Direct observation of dynamical heterogeneities near the attraction driven glass

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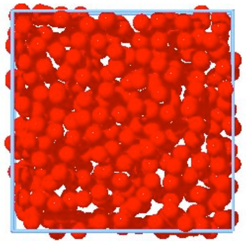
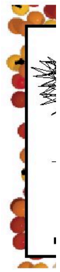
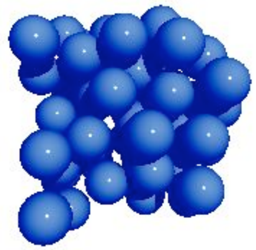
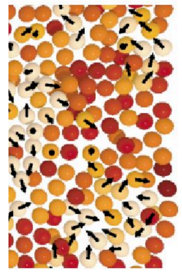
McGill

Dynamical heterogeneity and intermittence

- *Conventional liquids*: dynamical relaxation is achieved through continuous Brownian motion



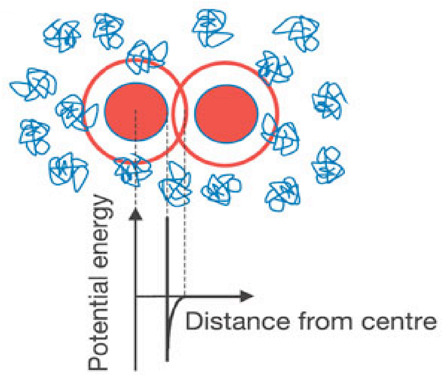
- *Supercooled liquids*: dynamics becomes localized and shows heterogeneity and discontinuity due to cage break-up

Heuer *et al*. *PRL* (1998)

Glotzer *et al*. *PRE* (1999);
Weeks *et al*. *PRL* (2002);

- *Attractive systems*: dynamics shows heterogeneity and intermittence due to bond breaking and forming



Light scattering+MCT: Manley *et al.* (2005)

MD Simulation: Cates *et al.* (2004)

Outline

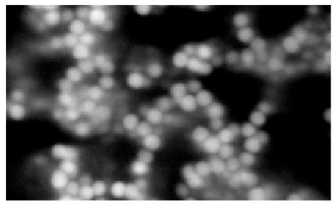
- Attractive colloidal physics
- Metrics used to study dynamics at the single particle level: space time correlation functions, MSD, NGP

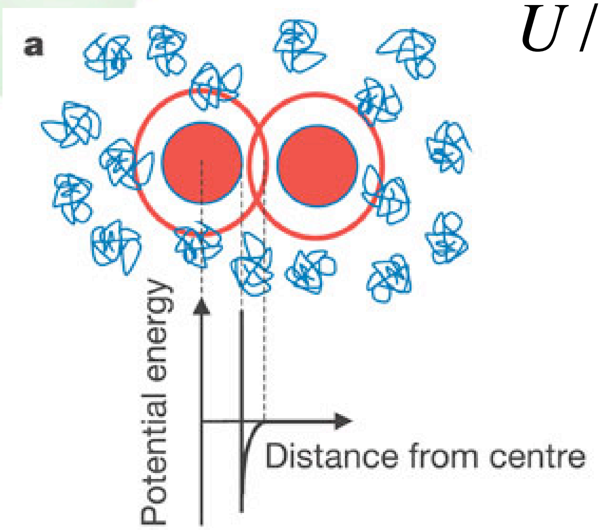
Questions:

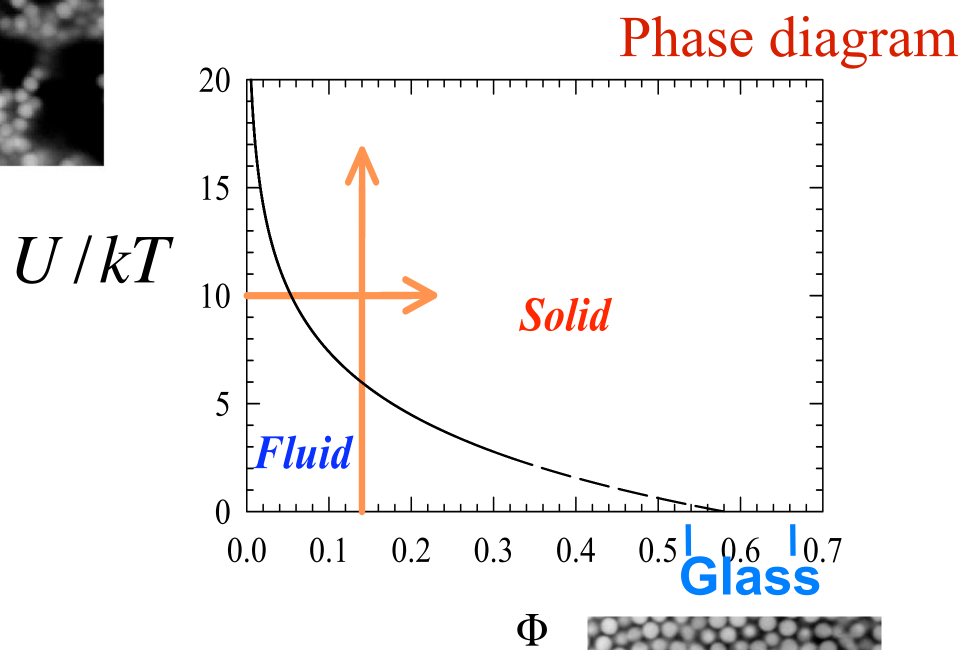
- Contribution of mobile and immobile particles to structural relaxation
- Correlation between structural and dynamical heterogeneities in this system
- Comparison of immobile population to supercooled hard sphere liquids
- Origin of the exponential tails in SvH
- Spatial correlation in mobile particles

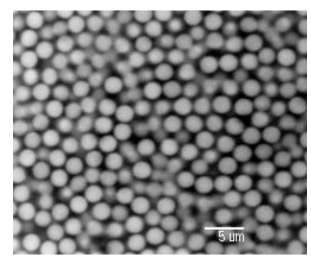
Fluid-Solid Transition

Weakly Attractive Systems

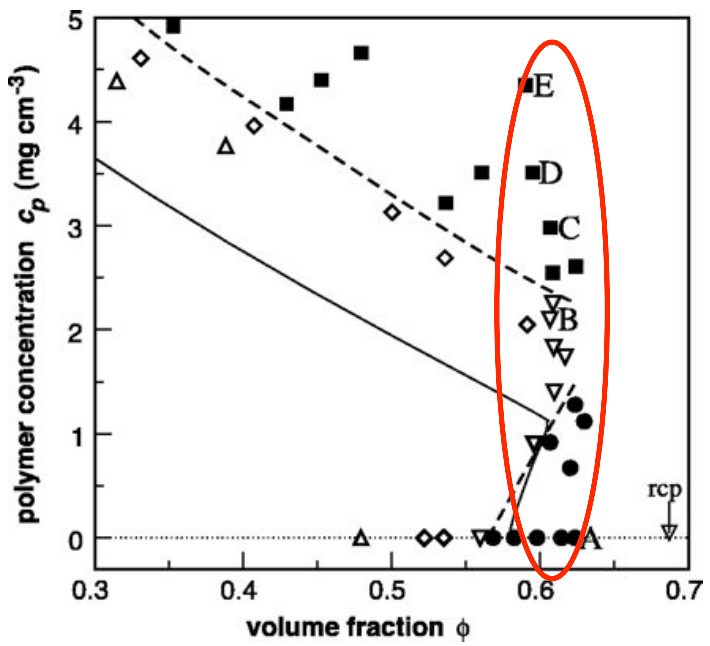


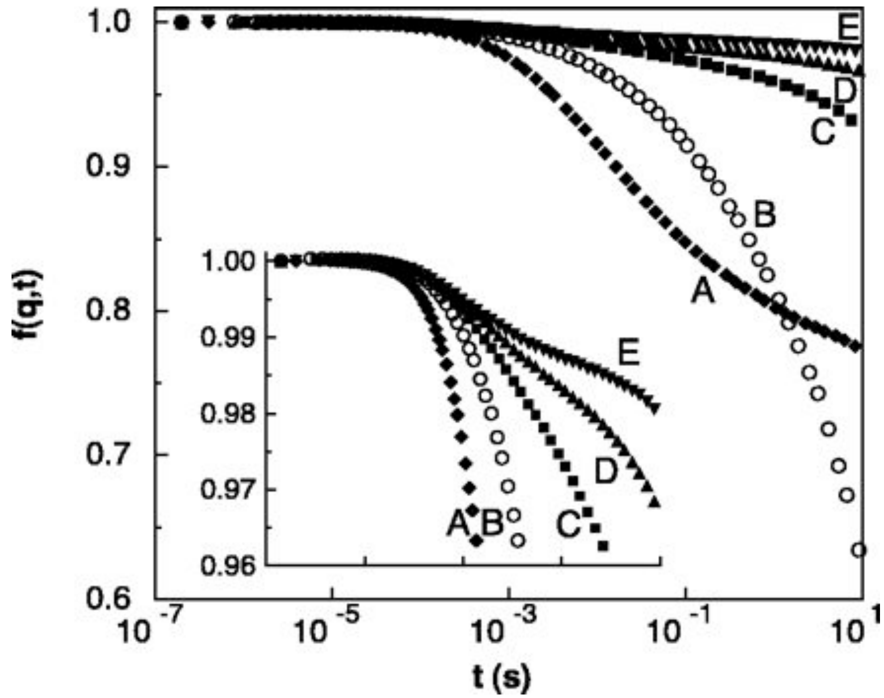






New type of colloidal glass: “Attractive Glass”

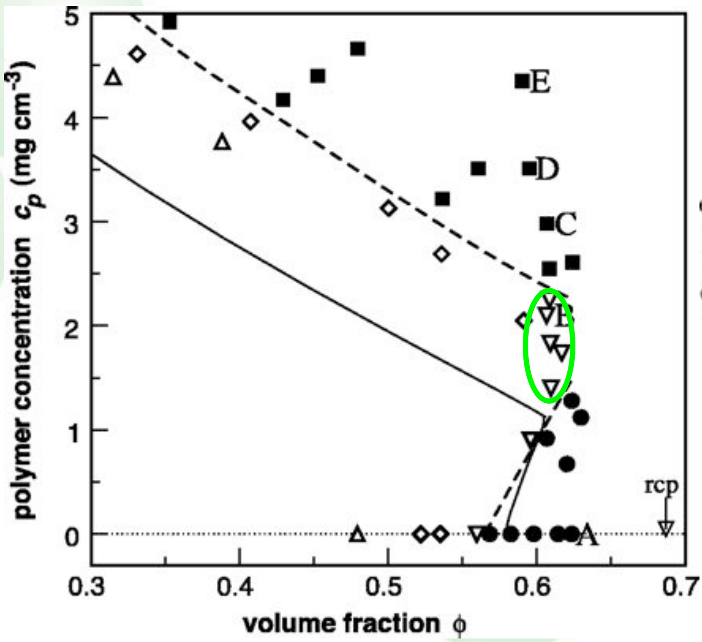


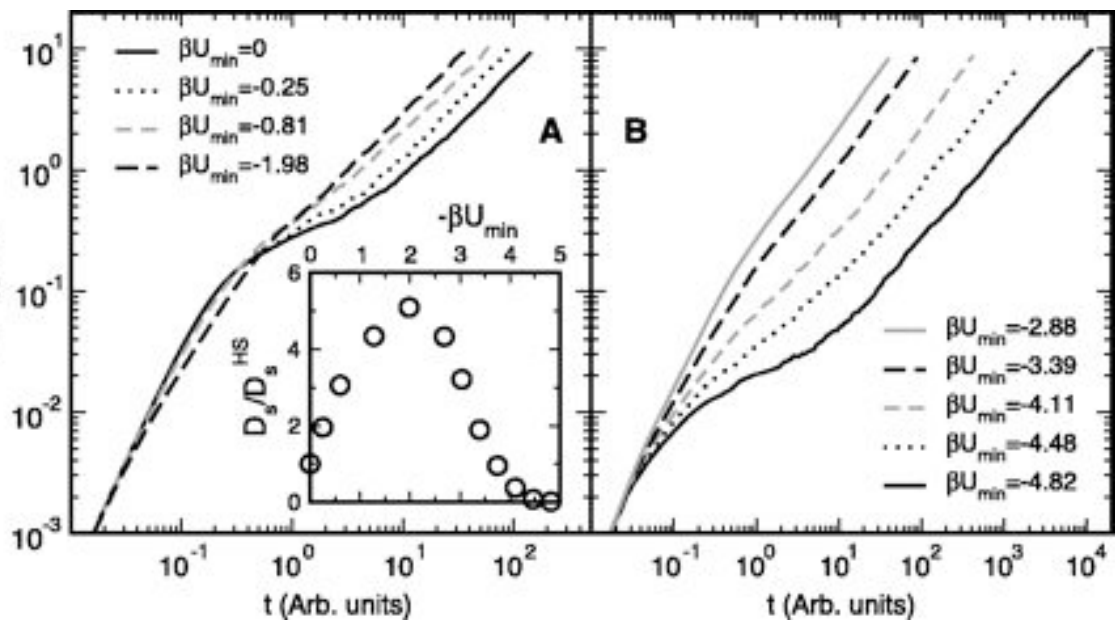


Light scattering: normalized dynamic structure factor

K.N.Pham *et al.*, *Science* 296,104 (2002)

New type of colloidal glass: "Attractive Glass"

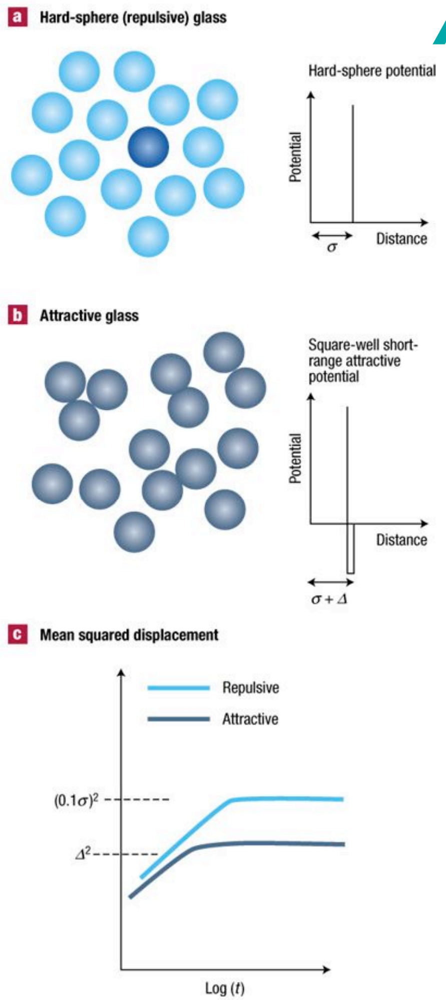




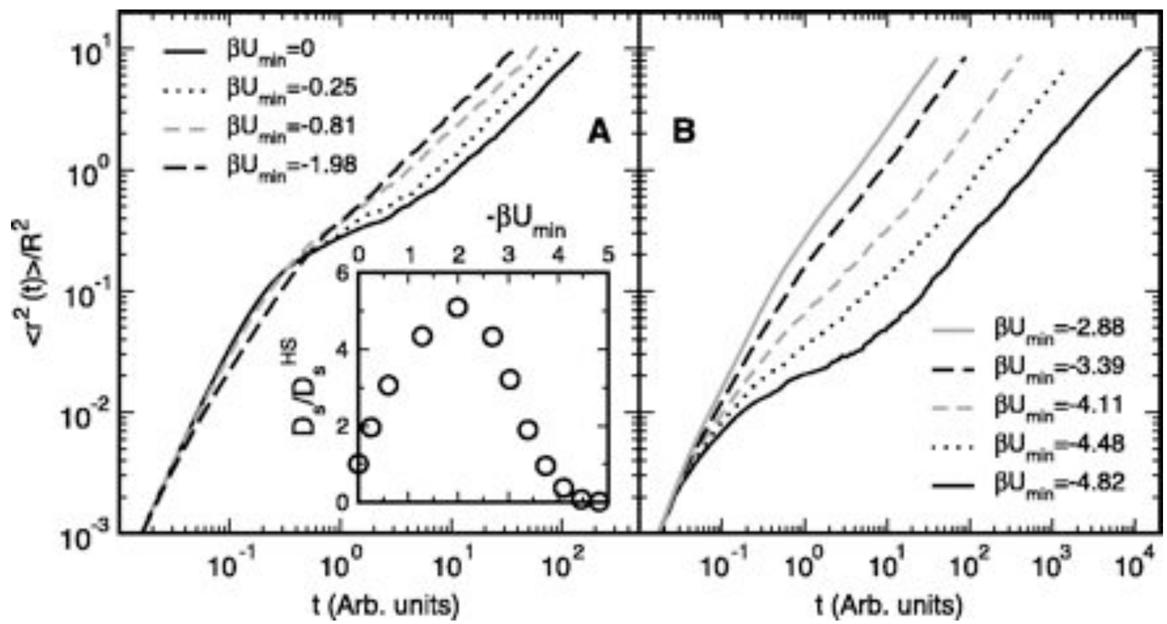
Computer simulation of glass reentrant from repulsive to attractive

