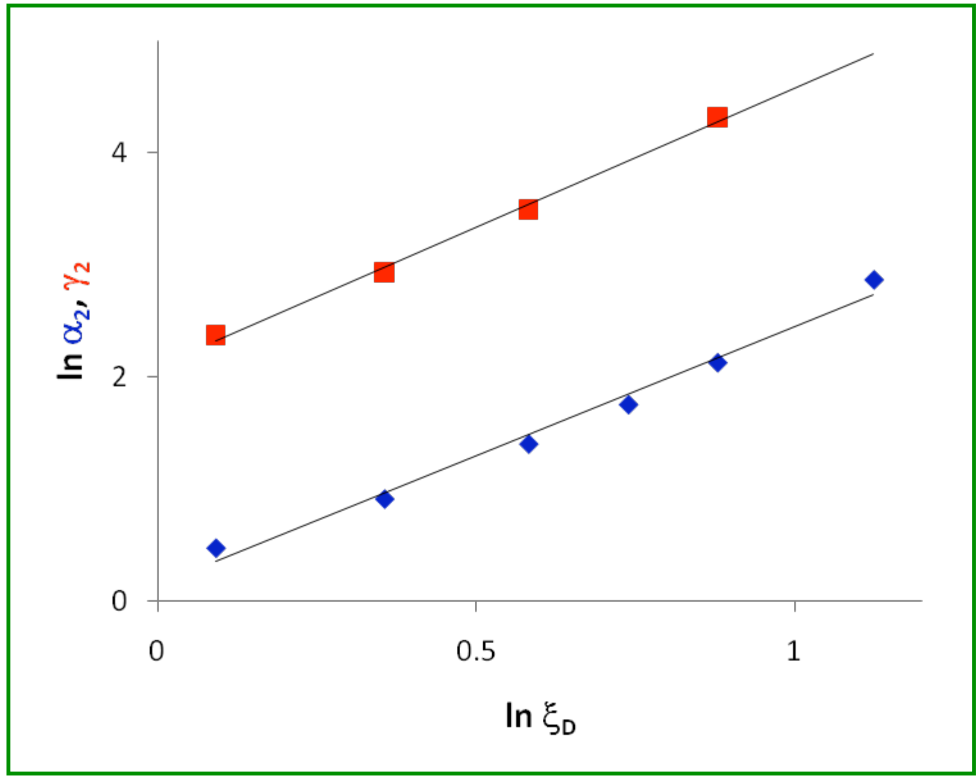
$$\alpha_{2,max} \propto \gamma_{max} \propto (\tau^*)^{0.56} \propto \xi_D^{2.4}$$

Heterogeneity of EARLY stages of Cage Escape and FINAL Relaxation strongly COUPLED

