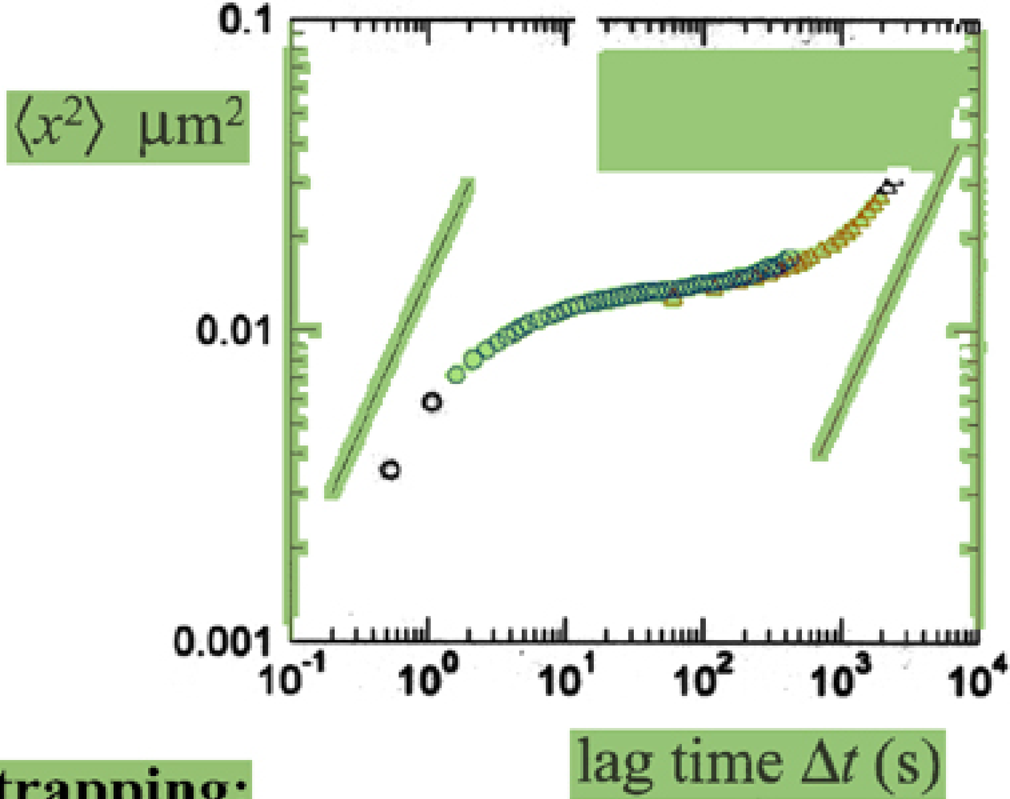
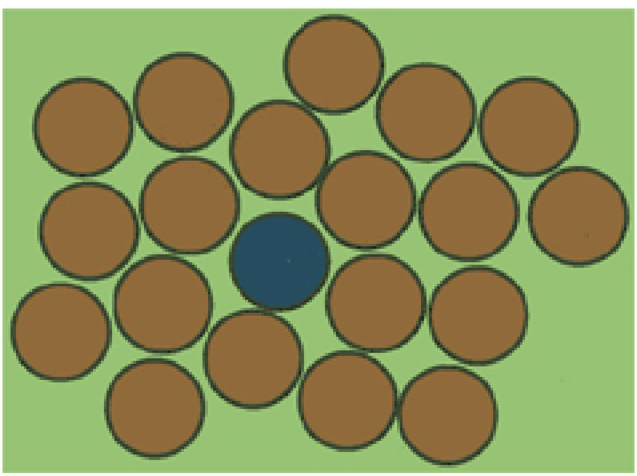
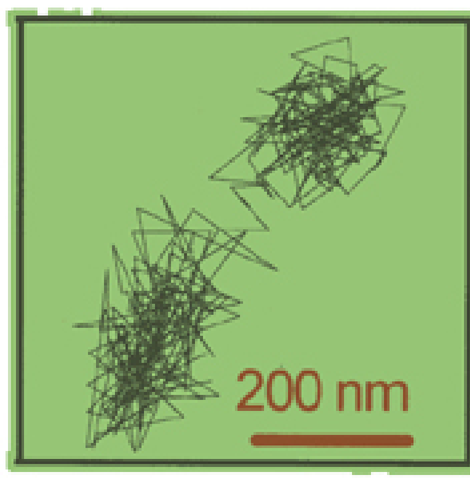


