Direct observation of dynamical heterogeneities near the attraction driven glass

Maria Kilfoil    McGill University

Co-worker: Yongxiang Gao, PhD student

http://www.physics.mcgill.ca/~kilfoil
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
  - Glotzer *et al.* *PRE* (1999); Weeks *et al.* *PRL* (2002);

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

Phase diagram

$U/kT$

Potential energy

Distance from centre

Fluid

Solid

Glass
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

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New type of colloidal glass: "Attractive Glass"

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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:

System: PMMA ($\sigma = 1.326 \, \mu m$) and $\Delta \sim 0.14 \, \sigma$ in refractive index-matching and buoyancy-tunable suspending fluids Decalin/Tetralin/CXB

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

Side view:
Confocal microscopy 3D real-space imaging
typical volume: (22.6 X 22.6 X 10)$\mu m^3$

Phase diagram of attractive colloidal systems

$U_{\text{dep}}$ from top to bottom is:
- $4.60 \, k_B T$
- $3.77 \, k_B T$
- $2.86 \, k_B T$
- $1.21 \, k_B T$

$\xi = 0.14$

1. $\xi = 0.08$ (MCT) (Poon et al.)
2. $\xi = 0.24$ (exp) (Poon et al.)

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

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

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

\[ G_d(r, \tau) = \frac{1}{N} \left\langle \sum_i \sum_{j \neq i} \delta \left[ r - |r_i(0) - r_j(\tau)| \right] \right\rangle \]
Distinct part of the van Hove space time correlation function

Geometry for calculating dvH

Simulation of a colloidal gel
Cates et al.
PRE 2003

Age: 15.7 h
Early stage, fluid like

Age: 52.0 h
Gel structure formed

Y. Gao and MLK, PRL 2007
Self part of the van Hove space time correlation function...

volume fraction 0.386, as $\tau$ increases

Single gaussian fit

![Graphs](image)
**But.. Two-Gaussian behaviour emerges in the Self part of van Hove Correlation Function**

*volume fraction 0.386, as \( \tau \) increases*

- Single gaussian fit
- Two gaussian fit (green line: fast branch; blue line: slow branch)
Populations of fast and slow particles

- Slow particles: \( n_{\text{slow}} = 1062 \)
- Fast particles: \( n_{\text{fast}} = 416 \)

\( \phi = 0.429 \)

5 \( \mu \)m thick slab
Distinct part of Van Hove correlation function for fast and slow particles

\[ \Delta r^2 (\mu m^2) \]

\[ \tau (s) \]

\( \phi = 0.429 \)

Y. Gao and MLK, PRL 2007
Microscopic dynamics for mobile particles in gel/attraction-driven glass regime

Mean squared displacement

Fast particles $\rightarrow$ Gaussian behavior at long time

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

$\phi = \phi_G = 0.442$
Microscopic dynamics for *immobile particles*

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

\[ \text{Mean squared displacement} \]

\[ \langle (\Delta r)^2 \rangle / \sigma^2 \]

\[ \phi = \]

\[ \phi_G = 0.442 \]

\[ \alpha \]

\[ \tau (s) \]

\[ \times 10^1, 10^2, 10^3, 10^4, 10^5 \]

Microscopic dynamics for **immobile particles**

Mean squared displacement

![Graph showing mean squared displacement](image)

Can local volume explain these results?

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

Blue: slow particle; Green: 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.

Global $\phi = 0.370$
Can local volume explain these results?

Distribution of local volume fraction obtained from Voronoi volumes

\[ \text{global } \phi = 0.440 \]
Intermittent dynamics
representative trajectories

slow particles $\phi = 0.370$

fast particles

\[
\begin{align*}
\Delta x \text{ (\textmu m)} & \quad 0 & \quad 0.6 \\
0 & 100 & 200 & 300 & 400 & 500 & 600 & t \text{ (s)}
\end{align*}
\]

\[
\begin{align*}
\Delta x \text{ (\textmu m)} & \quad -0.6 & \quad 0.6 \\
0 & 100 & 200 & 300 & 400 & 500 & 600 & t \text{ (s)}
\end{align*}
\]
The average jump time is defined as the average time scale between two successive jumps.

\[ \tau_{\text{jump}} = \frac{1}{N} \sum_{i=1}^{N} \tau_i \]

where \( N \) is the total number of jumps over all the particles having at least two jumps and \( \tau_i \) is the time taken for the \( i \)th jump.
Average first jump time

\[ \Delta x \]

\[ x_{\text{cut}} \]

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

\[ \tau_{1st\text{-}jump} = \frac{1}{N} \sum_{i=1}^{N} \tau_{i}^{1st} \]

where N is the total number of particles who have at least two jumps, and \( \tau_{i} \) 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

\[ \tau_{\text{jump}} \] [s]

\[ \phi \]