Amplitude of NGP and a-NGP *…analog of peak of chi_4(q=0,t) ?*

ϕ=0.5 —> 0.57

Barrier ~ 1.5 --> 6.7

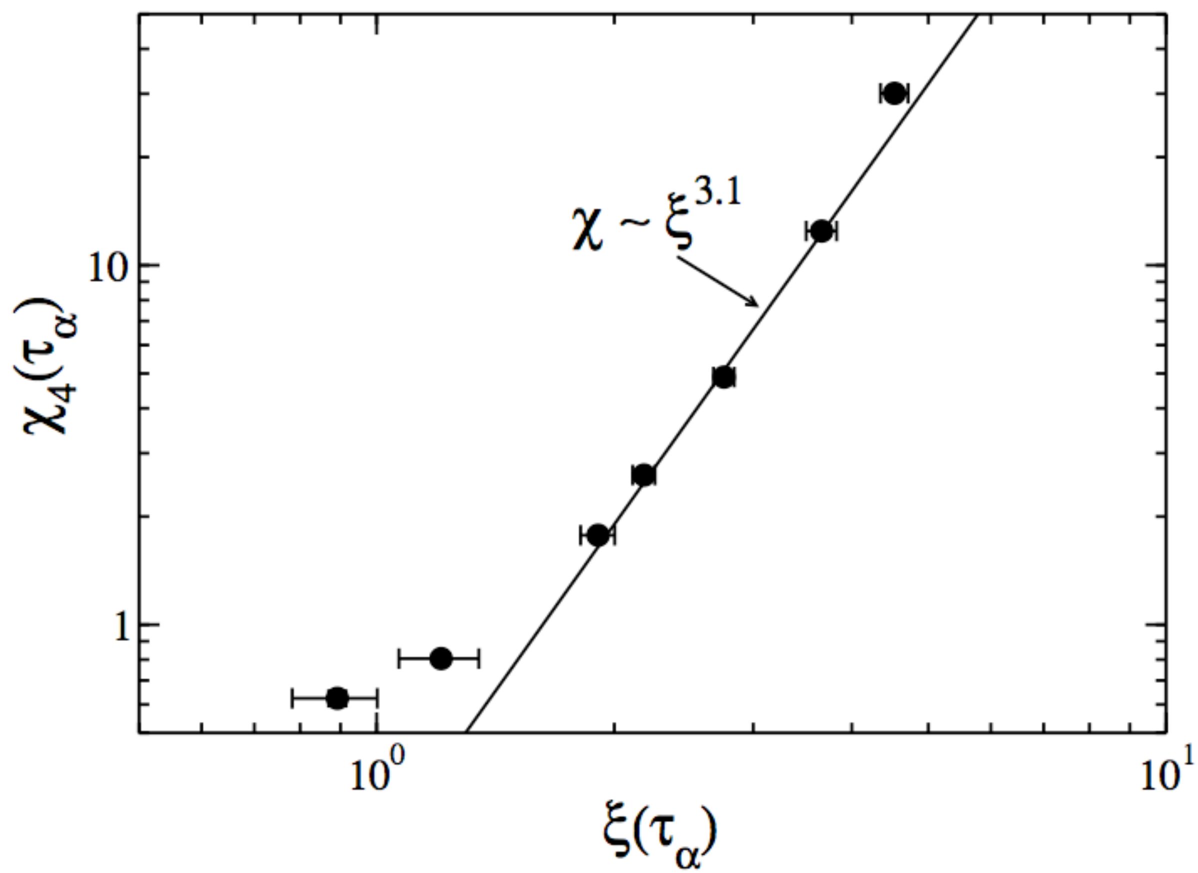


Fit exponents = 2.30 (standard ngp),
2.47 (alt ngp)

$$\textit{Peak Amplitude} \propto \xi_D^{2.4\pm0.1}$$

psi_D = NonFickian crossover length ~ Jump Length ~ Decoupling length
from F_s(q,t) scaling collapse via D(q)~Lorenztian,
ala time peak S4(q))