K.N.Pham *et al*., *Science* 296,104 (2002)

New type of colloidal glass: "Attractive Glass"



Sciortino, *Nature Materials* (2002)



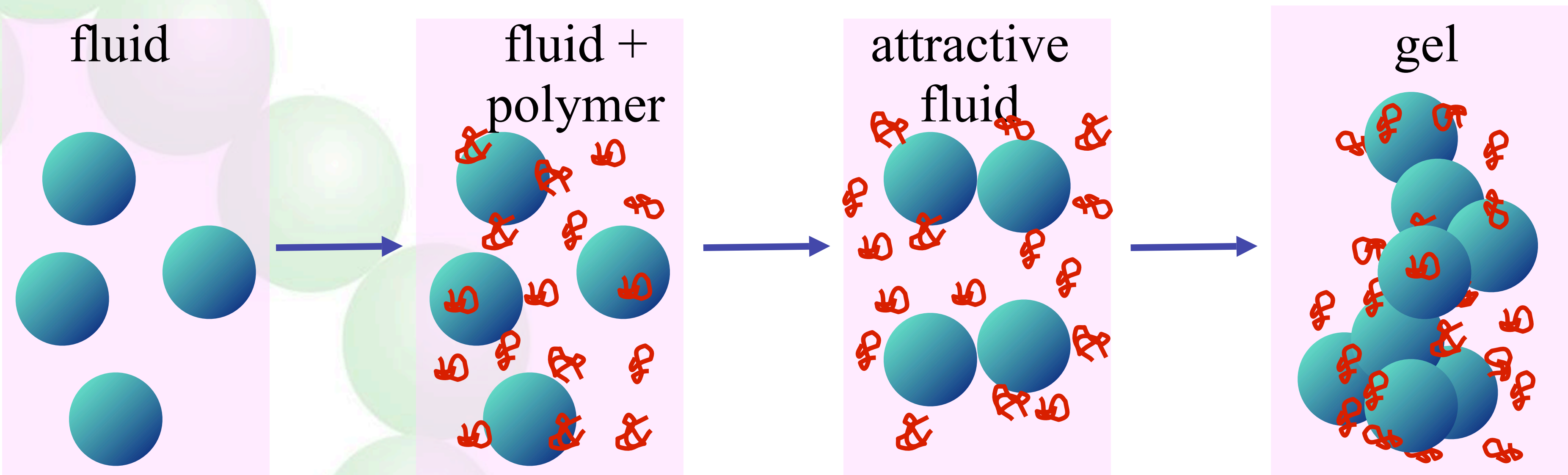
Computer simulation of glass reentrant from repulsive to attractive

K.N.Pham *et al*., *Science* 296,104 (2002)

Realization of weakly attractive systems:

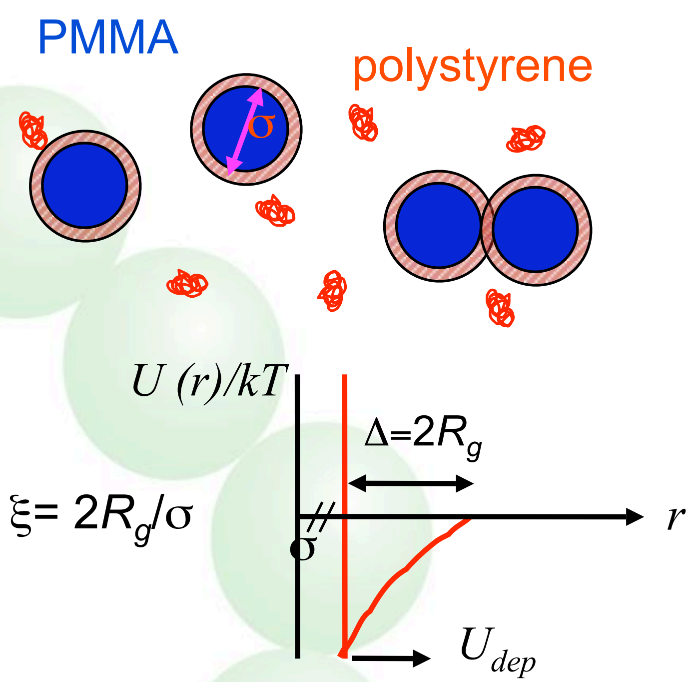
Colloid-polymer mixtures

Depletion attraction



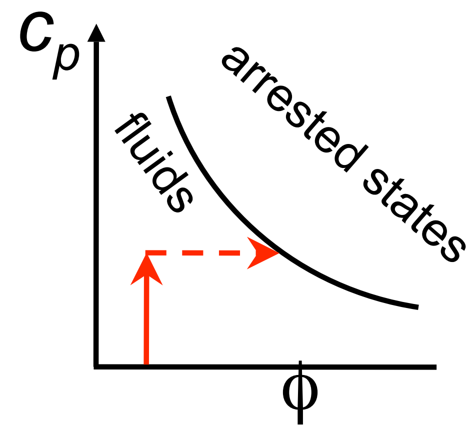
Polystyrene polymer, R_g=46 nm + PMMA spheres, r_c=660 nm

Realization of weakly attractive systems:



PMMA as colloids
PS nonadsorbing polymer as depletant

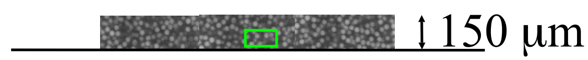
Asakura and Oosawa, *J. Polym. Sci* (1958)



System: PMMA (σ =1.326 μm) and Δ~0.14 σ in refractive index-matching and buoyancy-tunable suspending fluids Decalin/Tetralin/CXB

$\Delta n = 0$ and $\Delta\rho = 0.011 g/cm^3$

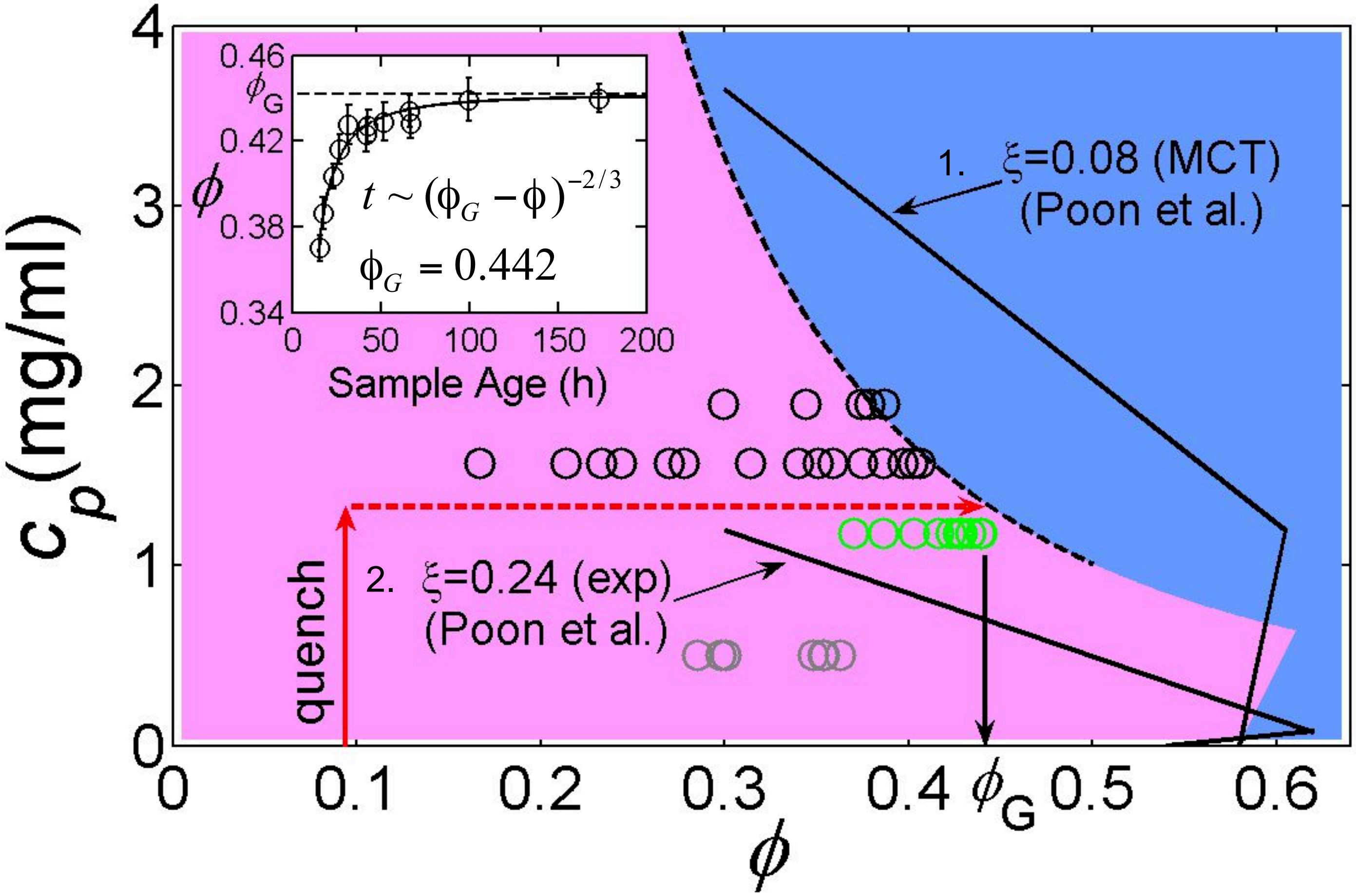
Side view:



Confocal microscopy 3D real-space imaging

typical volume:
(22.6 X 22.6 X 10)μm^3

Phase diagram of attractive colloidal systems



U_{dep} from top to bottom is:

4.60 $k_B T$

3.77 $k_B T$

2.86 $k_B T$

1.21 $k_B T$

ξ= 0.14

1. Pham *et al*., *Science* 296,104 (2002)
2. W. C. K. Poon *et al., PRE* 51, 1344 (1995)

van Hove space-time correlation function: self and distinct parts

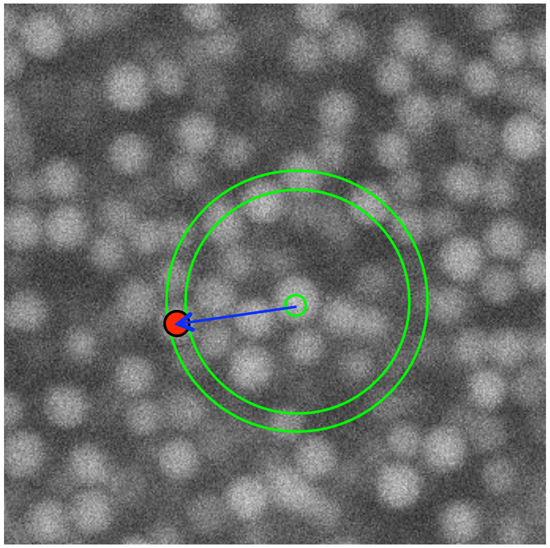
Self part

$$G_s(r,\tau) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \delta\left[r - |r_i(0) - r_i(\tau)|\right]\right\rangle$$

$$\approx \frac{1}{\left[\frac{4}{6}\pi < \Delta r^2(\tau) >\right]^{3/2}} \exp\left[-\frac{r^2}{\frac{4}{6} < \Delta r^2(\tau) >}\right]$$

Distinct part

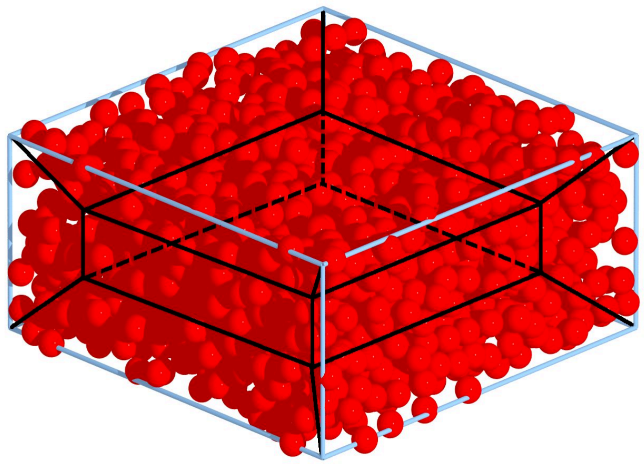
$$G_d(r,\tau) = \frac{1}{N}\left\langle \sum_{i}\sum_{j\neq i} \delta\left[r - \left|r_i(0) - r_j(\tau)\right|\right]\right\rangle$$

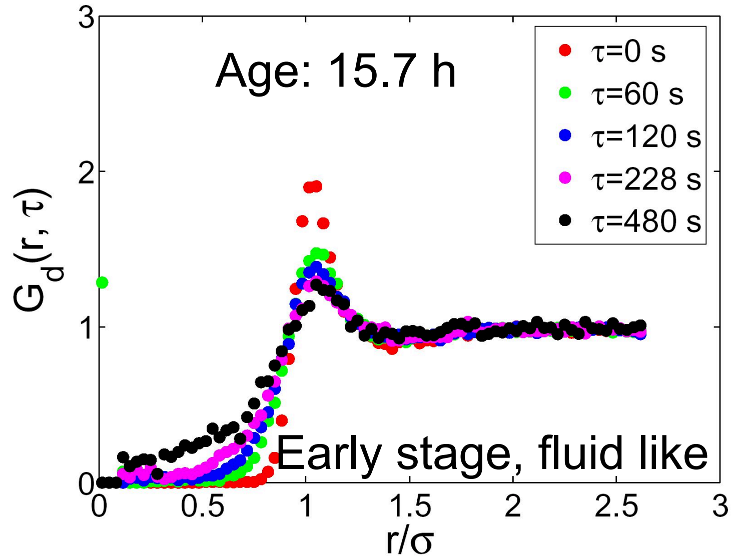


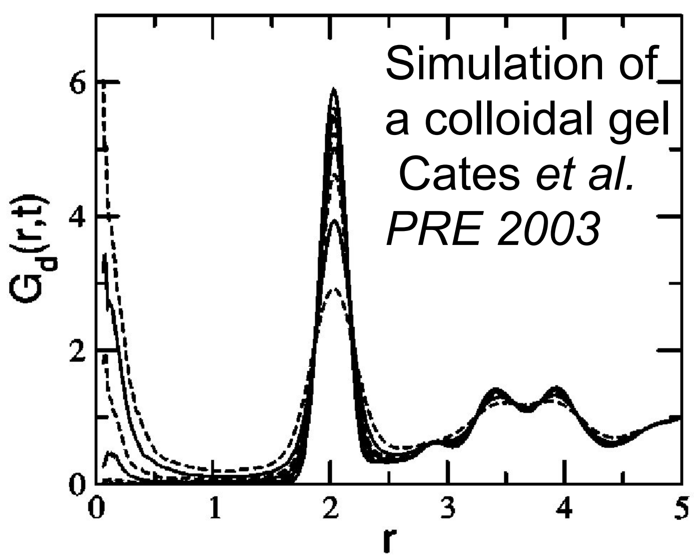
Distinct part of the van Hove space time correlation function