- slow_avg
- fast_avg
- fast_1st
- slow_1st
- slow_NGP
- fit of slow_NGP
Jump times are distributed exponentially

Immobile component, $\phi=0.370$

$$P(\tau_{\text{jump}}) \propto \exp\left(-\frac{\tau_{\text{jump}}}{\tau_0}\right)$$

$\tau_0=140.0 \text{ s}$

$\phi=0.429$

$$P(\tau_{\text{jump}}) \propto \exp\left(-\frac{\tau_{\text{jump}}}{\tau_0}\right)$$

$\tau_0=8017.9 \text{ s}$
Exponential wings in self van Hove correlation function

volume fraction 0.386, as $\tau$ increases

* Occurs in a broad class of materials close to glass and jamming transitions
Exponential wings in self van Hove correlation function

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

$\Delta x_0$ is the characteristic length scale

$\Delta x_0 = 0.0756$

$\phi = 0.370$
Exponential wings in self van Hove correlation function

\[ \Delta x_0 = 0.1574 \quad \phi = 0.370 \]
Exponential wings in self van Hove correlation function

Characteristic length scale increases only slowly with $\tau$
Exponential wings in self van Hove correlation function

Characteristic length scale increases only slowly with $\tau$
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:
  \[ f_{\text{vib}}(r), \ f_{\text{jump}}(r), \ \tau_{\text{jump}}, \ \tau_{\text{jump}}^{1st} \]
Range of data over which exponential wings in self van Hove are observed

Exponential tails

bimodal Gaussian
Are there correlated motions involved in the dynamical heterogeneities?

\[ \phi = 0.370 (\Delta t=12 \text{ s}), \ t^*=84 \text{ s} \]

**Weeks et al. definition**

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

- \( \Delta r > 0.5 \mu m \)
- \( 0.5\mu m > \Delta r > 0.4 \mu m \)
- \( 0.4\mu m > \Delta r > 0.3 \mu m \)
- \( 0.3\mu m > \Delta r > 0.25 \mu m \)
- \( 0.25\mu m > \Delta r > 0.2 \mu m \)
- \( 0.2\mu m > \Delta r > 0.15 \mu m \)
- \( 0.15\mu m > \Delta r > 0.1 \mu m \)
- \( 0.1\mu m > \Delta r > 0.07 \mu m \)
- \( 0.07\mu m > \Delta r > 0.04 \mu m \)
- \( 0.04\mu m > \Delta r \)
\[ \phi = 0.370 \ (\Delta t=12 \text{ s}), \ t^* = 84 \text{ s} \]

Glotzer et al. definition

\[ \Delta r = \max \{|r(t) - r(0)|\} \]
\[ t \in [0, t^*] \]
\[ \Delta r > 0.5 \ \mu \text{m} \]
\[ 0.5 \mu \text{m} > \Delta r > 0.4 \ \mu \text{m} \]
\[ 0.4 \mu \text{m} > \Delta r > 0.3 \ \mu \text{m} \]
\[ 0.3 \mu \text{m} > \Delta r > 0.25 \ \mu \text{m} \]
\[ 0.25 \mu \text{m} > \Delta r > 0.2 \ \mu \text{m} \]
\[ 0.2 \mu \text{m} > \Delta r > 0.15 \ \mu \text{m} \]
\[ 0.15 \mu \text{m} > \Delta r > 0.1 \ \mu \text{m} \]
\[ 0.1 \mu \text{m} > \Delta r > 0.07 \ \mu \text{m} \]
\[ 0.07 \mu \text{m} > \Delta r > 0.04 \ \mu \text{m} \]
\[ 0.04 \mu \text{m} > \Delta r \]
Average step size definition

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

- $\Delta r > 0.3 \, \mu m$
- $0.3 \, \mu m > \Delta r > 0.25 \, \mu m$
- $0.25 \, \mu m > \Delta r > 0.2 \, \mu m$
- $0.2 \, \mu m > \Delta r > 0.18 \, \mu m$
- $0.18 \, \mu m > \Delta r > 0.16 \, \mu m$
- $0.16 \, \mu m > \Delta r > 0.14 \, \mu m$
- $0.14 \, \mu m > \Delta r > 0.12 \, \mu m$
- $0.12 \, \mu m > \Delta r > 0.10 \, \mu m$
- $0.10 \, \mu m > \Delta r > 0.08 \, \mu m$
- $0.08 \, \mu m > \Delta r$
\[ \phi = 0.386 (\Delta t=30 \text{ s}), \ t^*=330 \text{ s} \]

- Weeks et al. definition
- Glotzer et al. definition

Average step size definition
\[ \phi = 0.429 (\Delta t=960s), t^* = 12480s \]

**Weeks et al. definition**

**Glotzer et al. definition**

**Average step size definition**
\[ \phi = 0.439 \ (\Delta t=1500 \text{ s}), \ t^*=25500 \text{ s} \]

**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

- **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

ϕ = 0.429
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?