Szamel chi4(t) : BHSM

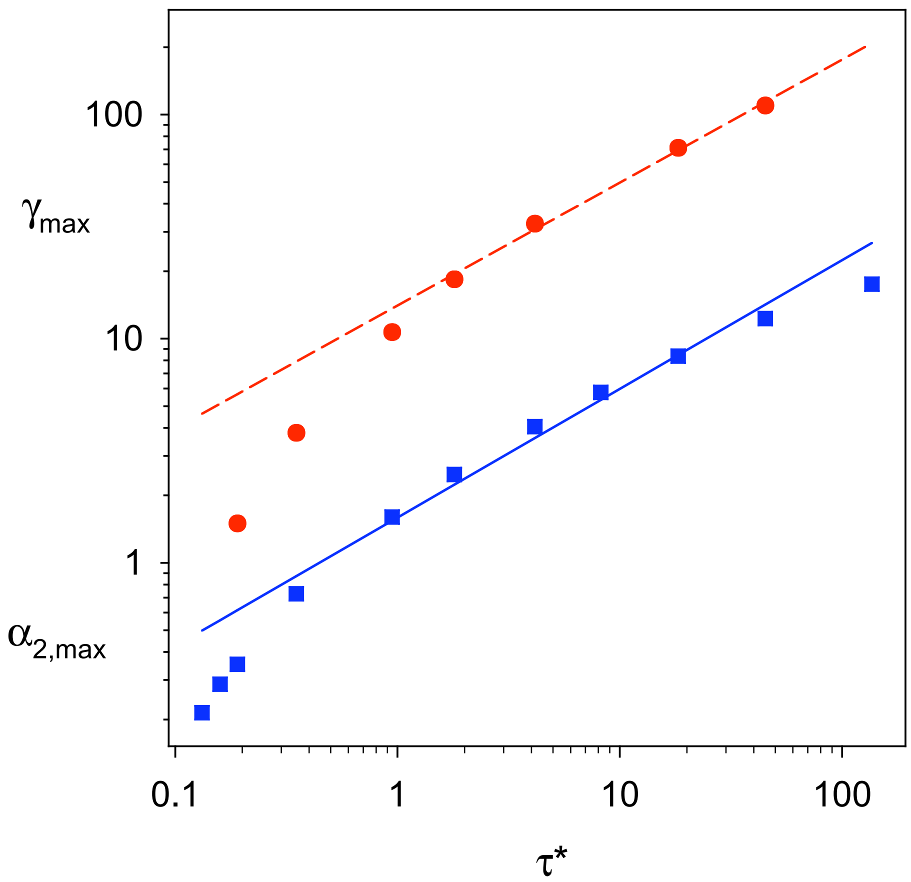


Dasgupta & Sastry (PRL 2010) : exponent ~ **2.2-2.5** for BLJM ~ NLE theory

IMCT : exponent ~ 4 …poor despite good empirical MCT fit in this regime

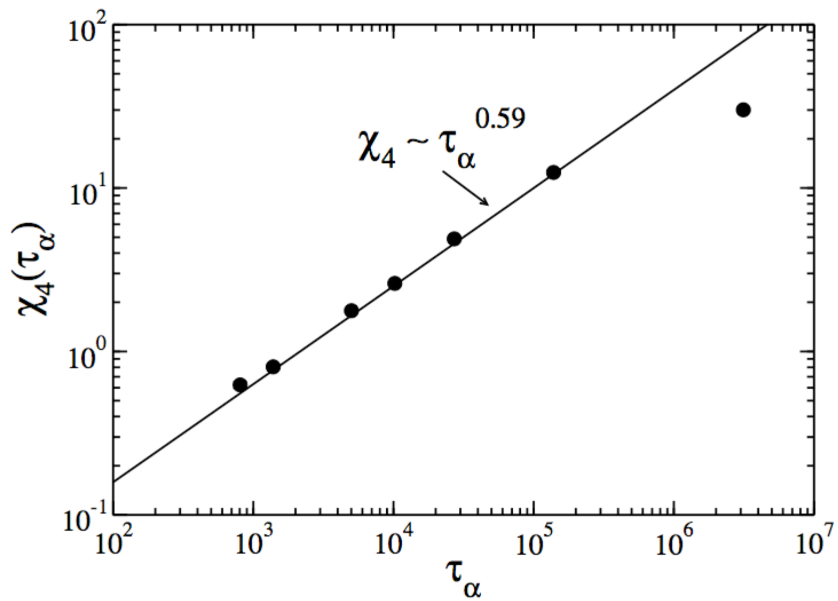
Peak Amplitude of NGP and a-NGP vs. Alpha Time