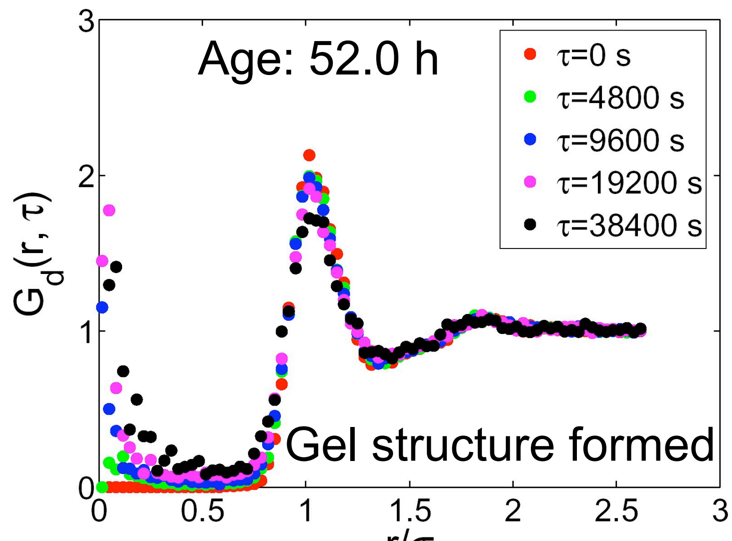
Y. Gao and MLK, PRL 2007

Geometry for calculating dvH





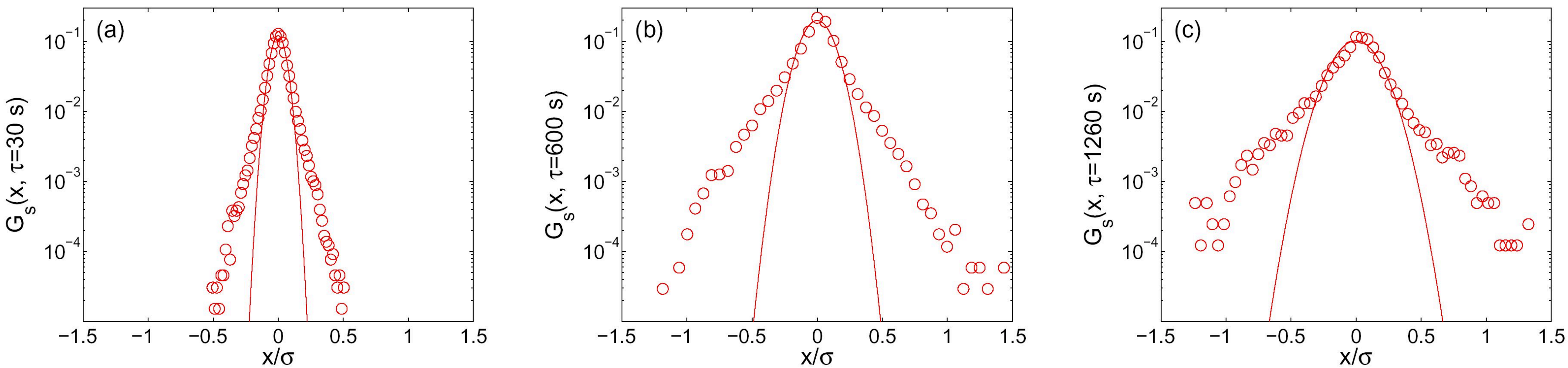




Self part of the van Hove space time correlation function…

volume fraction 0.386, as τ increases

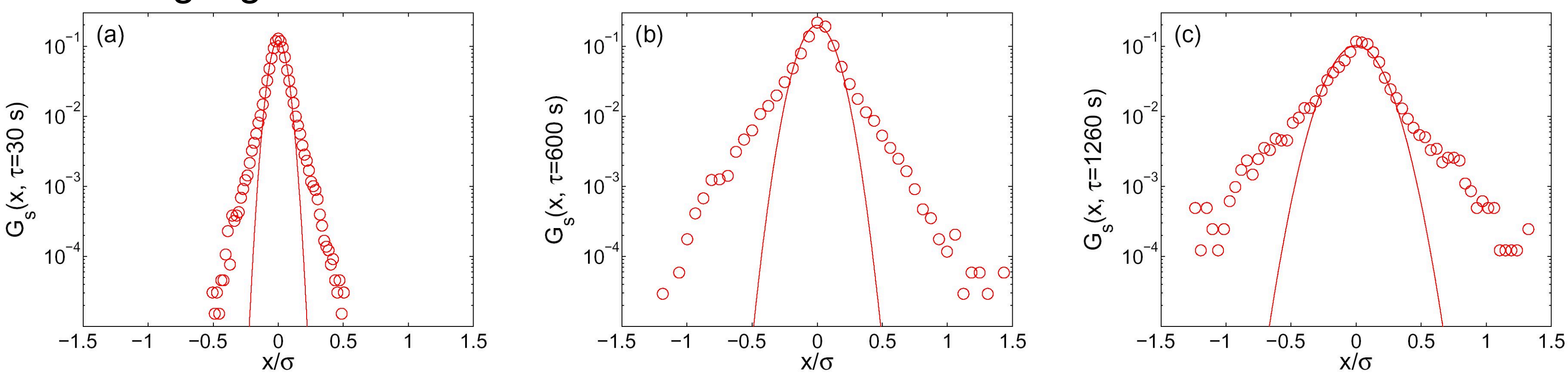
Single gaussian fit



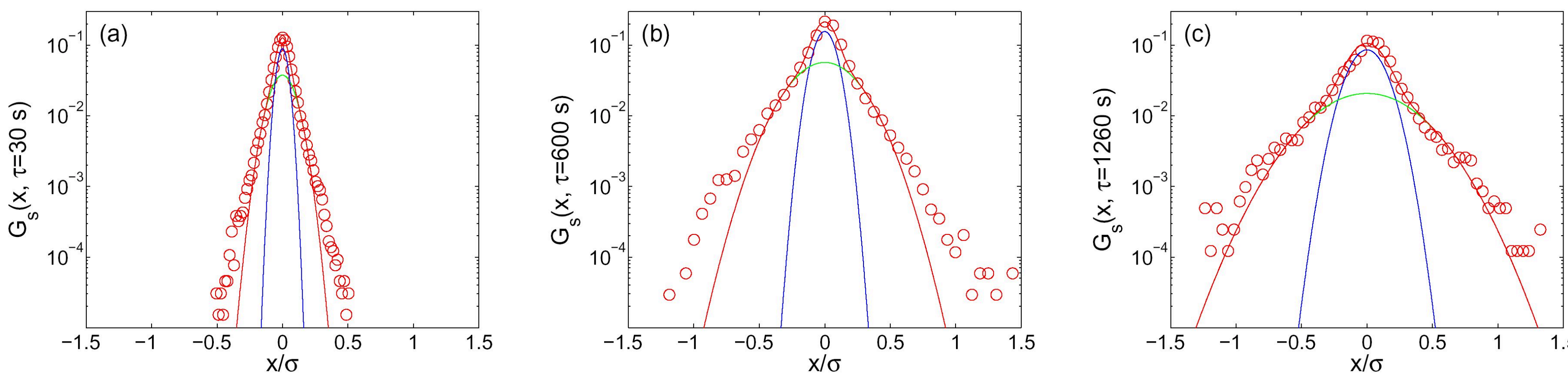
But.. Two-Gaussian behaviour emerges in the Self part of van Hove Correlation Function

volume fraction 0.386, as τ increases

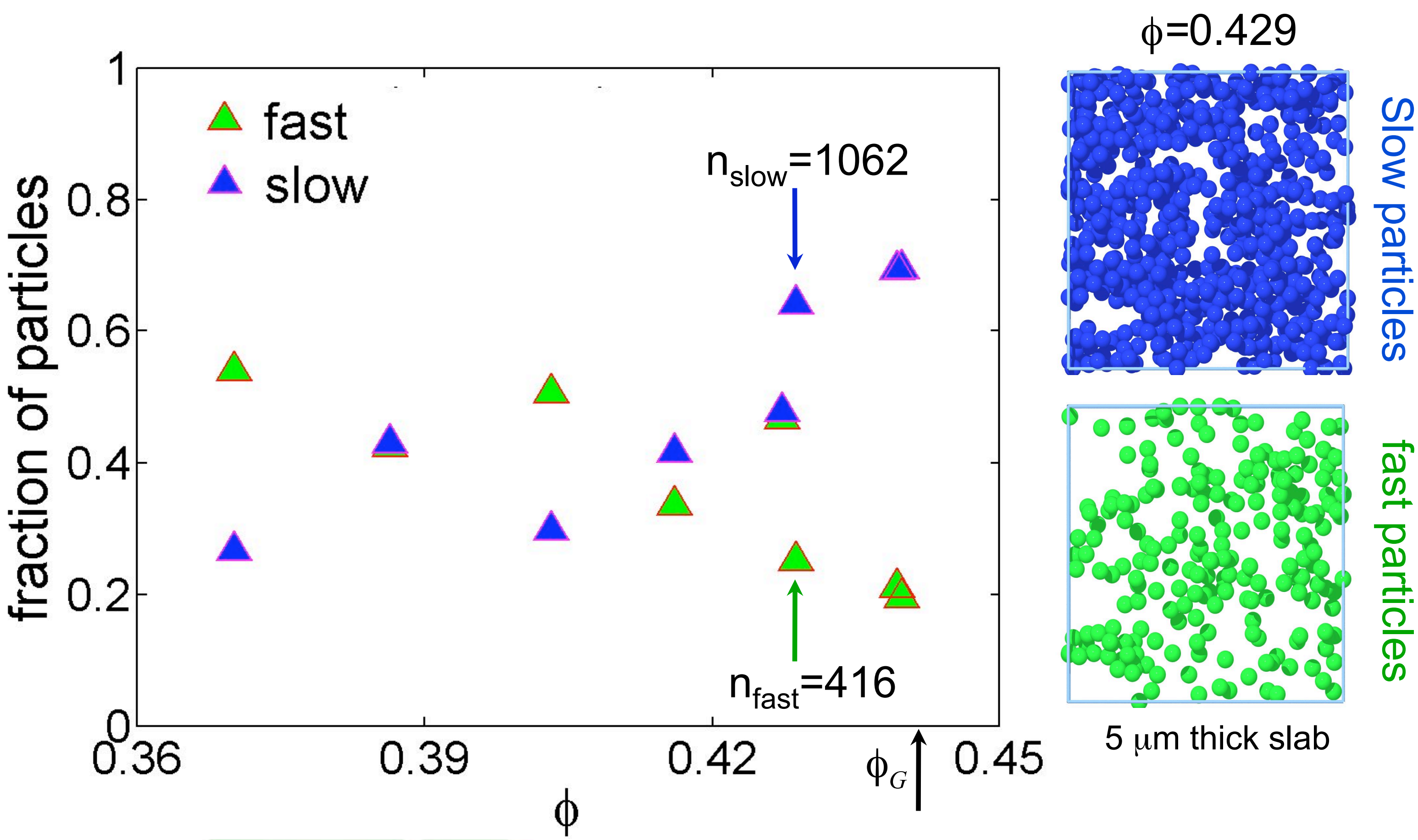
Single gaussian fit



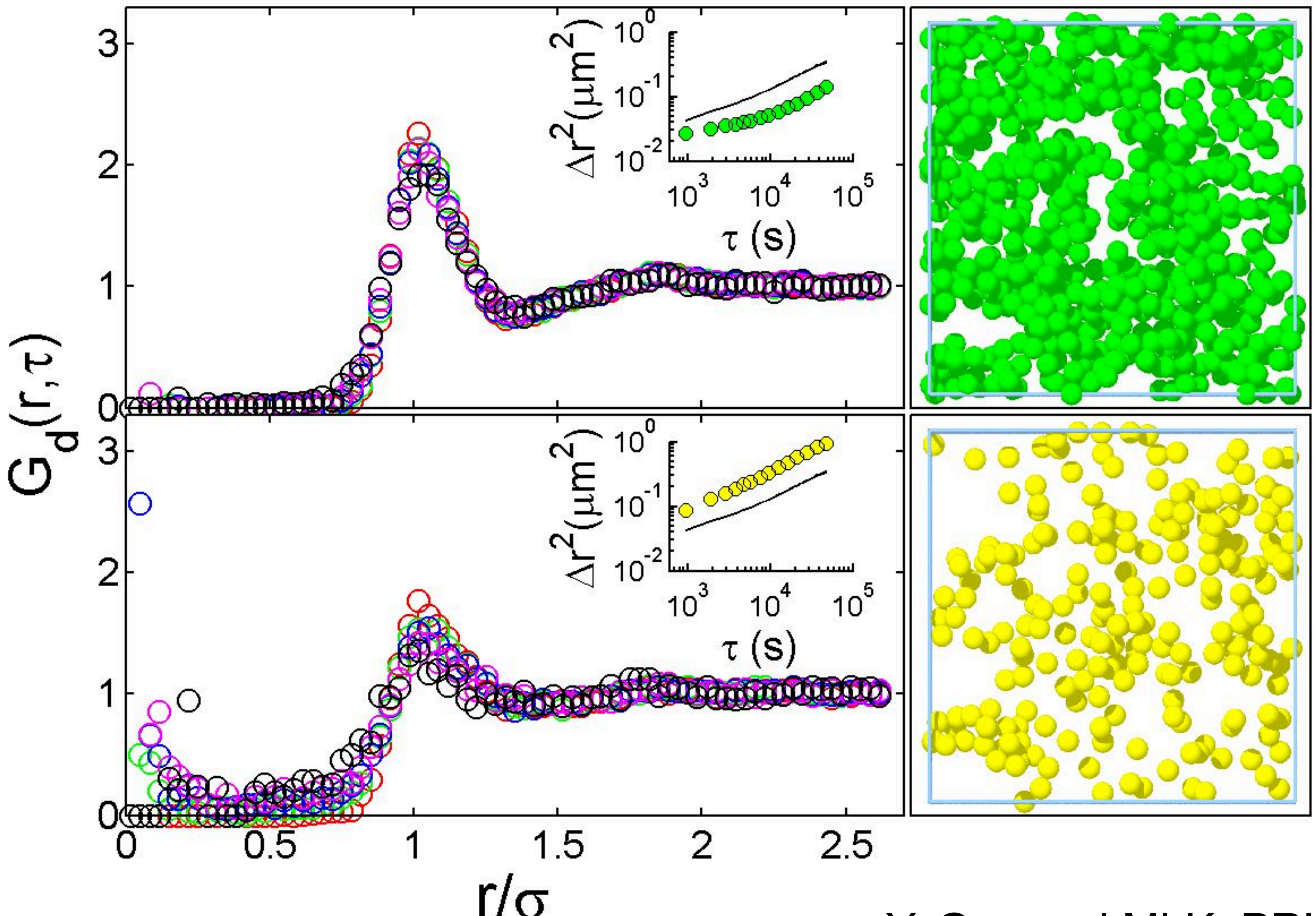
two gaussian fit (green line: fast branch; blue line: slow branch



Populations of fast and slow particles



Distinct part of Van Hove correlation function for fast and slow particles

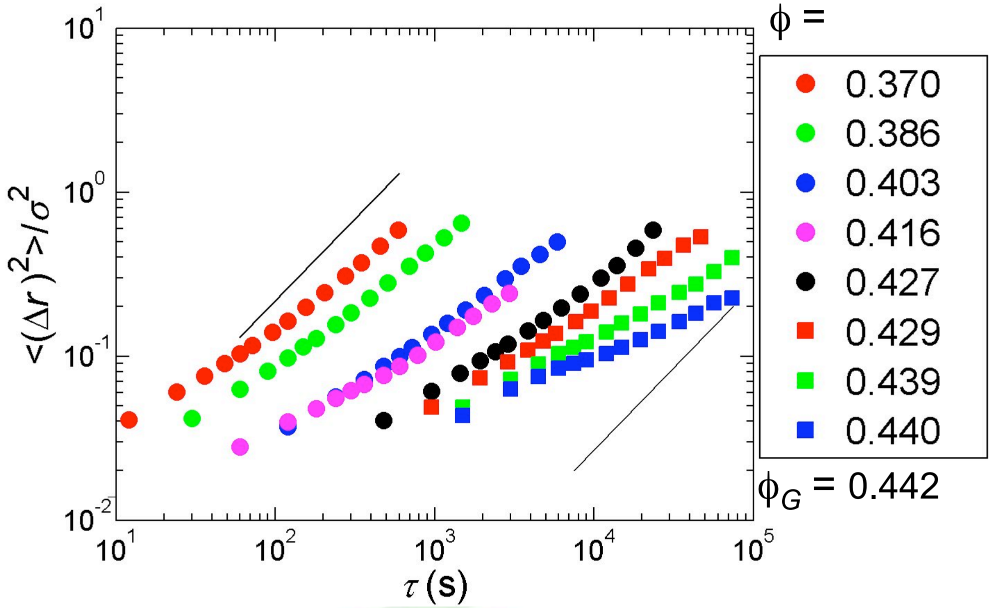


ϕ=0.429

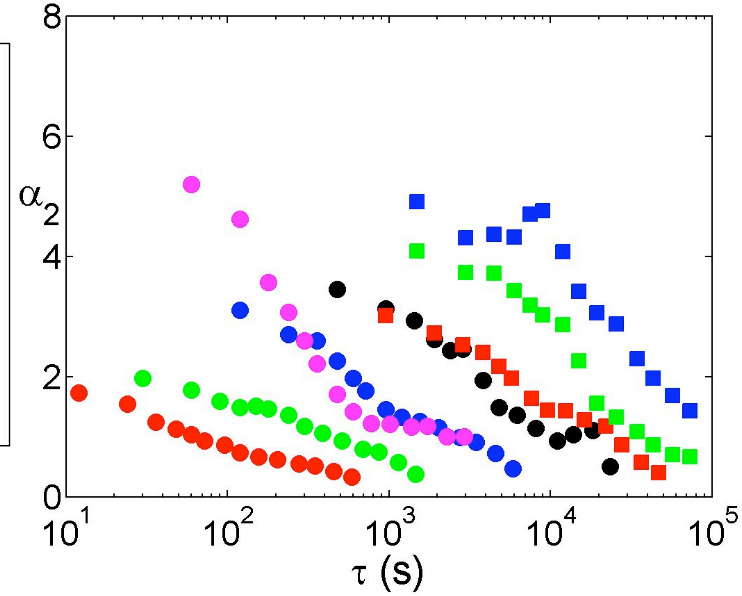
Y. Gao and MLK, PRL 2007

Microscopic dynamics for ***mobile particles*** in gel/attraction-driven glass regime

