Cage trapping:

\[ \langle x^2 \rangle \ \mu m^2 \]

lag time \( \Delta t \) (s)

- Short times: particles stuck in “cages”
- Long times: cages rearrange

\( \phi = 0.56, 100 \text{ min} \) (supercooled fluid)

200 nm
Volume fraction $\phi=0.3$ "supercooled fluid"

$\langle x^2 \rangle \mu m^2$

3D

2D

lag time $\Delta t$ (s)

$\Delta t = 1000$ s

$P(\Delta x)$

$\Delta x (\mu m)$
Nongaussian Parameter $\alpha_2$

$$\alpha_2 = \frac{\left\langle x^4 \right\rangle}{3\left\langle x^2 \right\rangle^2} - 1$$

Rahman, 1964

Gaussian: $\alpha_2 = 0$

Exponential: $\alpha_2 = 1$

$\alpha_2 = 1.2$
Time scale:
\[ \Delta t^* \]
when nongaussian parameter \( \alpha_2 \) largest

Length scale:
\[ \Delta r^* \]
on average, 5% of particles have
\[ \Delta r (\Delta t^*) > \Delta r^* \]

\approx cage rearrangements

\[ P(\Delta x) \]
\( \Delta x (\mu m) \)

95%
top 5% = tails of \( \Delta x \) distribution

(\( \phi = 0.53 \), supercooled fluid)
Voronoï polyhedra -- Delaunay triangulation

("Wigner-Seitz cell")

polyhedron face: set of all points equidistant from two particles

defines nearest neighbor particles
Supercooled fluid
\( \phi = 0.56 \)

Very large fluctuations

- Sample is not ergodic

\( \Delta t^* \)
Glass Transition
supercooled fluid $\phi=0.56$

glass $\phi=0.61$

top 5%
Particles move towards neighbors

$P(d)$

Particles move in the same direction as neighbors

$P(\theta)$

$\Delta r^*$

$d$

Angle $\theta$

$(P(\theta)$ corrected for spherical projection)
Particles follow neighbors

\[ P(\theta) \]

Angle \( \theta \)

\( P(\theta) \) corrected for spherical projection

\( \theta \approx 0^\circ \)
common

\( \theta \approx 180^\circ \)
rare
Look for local orientational order:

- $q_{6m}(i)$ forms a 13-dimensional vector
- find unit vectors $q_{6m}(i)$
- if $q_{6m}(i) \cdot q_{6m}(j) > 0.5$, then bond (ij) is “crystal-like”
- if particle has $\geq 8$ “crystal-like” bonds, it is a crystal-like particle

rotationally invariant, insensitive to type of crystal
Number $N_f$ of fast neighbors to a fast particle:

Fractal dimension:

$N \sim R_g^{d_f}$

$d_f = 2.0$

$\phi = 0.56$

supercooled fluid
Cluster size grows as glass transition is approached.

Average cluster size

\[ \langle N_c \rangle \]

\( \approx \phi_G \)

\( \phi \) volume fraction
mean square displacement
\[ <X^2> (\mu m^2) \]

nongaussian parameter

average cluster size

\[ \frac{N_o}{N} \]

supercooled liquids

glasses

\[ \Delta t (s) \]
Relaxation modes of glasses & supercooled fluids

“α” and “β” relaxation processes:
cage breakdown for fluids
short time scale relaxations, both fluids & glasses

Our results: cluster structure similar for
• Supercooled fluids, small Δt (“β”)
• Glasses, all Δt (“β”)

![Diagram showing average cluster size over lag time for different values of φ.]
Dynamical Heterogeneity: possible *dynamic* length scale

Adam & Gibbs: “*cooperatively rearranging regions*” (1965)

NMR experiments:
- Schmidt-Rohr & Spiess (1991, polymers)
- Silleseu et al (1992, o-terphenyl)

Photobleaching:
- Cicerone & Ediger (1995, o-terphenyl)

Simulations:
Molecular Dynamics Simulations:

W. Kob, S. C. Glotzer, C. Donati, P. H. Poole,...

1997 - now

• Binary mixture of Lennard-Jones particles

• Equilibrium supercooled liquids

• 8000 particles, 3D