PRE 2006
JPCM 2008



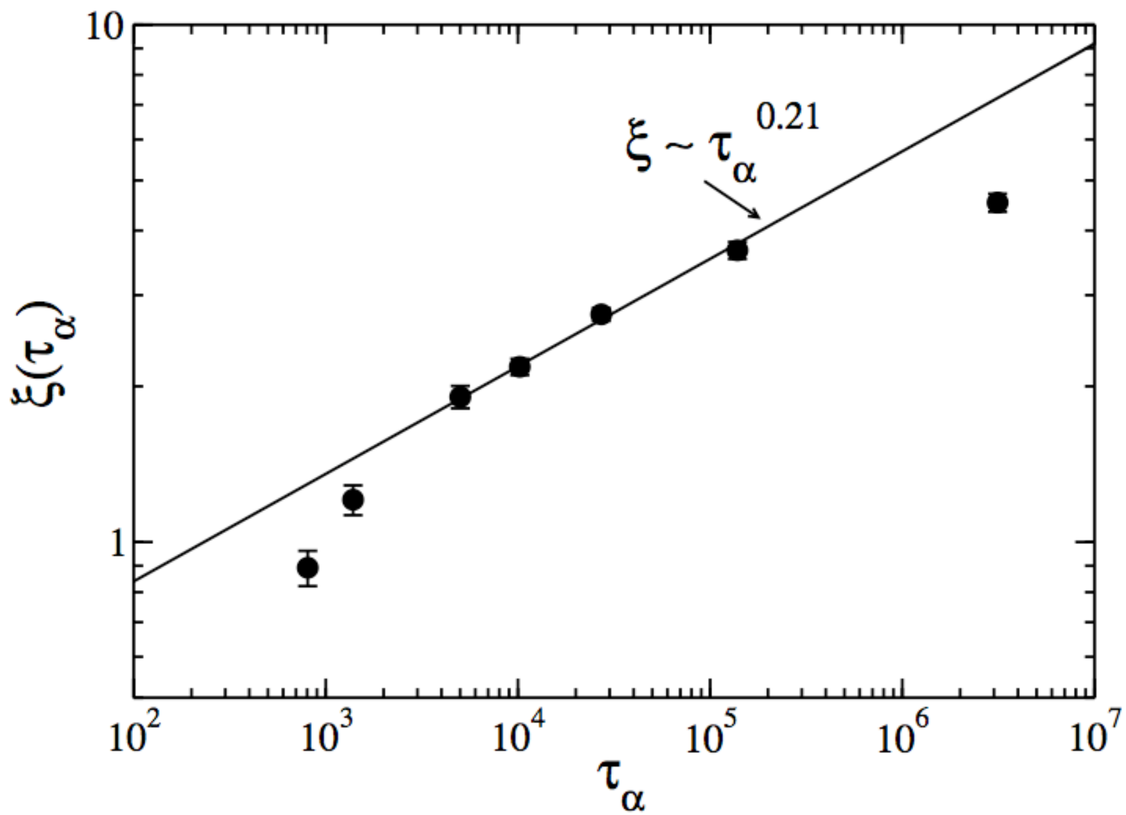
Scaling Exponent ~0.55-0.57

Ala Chi4 (Szamel)



Really more logarithmic ?? ;
intermediate power laws per chi4
deviations in HIGH and LOW barrier regimes

Szamel chi4(t)