Mean squared displacement



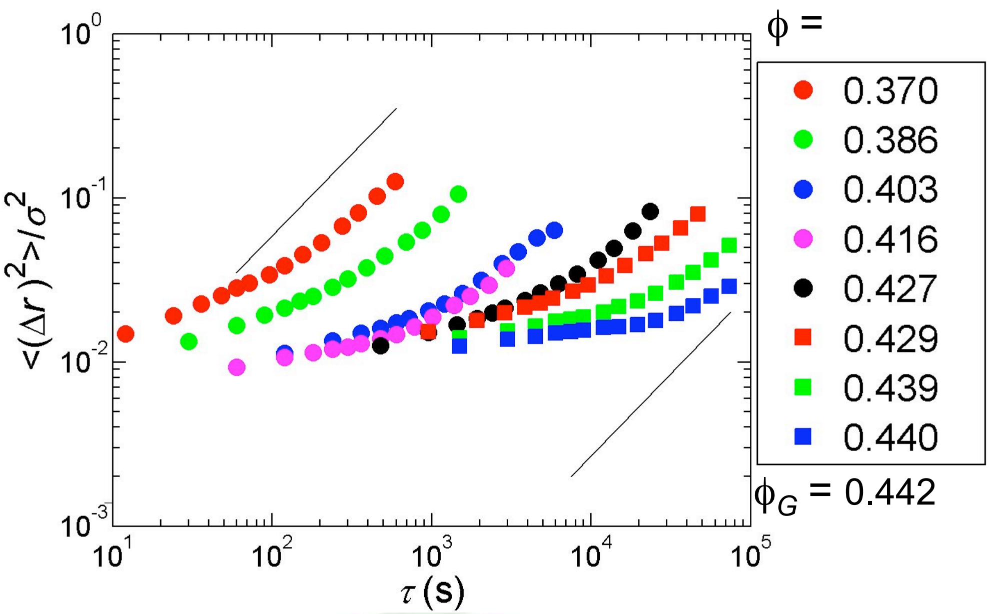
Non-Gaussian parameter $\alpha_2 = \frac{<\Delta x^4>}{3<\Delta x^2>^2} - 1$



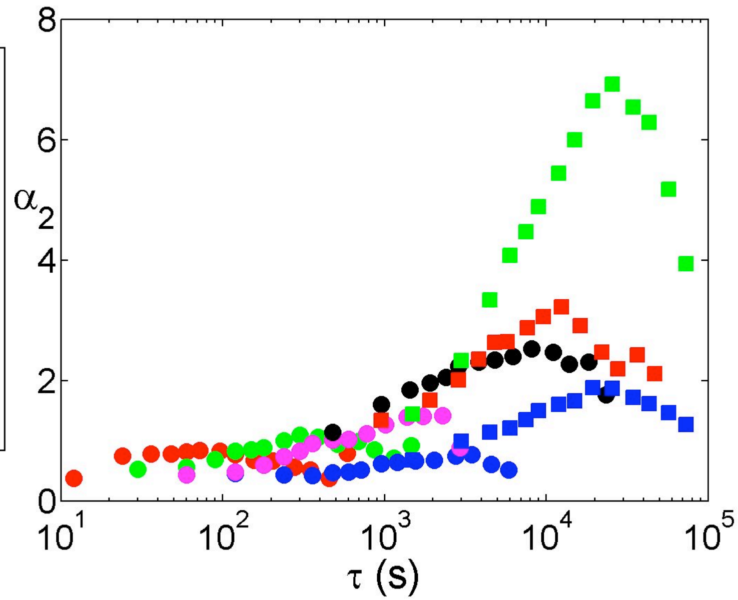
Fast particles → Gaussian behavior at long time

Microscopic dynamics for ***immobile particles***

Mean squared displacement



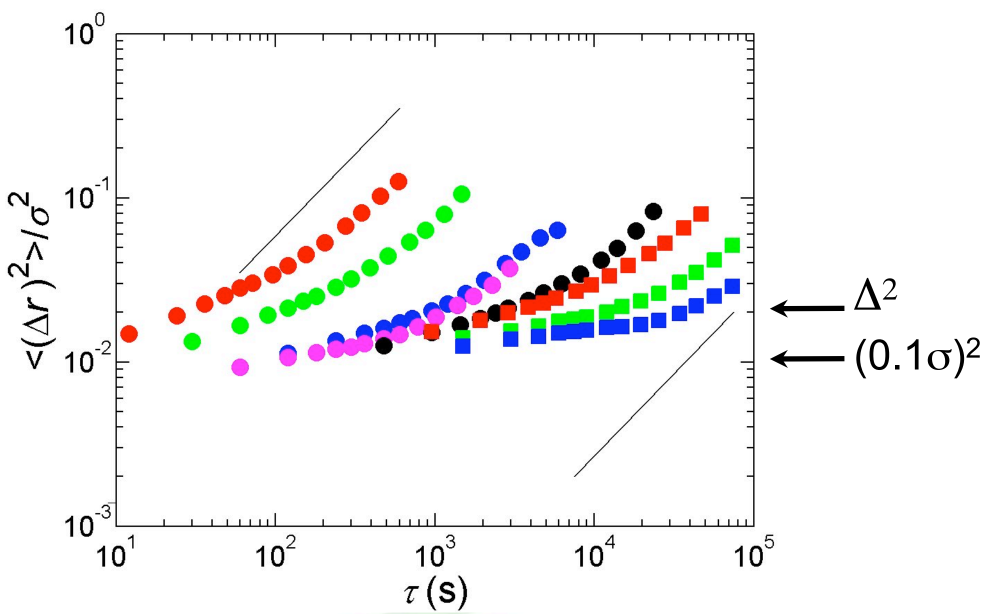
Non-Gaussian Parameter

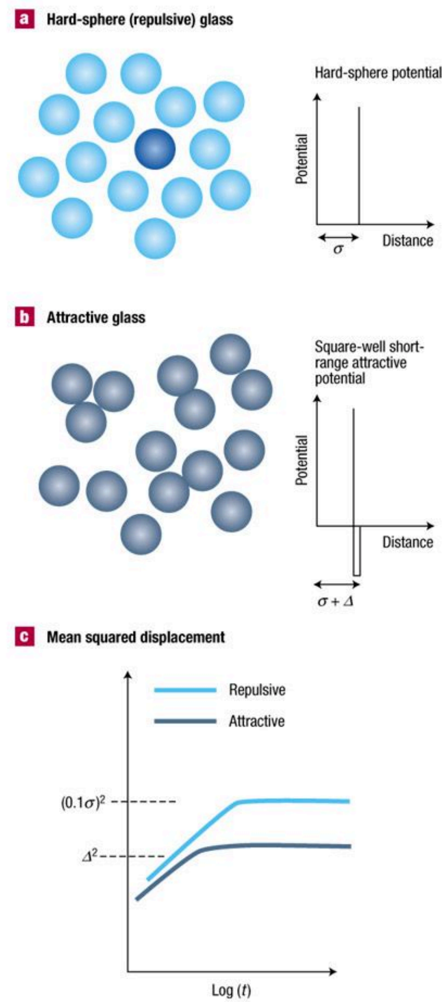


- MSD shows a plateau as transition is approached
- Non-Gaussian parameters exhibit similar behavior to HS supercooled liquids

Microscopic dynamics for ***immobile particles***

Mean squared displacement

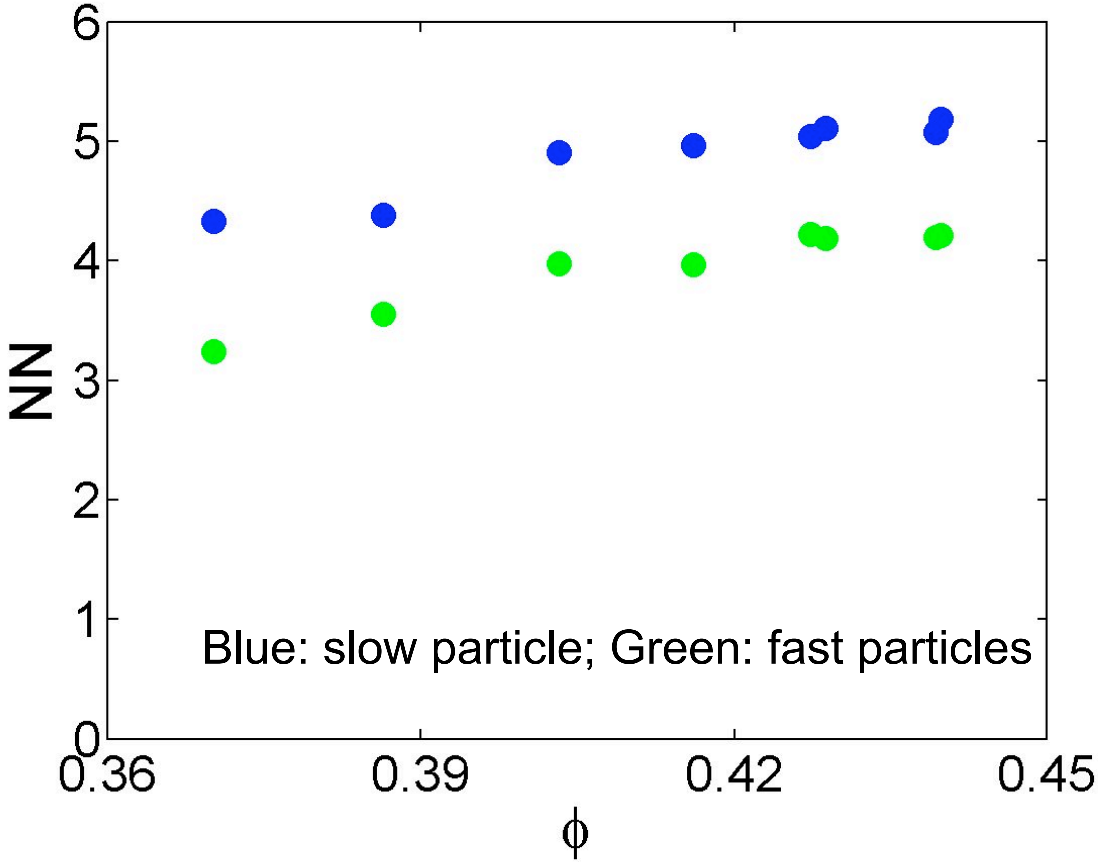




Sciortino, *Nature Materials* (2002)

Can local volume explain these results?

Number of nearest neighbors for fast and slow particles

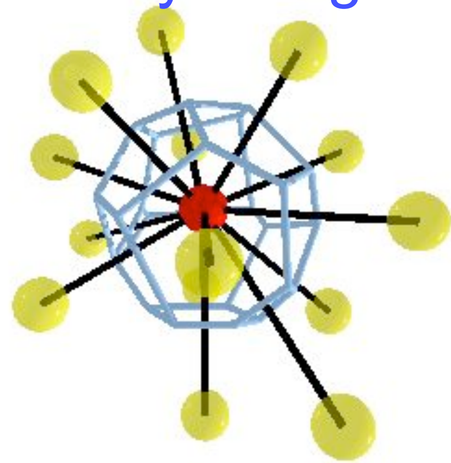


Overall, slow particles have about one more nearest neighbors than fast particles

Local Crowding Parameter

define nearest neighbor particles

Voronoi polyhedra --
Delaunay triangulation

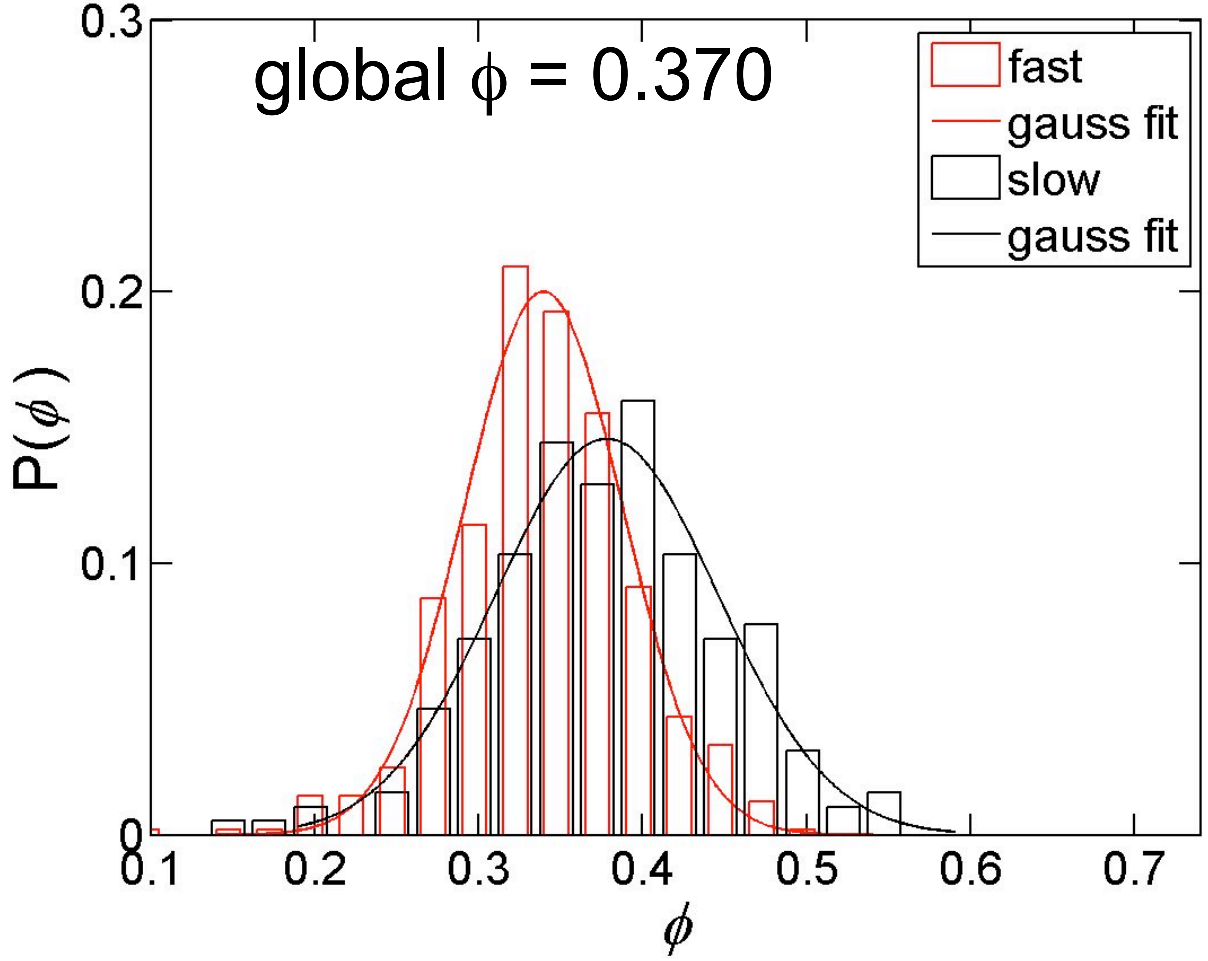


("Wigner-Seitz cell")

extract local density (volume fraction)

Can local volume explain these results?

Distribution of local volume fraction obtained from Voronoi volumes



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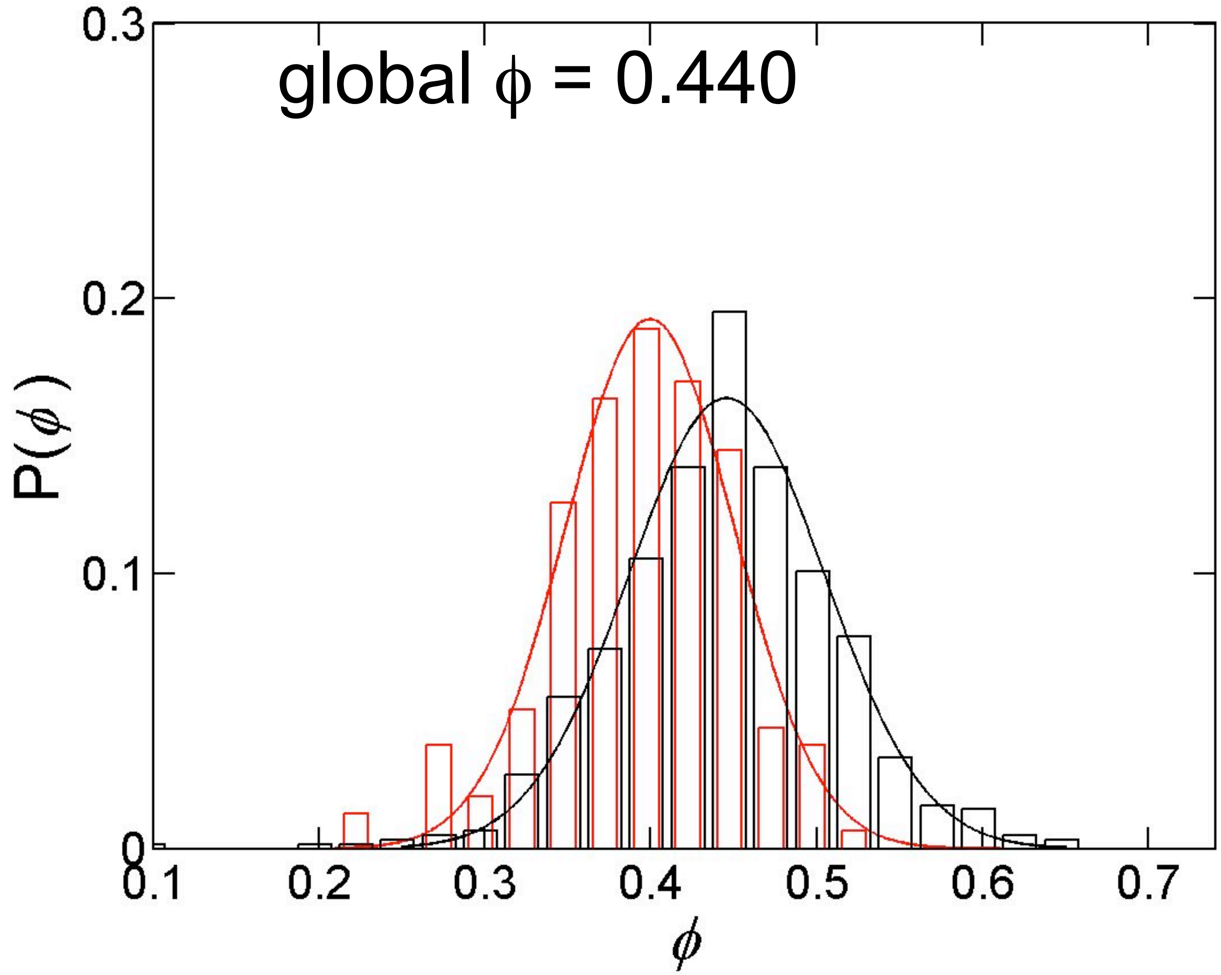


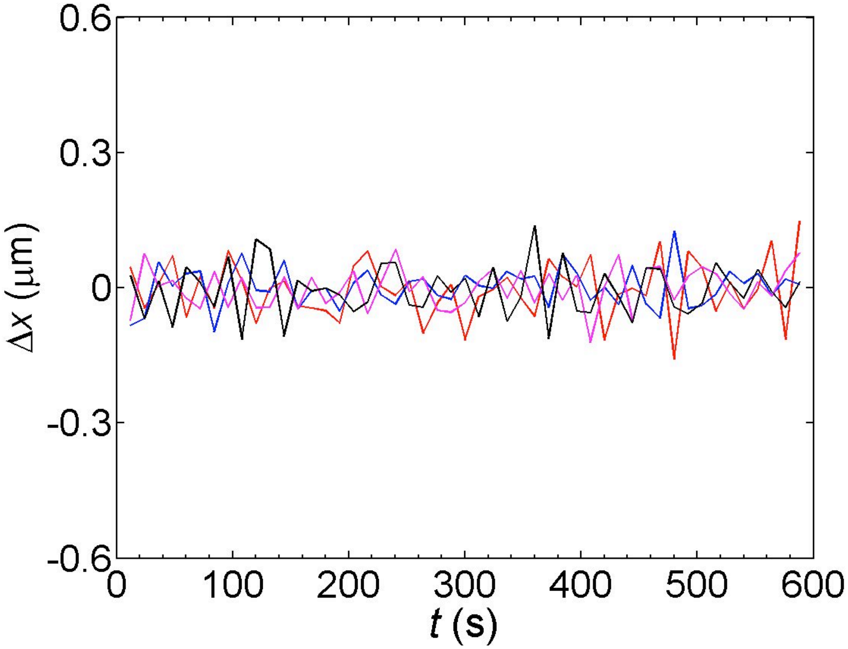
Intermittent dynamics

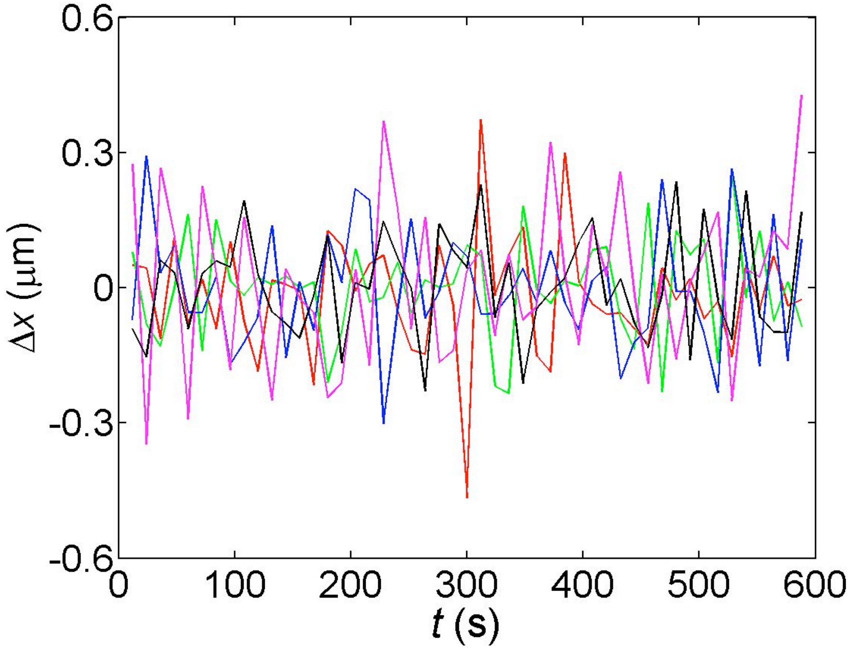
representative trajectories

slow particles

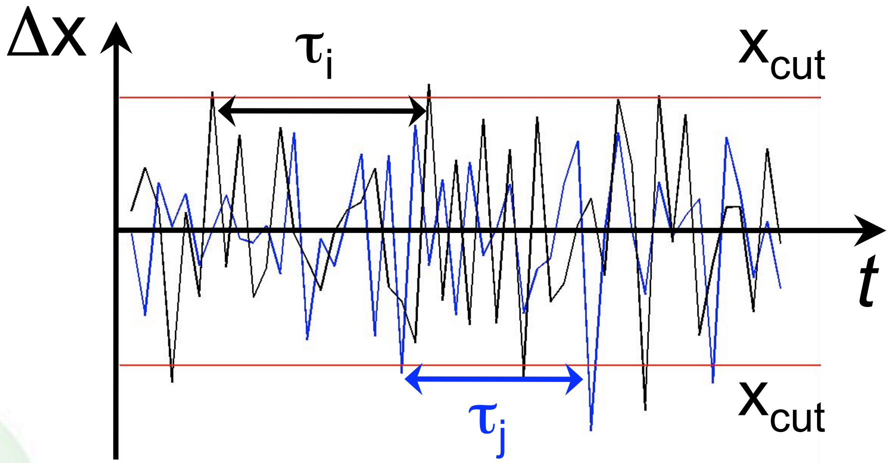
$\phi = 0.370$

fast particles





Average jump time

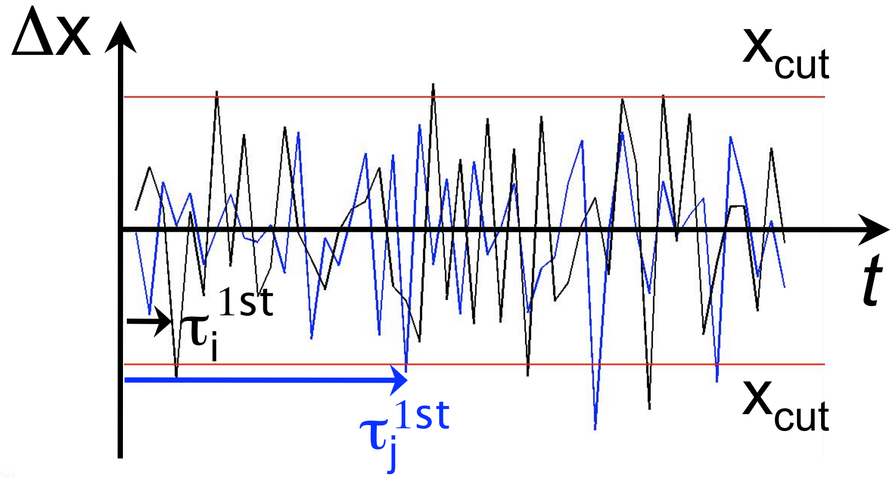


The average jump time is defined as the average time scale between two successive jumps.

$$\tau_{jump} = \frac{1}{N}\sum_{i=1}^{N}\tau_i$$

where N is the total number of jumps over all the particles having at least two jumps and τ_i is the time taken for the *ith* jump.

Average first jump time



Average time at which the first jump occurs for particles having at least two jumps:

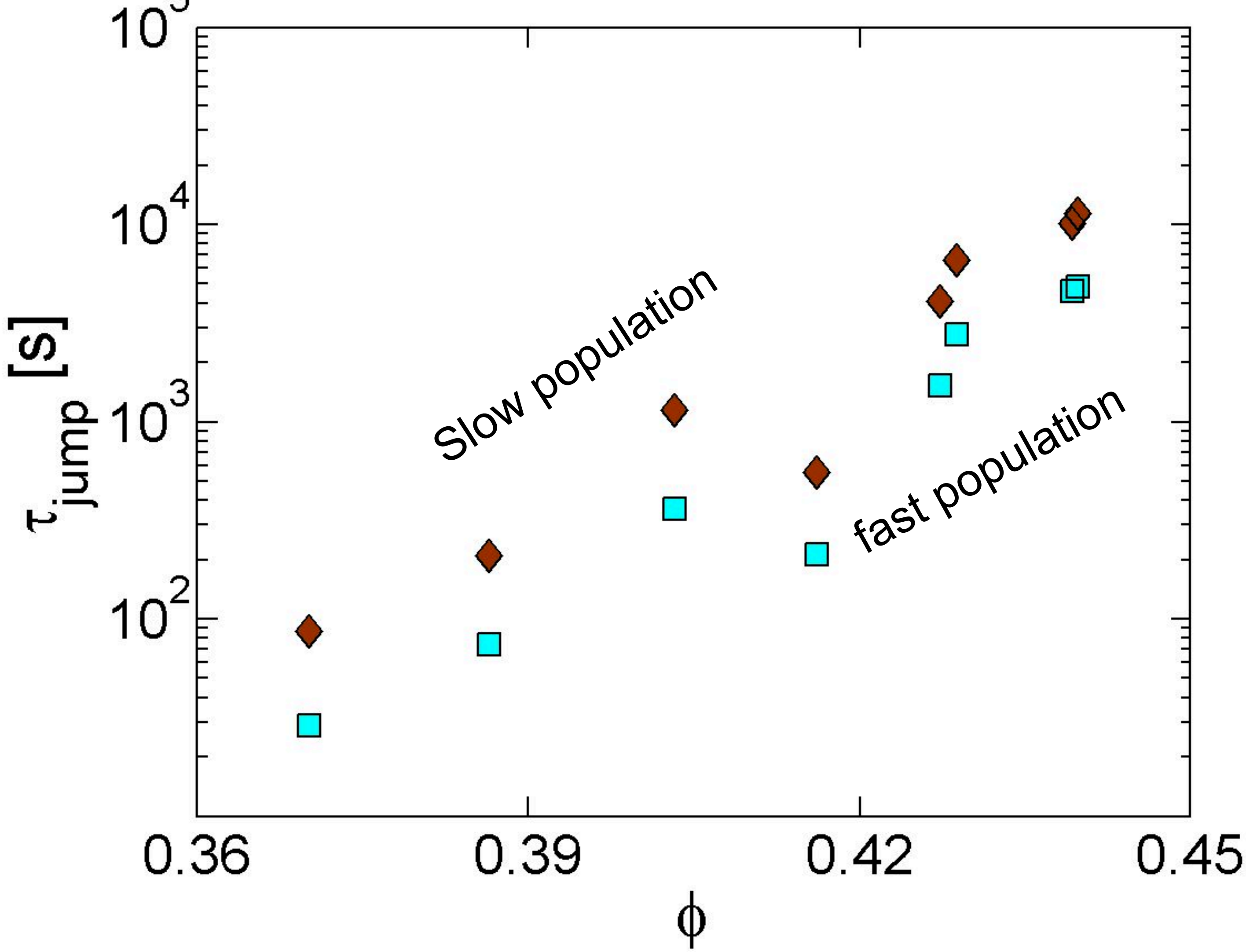
$$\tau_{1st-jump} = \frac{1}{N}\sum_{i=1}^{N}\tau_i^{1st}$$

where N is the total number of particles who have at least two jumps, and τ_i is the time the *ith* particle takes to have a jump.