~ NLE theory

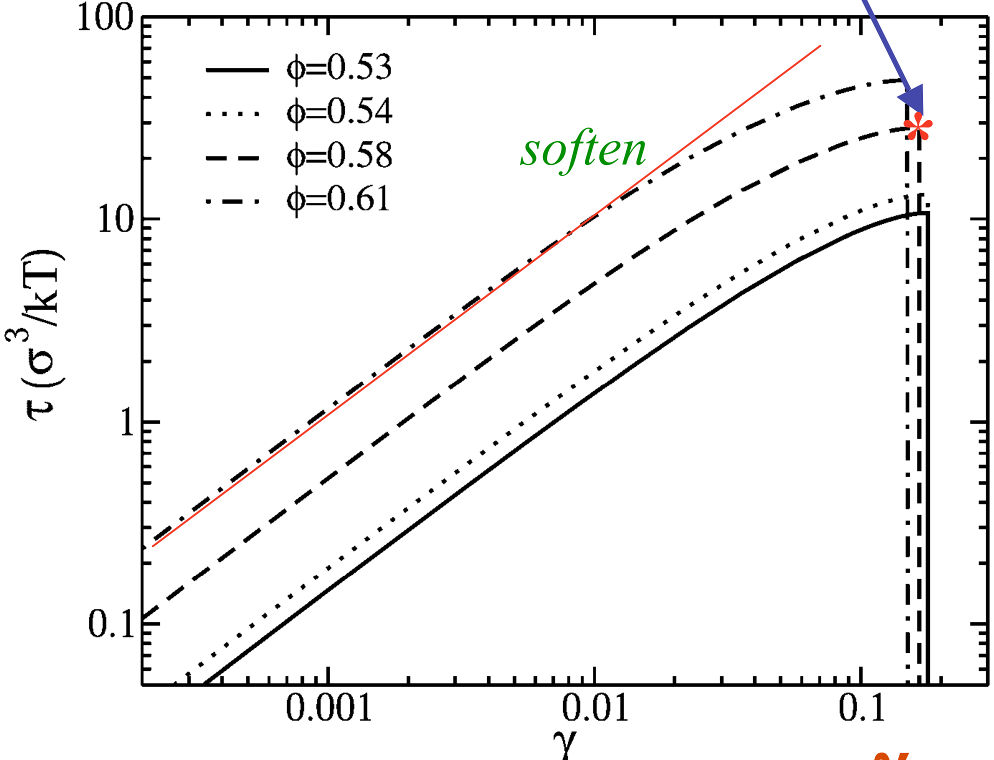
Private Communication:

Pretty good EXP, Barrier sub-linear with dynamic length ala D&S

Quasi-Static Limit (*no hopping*): ~ "solid-like" Step Strain Expt

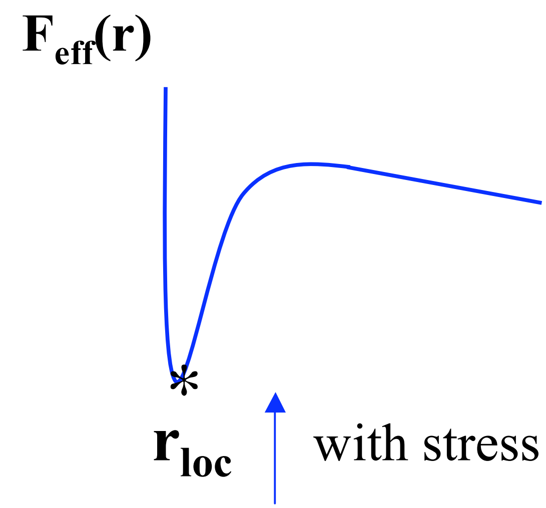
$$\boxed{\tau = G'(\tau)\gamma}$$

Absolute Yield:*destroy localized state*



$\tau_{y,abs}$

$\gamma_{y,abs}$ ~15%

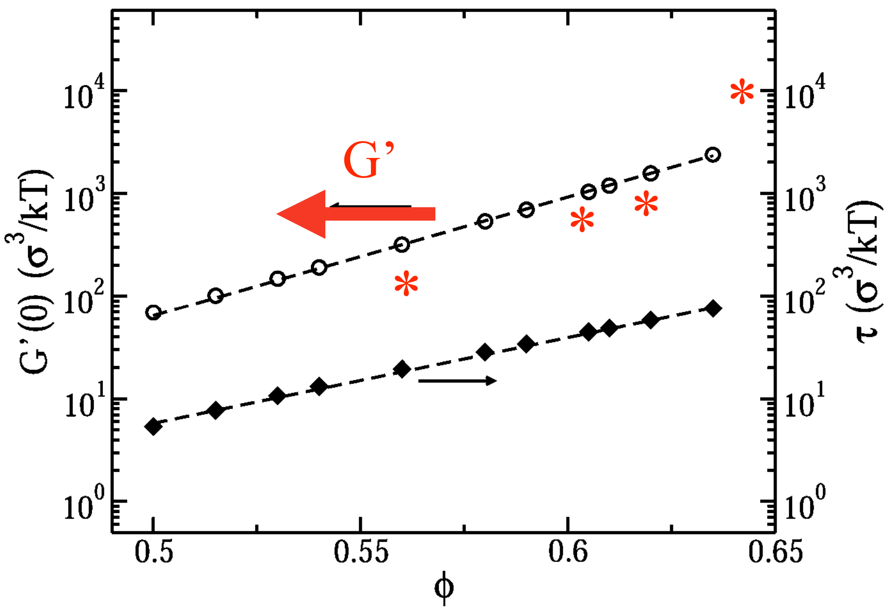


PRE, 2005

Linear Shear Modulus & Absolute Yield Stress

Units : kT/σ³ = 4 Pa for 100 nm

* *Petekedis et al Expt (PRE,2002)*



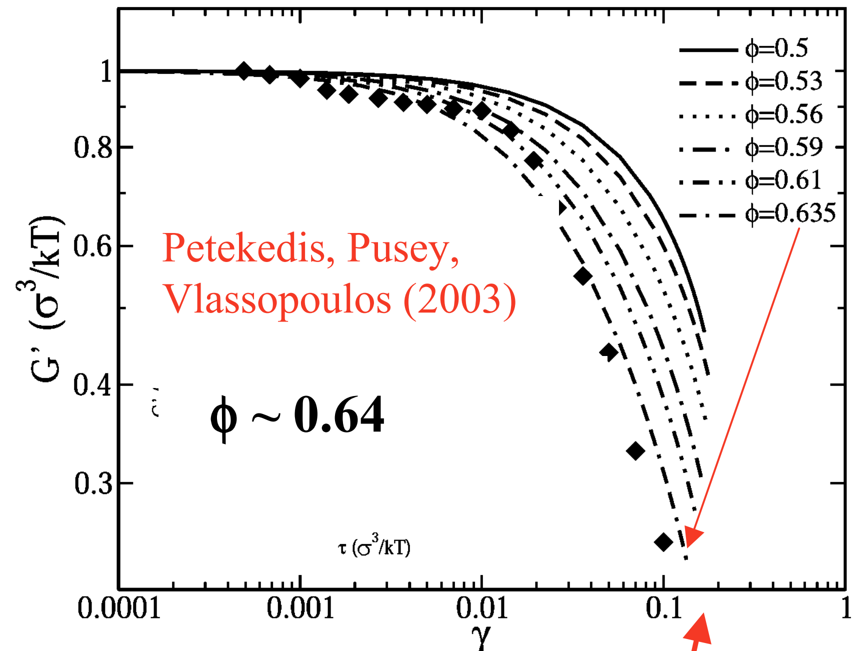
$$G' \propto e^{27\phi} \propto \phi^{14}$$

$$\tau_{y,abs} \propto e^{19\phi} \propto \phi^{11}$$

Strain Softening

Dynamic strain sweep Expt (100 Hz)

G'(strain)/G'(0)