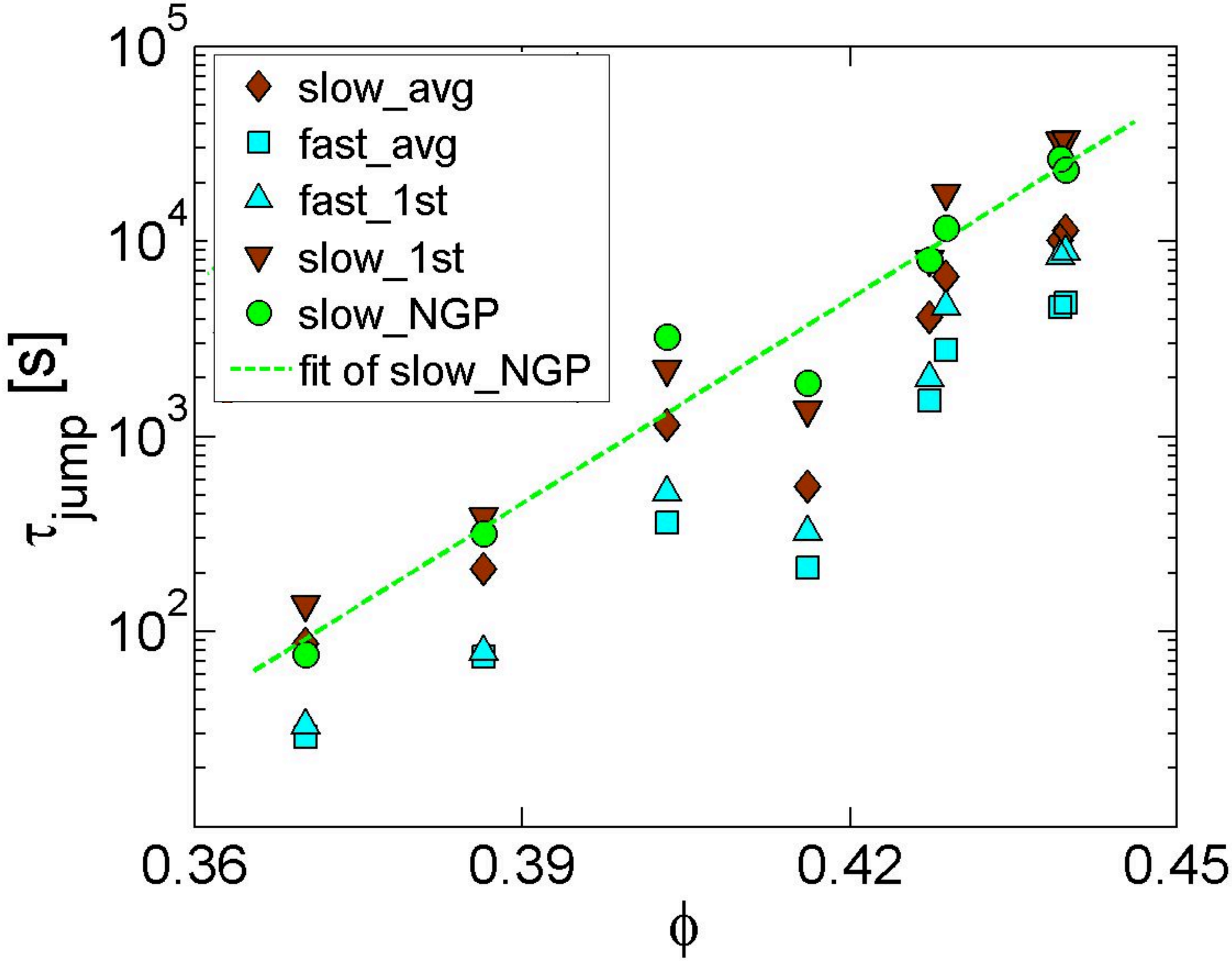
A particle belonging to a mobile region enhances its probability to move further -> prediction in kinetically constrained models

Berthier, et al, (2005); Y. Jung et al, PRE 2006

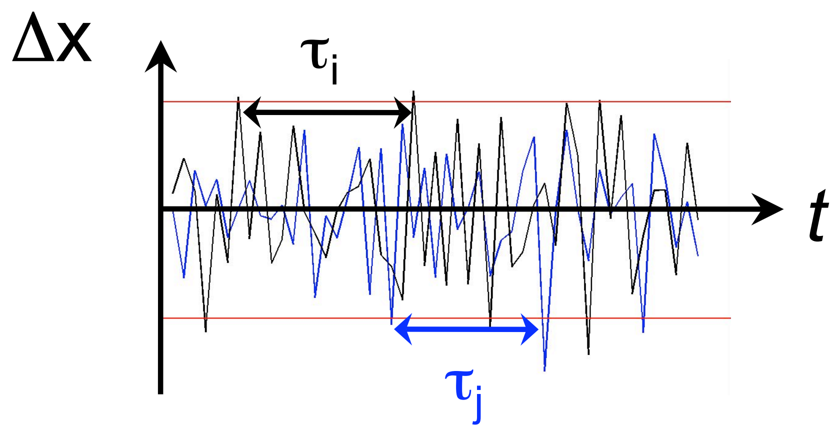
Timescale for jump dynamics



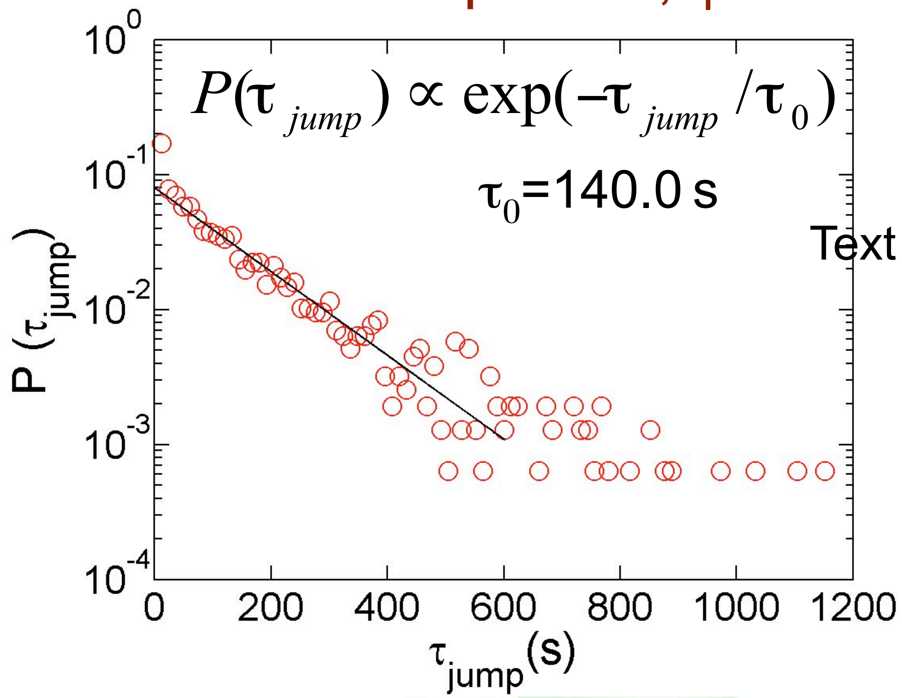
Comparison of dynamical timescales



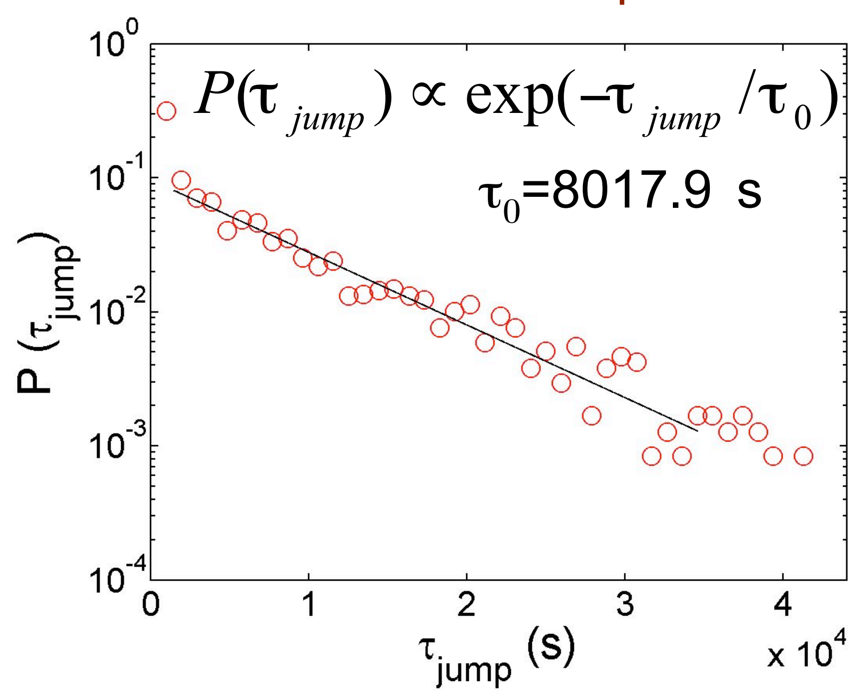
Jump times are distributed exponentially