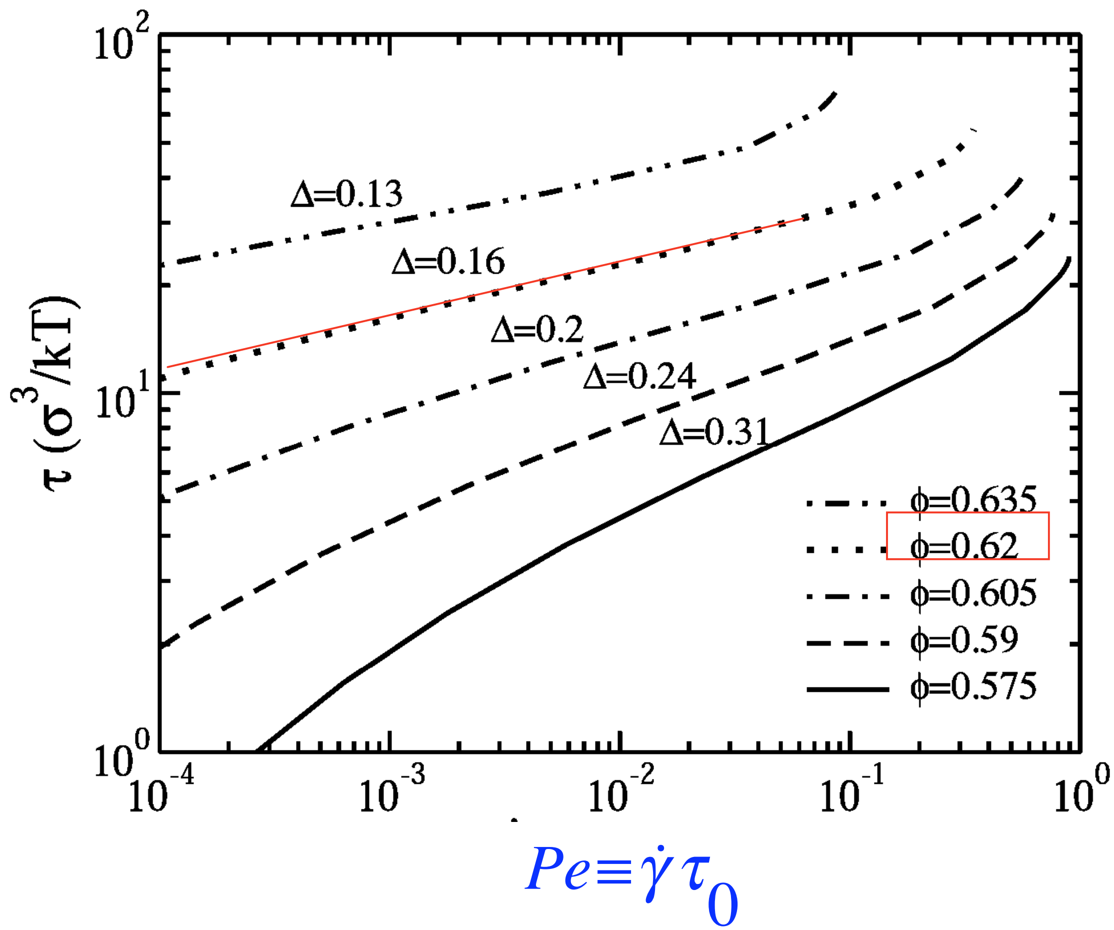


Softens by factor ~ 3-4 before Yield

Absolute Yield Strain ~ **10-20 %**

Magnitudes & Dependences Broadly consistent with variety of Expts

Steady State (homogeneous) **Flow Curves**



No rigorous plateau

….hopping restores ergodicity

Apparent Power Laws : $\boxed{\tau \propto \dot{\gamma}^{\Delta}}$ → *ϕ-dependent shear thinning exponent*

$\Delta(\phi) \sim 0.1\text{–}0.3$

Spaepen

$\phi \sim 0.61$
$\sigma \sim 1.5\,\mu m$

$$F_B(\tau) \cong F_B(0)\left[1-(\tau/\tau_{y,abs})\right]^{5/2}$$

~15 kT

Expt estimate of Stress : $\tau \simeq \gamma_0 G' \simeq (0.012)(0.056)Pa \simeq 7.7*10^{-4}$

Theory : $\tau_{y,abs} \simeq 60\dfrac{kT}{\sigma^3} \simeq 60 \bullet (4.2Pa)(1/15)^3 \cong 0.075$

Mechanical Barrier Reduction ~ $15 \bullet \dfrac{5}{2} \bullet \dfrac{7.7*10^{-4}}{0.075} \approx 0.38 \quad k_B T$

WITHIN FACTOR 2-3 OF EXPT ESTIMATE !