immobile component, ϕ=0.370

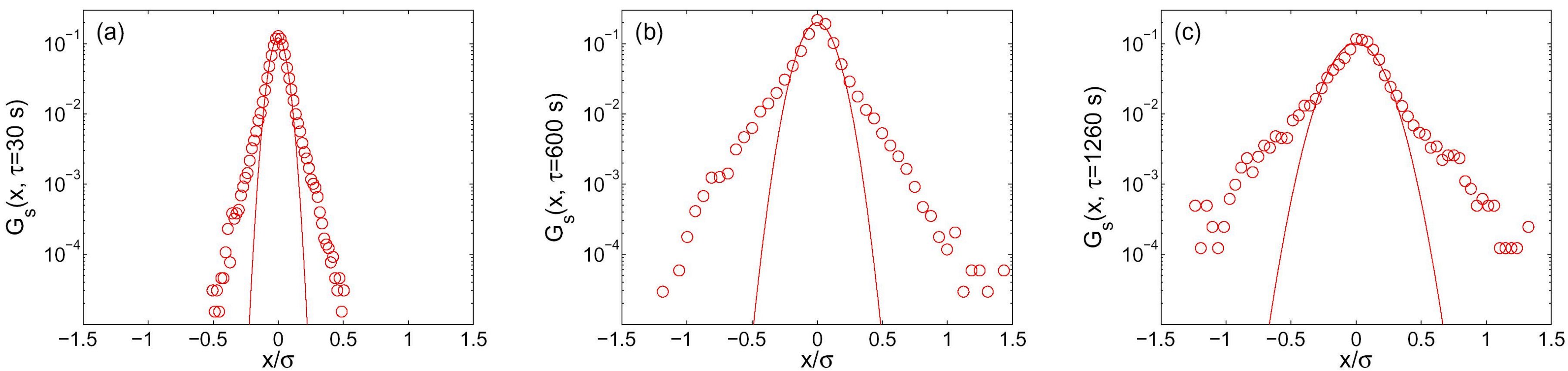


ϕ=0.429



Exponential wings in self van Hove correlation function

volume fraction 0.386, as τ increases

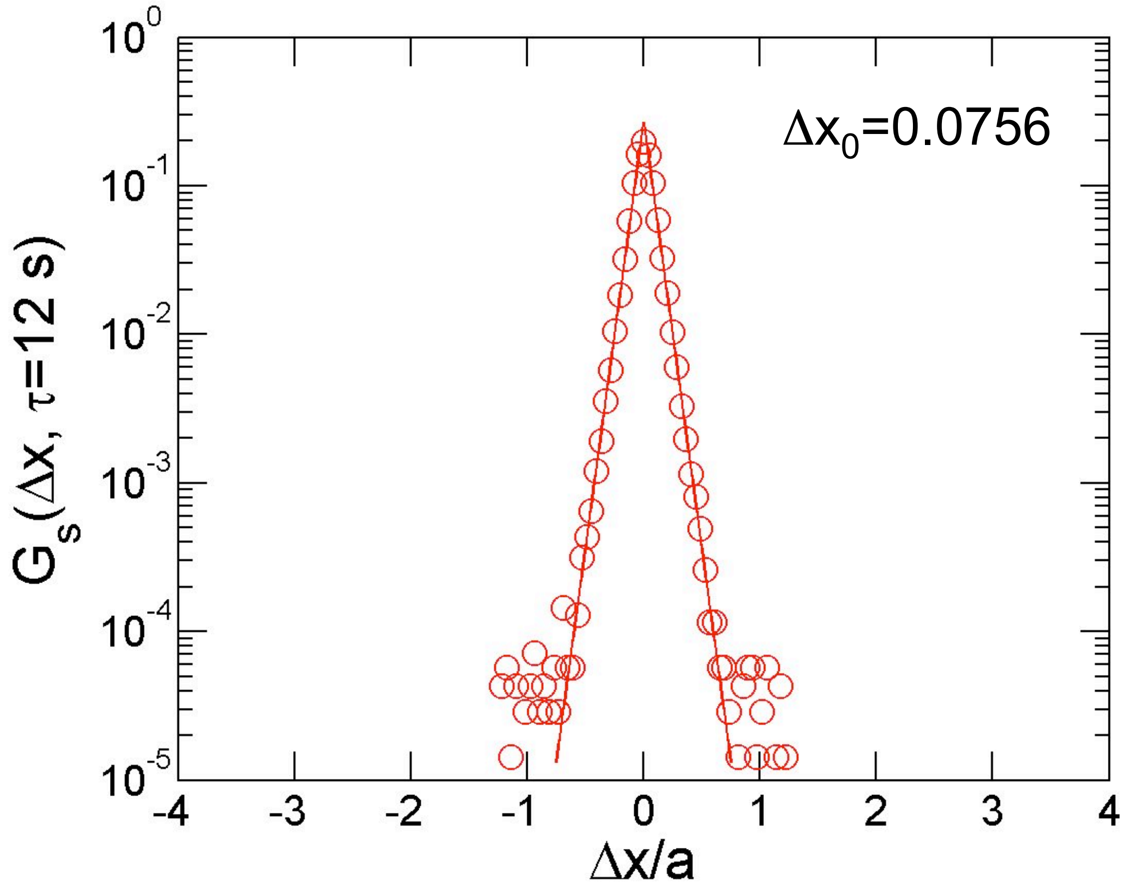


* Occurs in a broad class of materials close to glass and jamming transitions

Exponential wings in self van Hove correlation function

fit to: $P(\Delta x, \tau) \propto \exp(-|\Delta x| / \Delta x_0)$

Δx_0 is the characteristic length scale

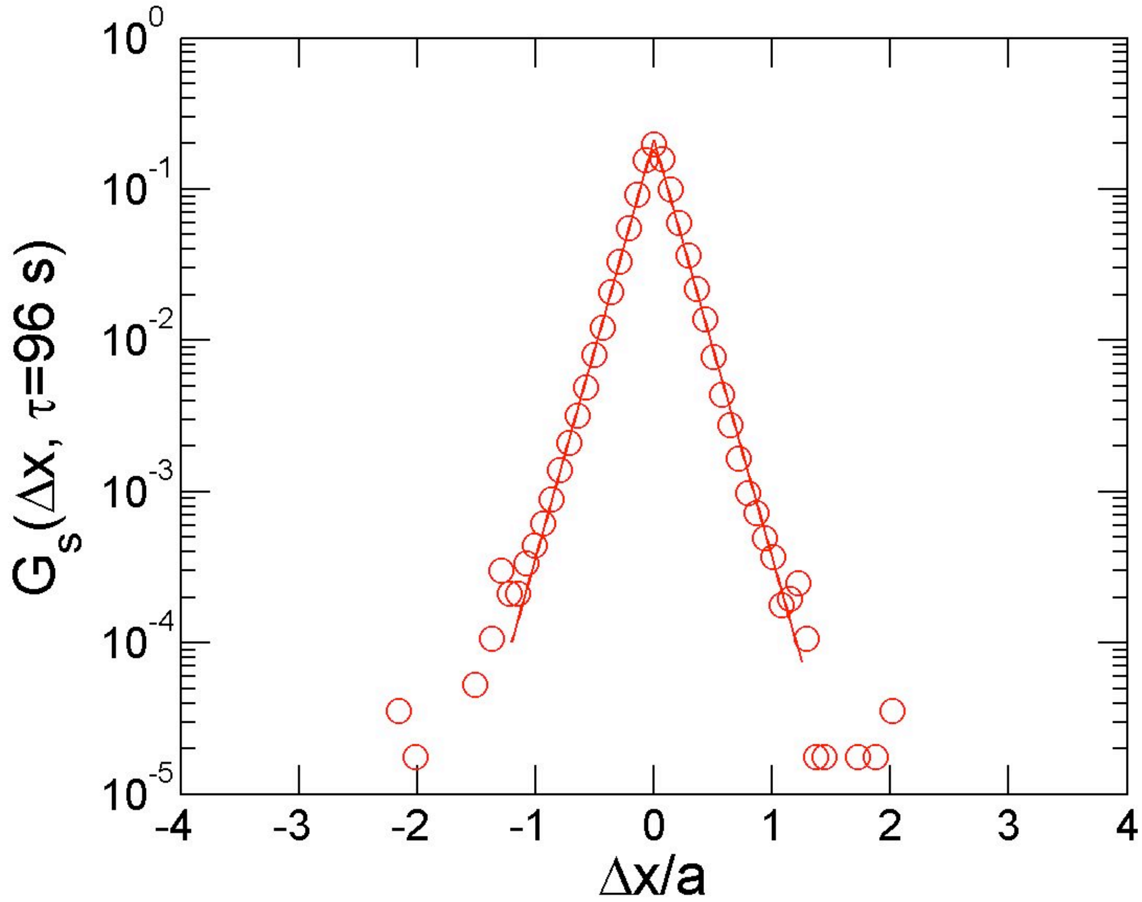


$\phi = 0.370$

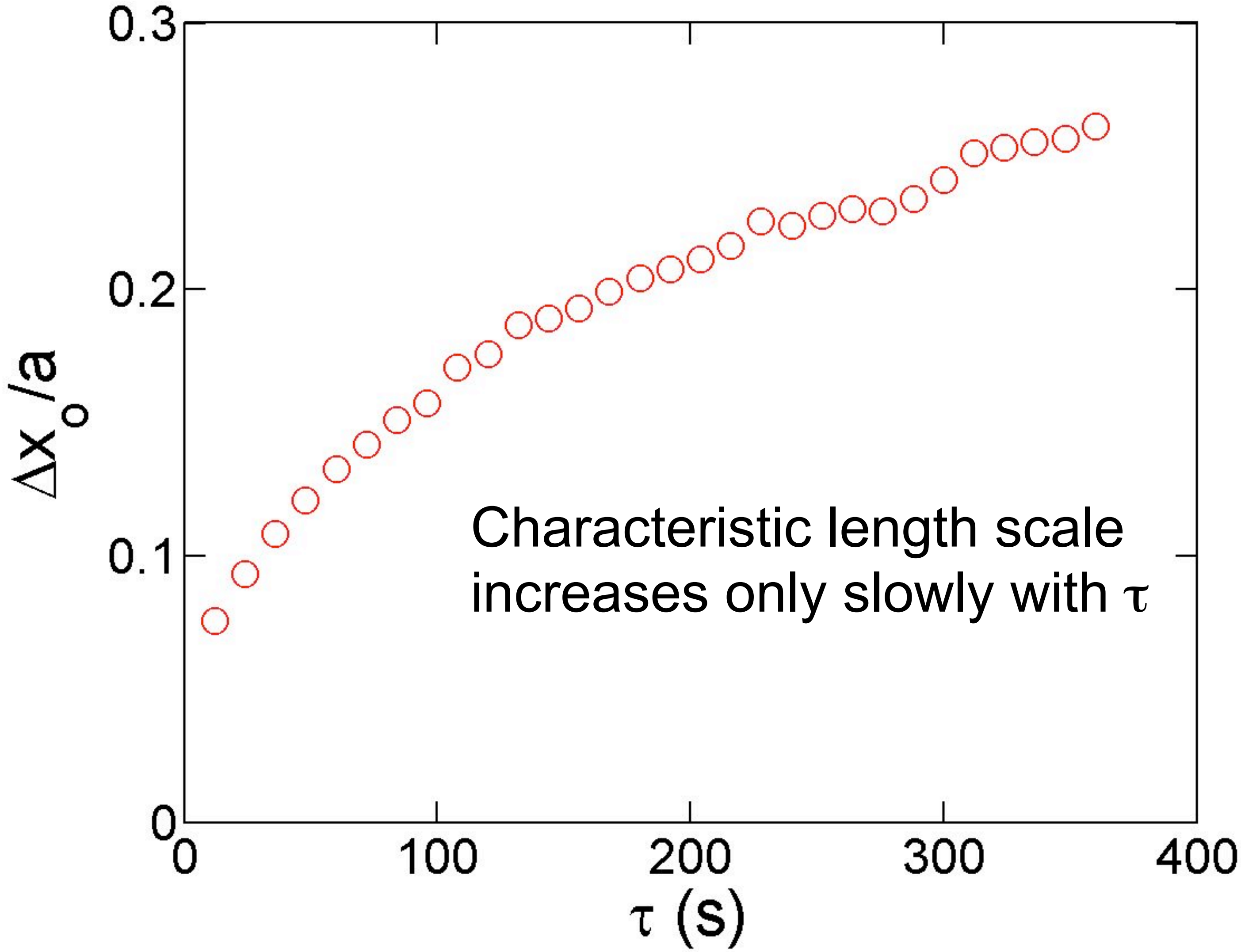
Exponential wings in self van Hove correlation function

ϕ = 0.370

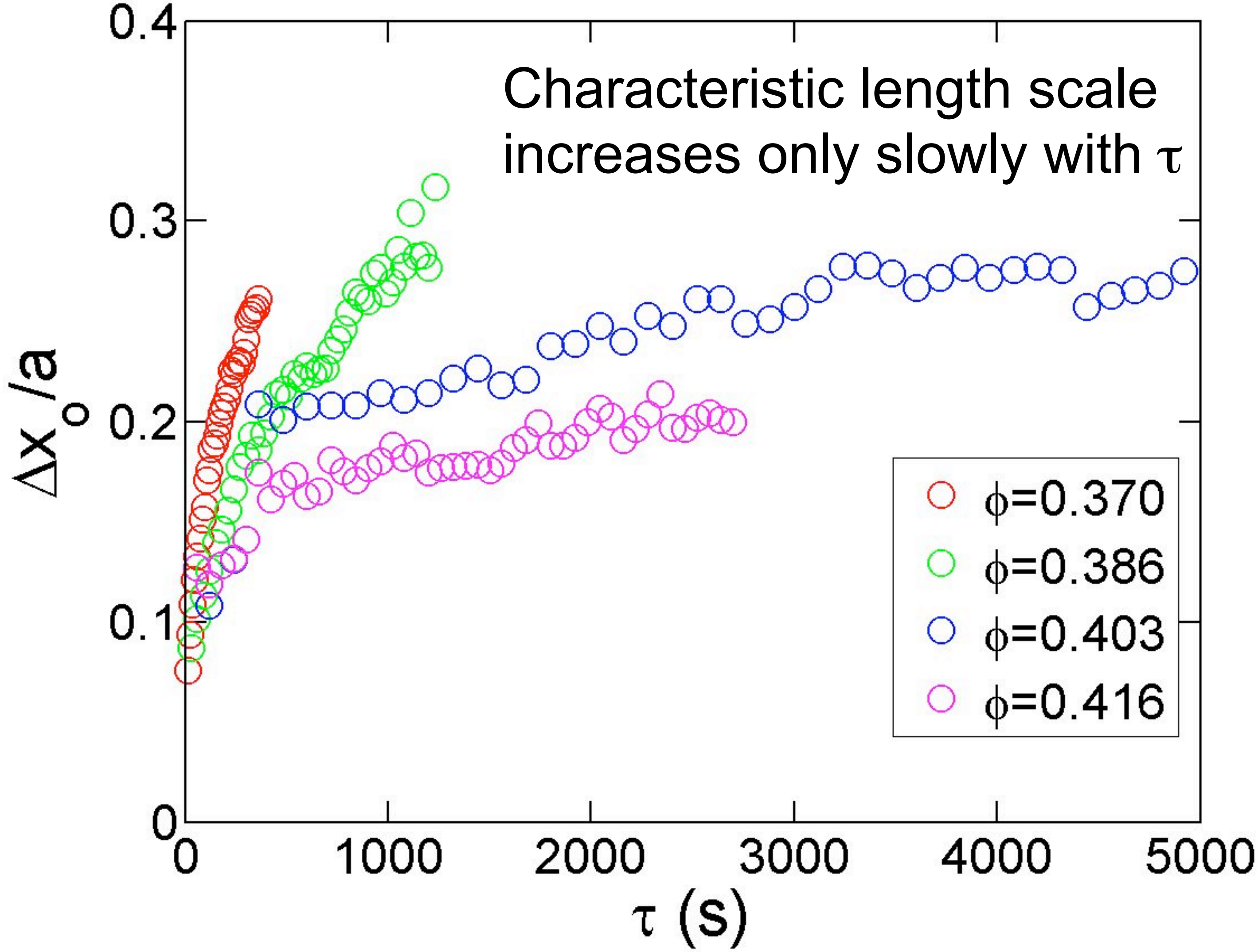
Δx_0=0.1574



Exponential wings in self van Hove correlation function



Exponential wings in self van Hove correlation function



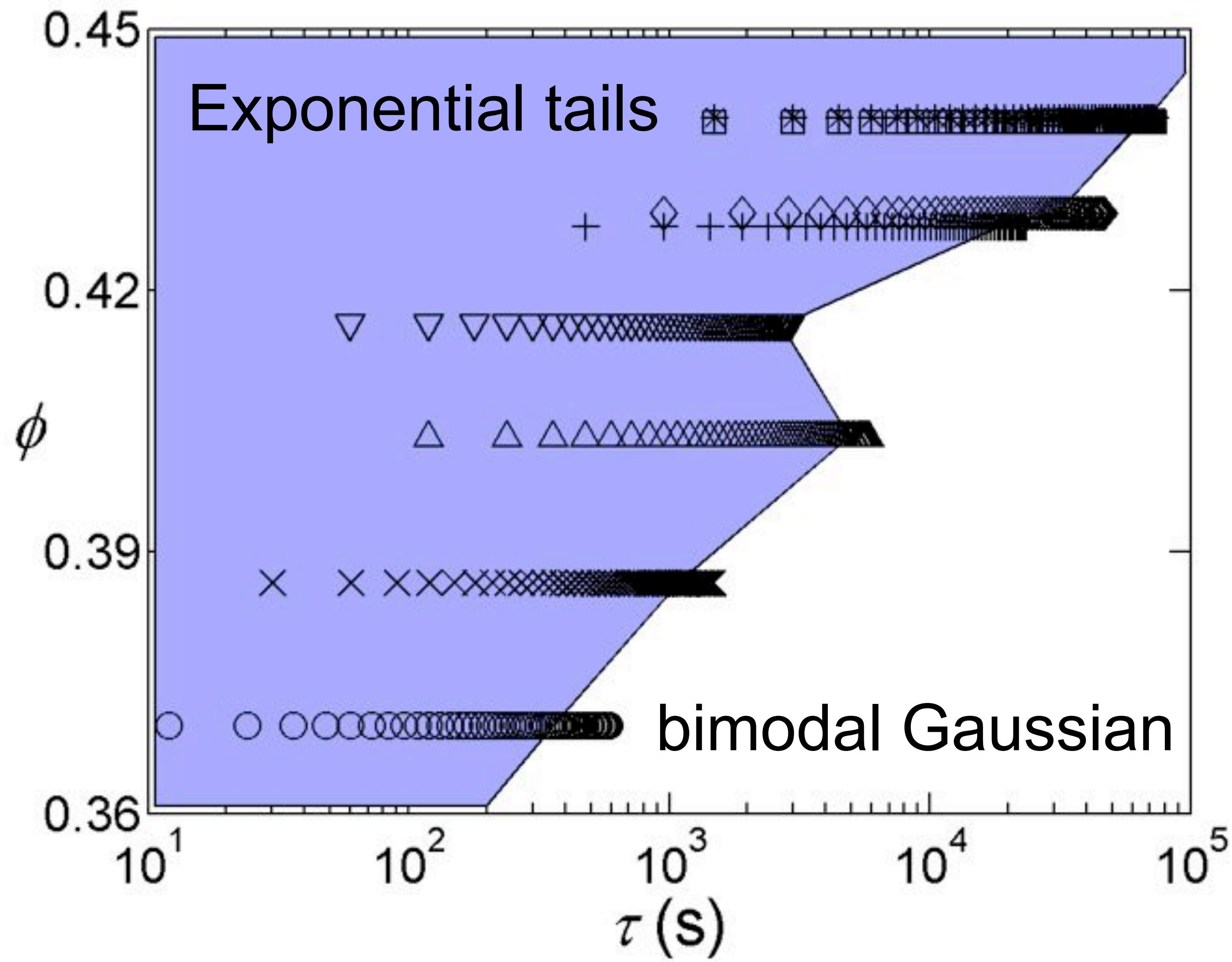
Exponential wings in self van Hove correlation function

* model of Berthier and Kob (Chaudhuri *et al.*, arXiv:0707.2095v1), suggests CTRW can describe the (universal) exponential tails

* have measurements of all the elements in the model:

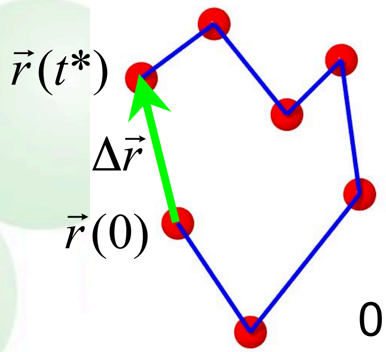
$f_{\mathrm{vib}}(r)$, $f_{\mathrm{jump}}(r)$, τ_{jump}, $\tau_{\mathrm{jump}}^{\mathrm{1st}}$

Range of data over which exponential wings in self van Hove are observed



Are there correlated motions involved in the dynamical heterogeneities?

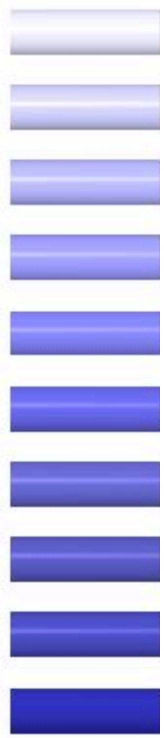
ϕ = 0.370 (Δt=12 s), t^*=84 s

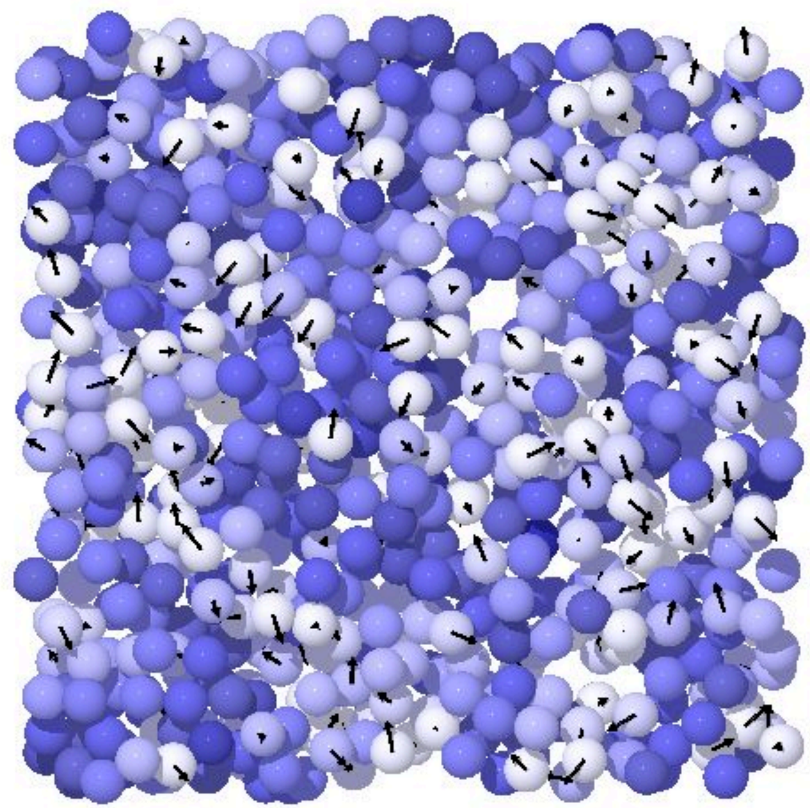


Weeks et al. definition

$$\Delta r = |\vec{r}(t^*) - \vec{r}(0)|$$

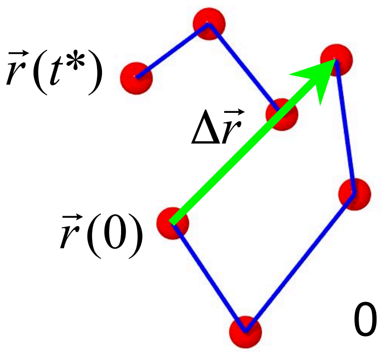
Δr>0.5 μm
0.5μm>Δr>0.4 μm
0.4μm>Δr>0.3 μm
0.3μm>Δr>0.25 μm
0.25μm>Δr>0.2 μm
0.2μm>Δr>0.15 μm
0.15μm>Δr>0.1 μm
0.1μm>Δr>0.07 μm
0.07μm>Δr>0.04 μm
0.04μm>Δr





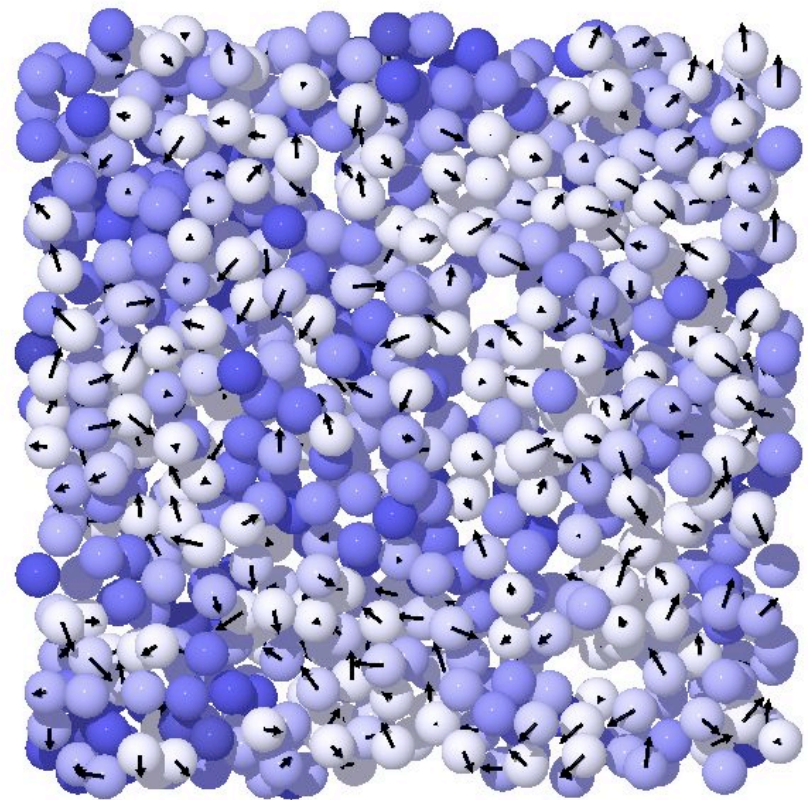
ϕ = 0.370 (Δt=12 s), t^*=84 s

Glotzer et al. definition



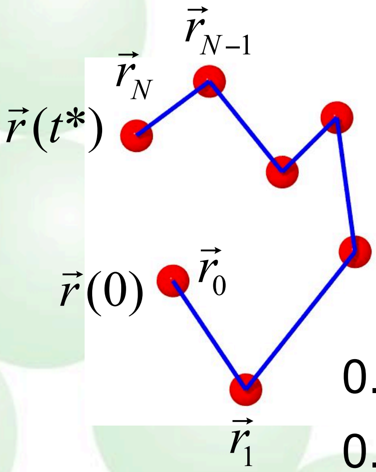
$$\Delta r = \max\{|r(t)-r(0)|\}$$
$$t\in[0,t^*]$$

- Δr>0.5 μm
- 0.5μm>Δr>0.4 μm
- 0.4μm>Δr>0.3 μm
- 0.3μm>Δr>0.25 μm
- 0.25μm>Δr>0.2 μm
- 0.2μm>Δr>0.15 μm
- 0.15μm>Δr>0.1 μm
- 0.1μm>Δr>0.07 μm
- 0.07μm>Δr>0.04 μm
- 0.04μm>Δr



ϕ = 0.370 (Δt=12 s), *t**=84 s

Average step size definition



$$\Delta r = \frac{1}{N}\sum_{i=1}^{N} |\vec{r}_i - \vec{r}_{i-1}|$$

Δr>0.3 μm

0.3μm>Δr>0.25 μm

0.25μm>Δr>0.2 μm

0.2μm>Δr>0.18 μm

0.18μm>Δr>0.16 μm

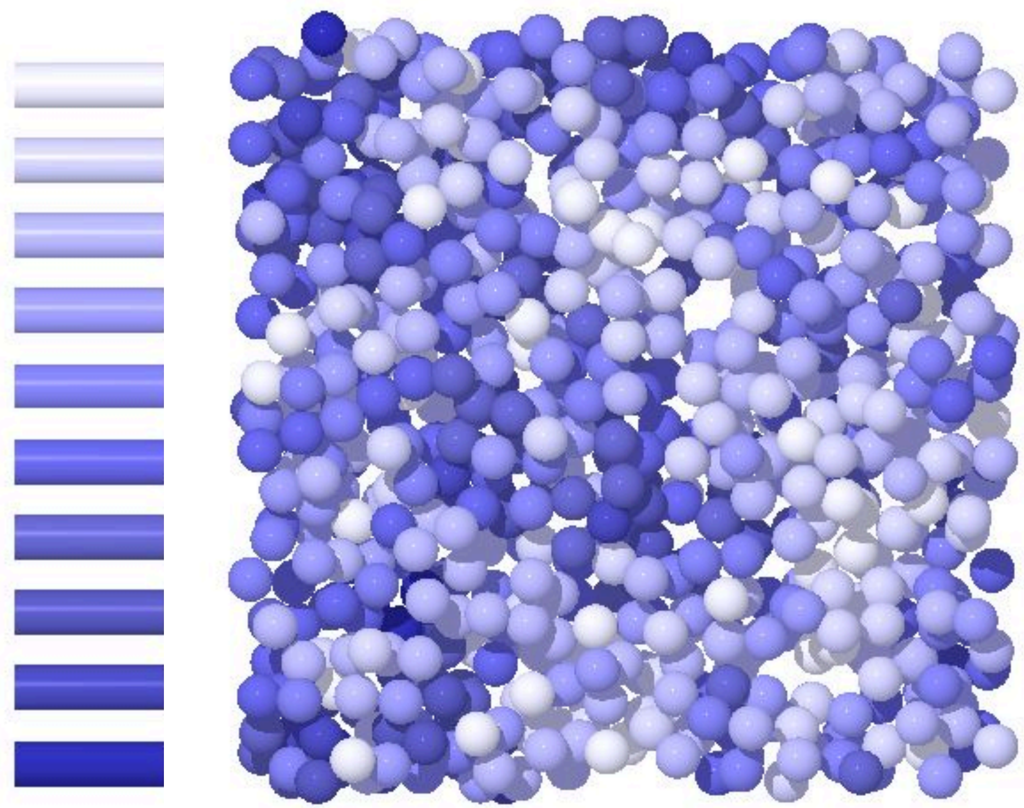
0.16μm>Δr>0.14 μm

0.14μm>Δr>0.12 μm

0.12μm>Δr>0.10 μm

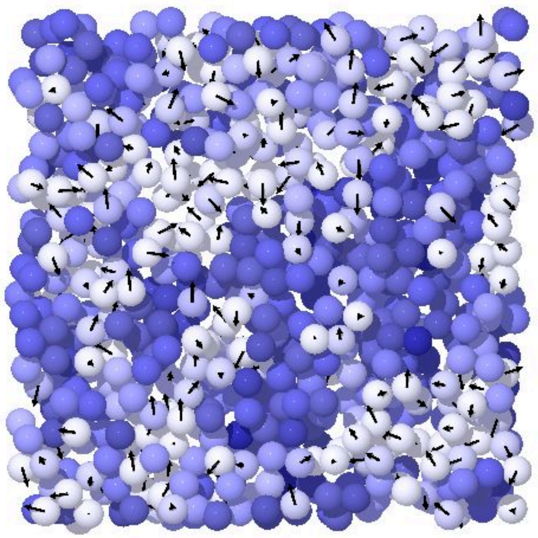
0.10μm>Δr>0.08 μm

0.08μm>Δr

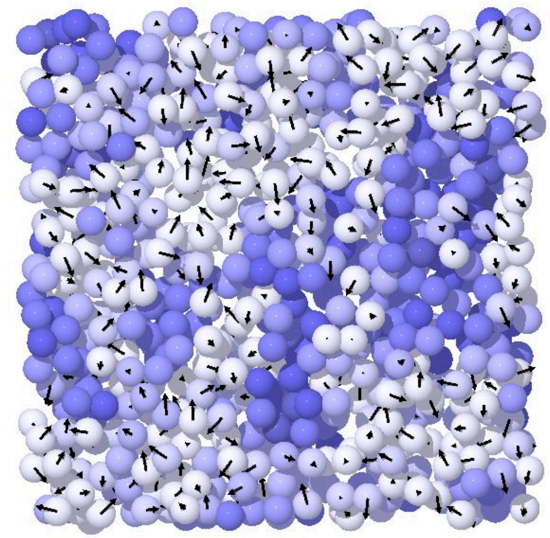


ϕ = 0.386 (Δt=30 s), t^*=330 s

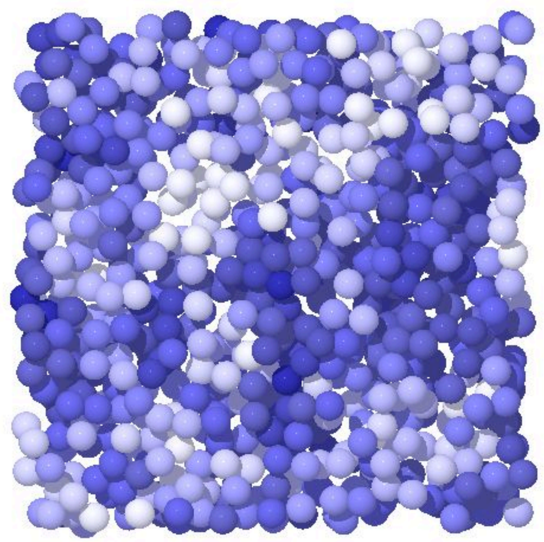
Weeks et al. definition



Glotzer et al. definition

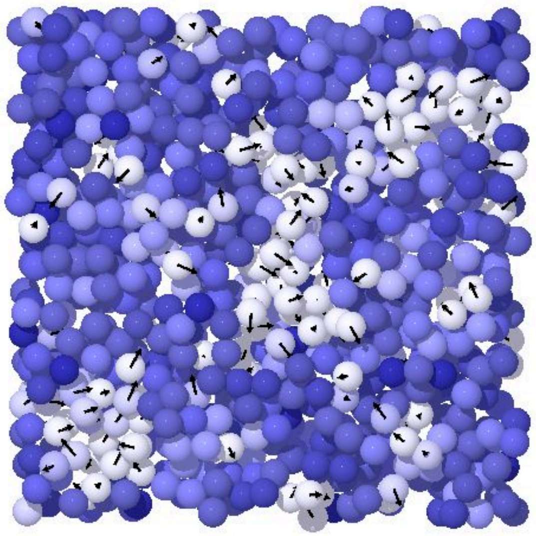


Average step size definition

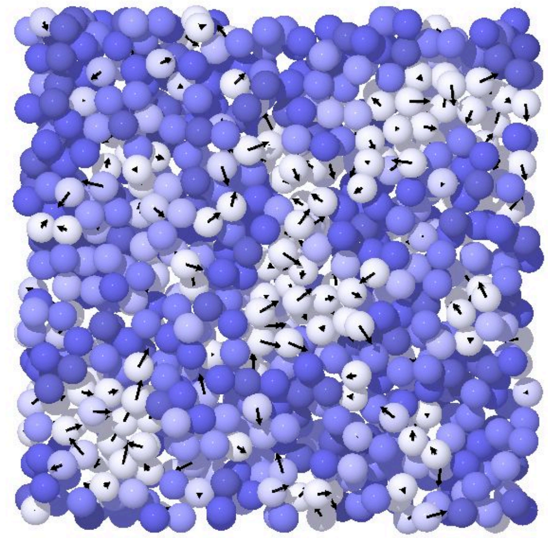


ϕ = 0.429 (Δt=960s), t^*=12480s

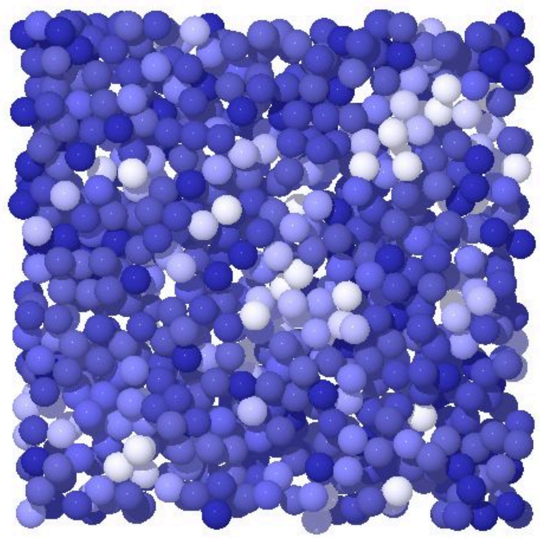
Weeks et al. definition



Glotzer et al. definition

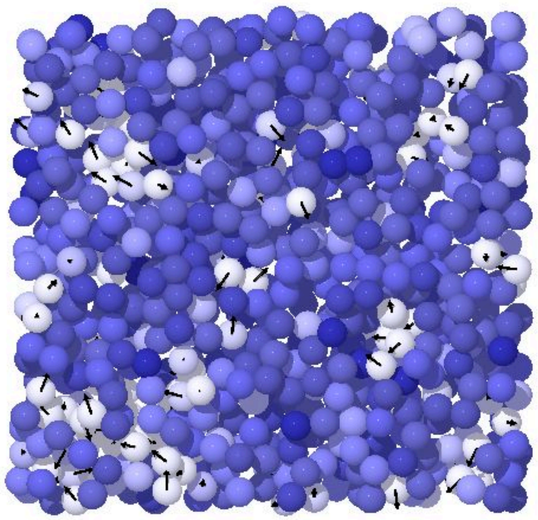


Average step size definition

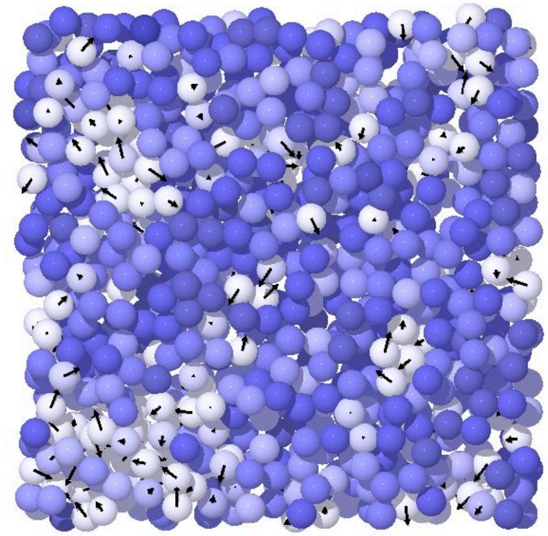


ϕ = 0.439 (Δt=1500 s), t^*=25500 s

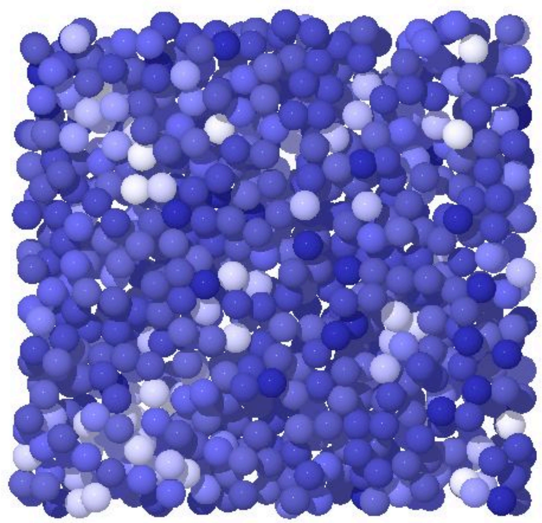
Weeks et al. definition



Glotzer et al. definition



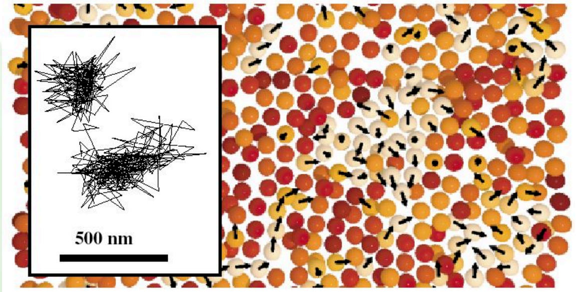
Average step size definition



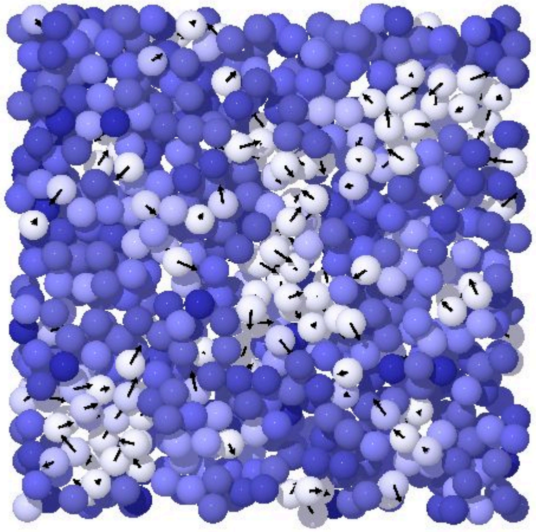
Conclusions

- Dynamics in attractive colloids close to the jamming transition shows heterogeneity
- Immobile population appears grows at the expense of the mobile population as system approaches the jamming transition.
- Immobile population shares features with the approach to the glass transition via the hard sphere route. Dynamics is localized vibrations. The mechanism for localization ~ combination of crowding and stickiness.
- The mobile population shows increasingly sluggish dynamics, with some fraction contributing to the broad tails in the van Hove function, emerging as Gaussian at long lag times.
- No strong correlation of dynamical and structural heterogeneities.

What do we NOT see



$\phi = 0.429$



- ***Different*** microscopic picture of the dynamical heterogeneities compared to hard sphere supercooled fluids
- Do not see large changes in local volume accompanying the huge dynamical effects on approach to jamming transition

Unresolved issues

- Is there a growing length scale in the approach to the transition here? --> study four-point correlation functions
- Do attractive and hard sphere glasses have the same behaviour?