Cage trapping:



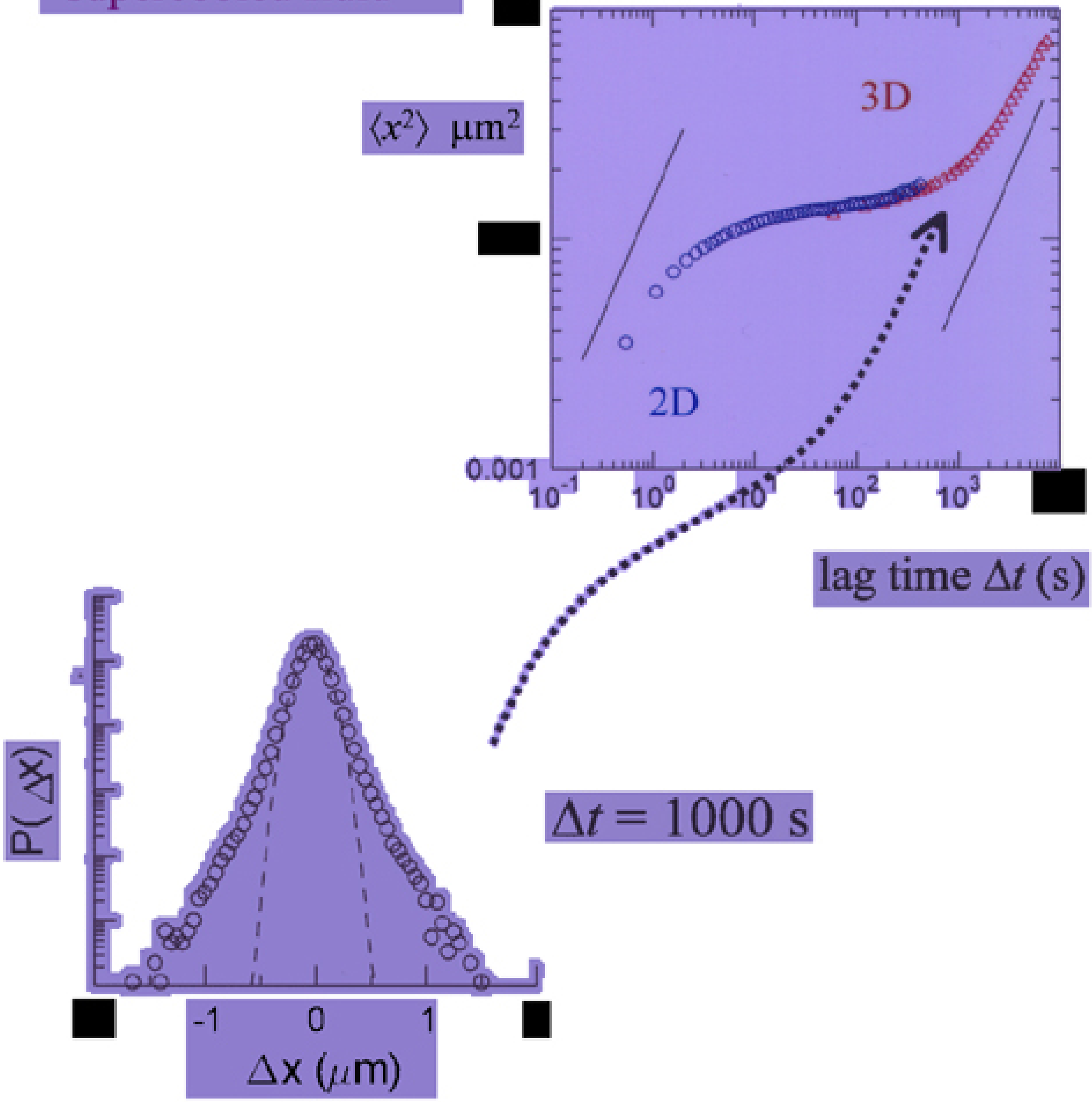


φ=0.56, 100 min
(supercooled fluid)

- Short times: particles stuck in "cages"
- Long times: cages rearrange

I ent

Volume fraction ϕ=0.5 [redacted]
"supercooled fluid"



[redacted]

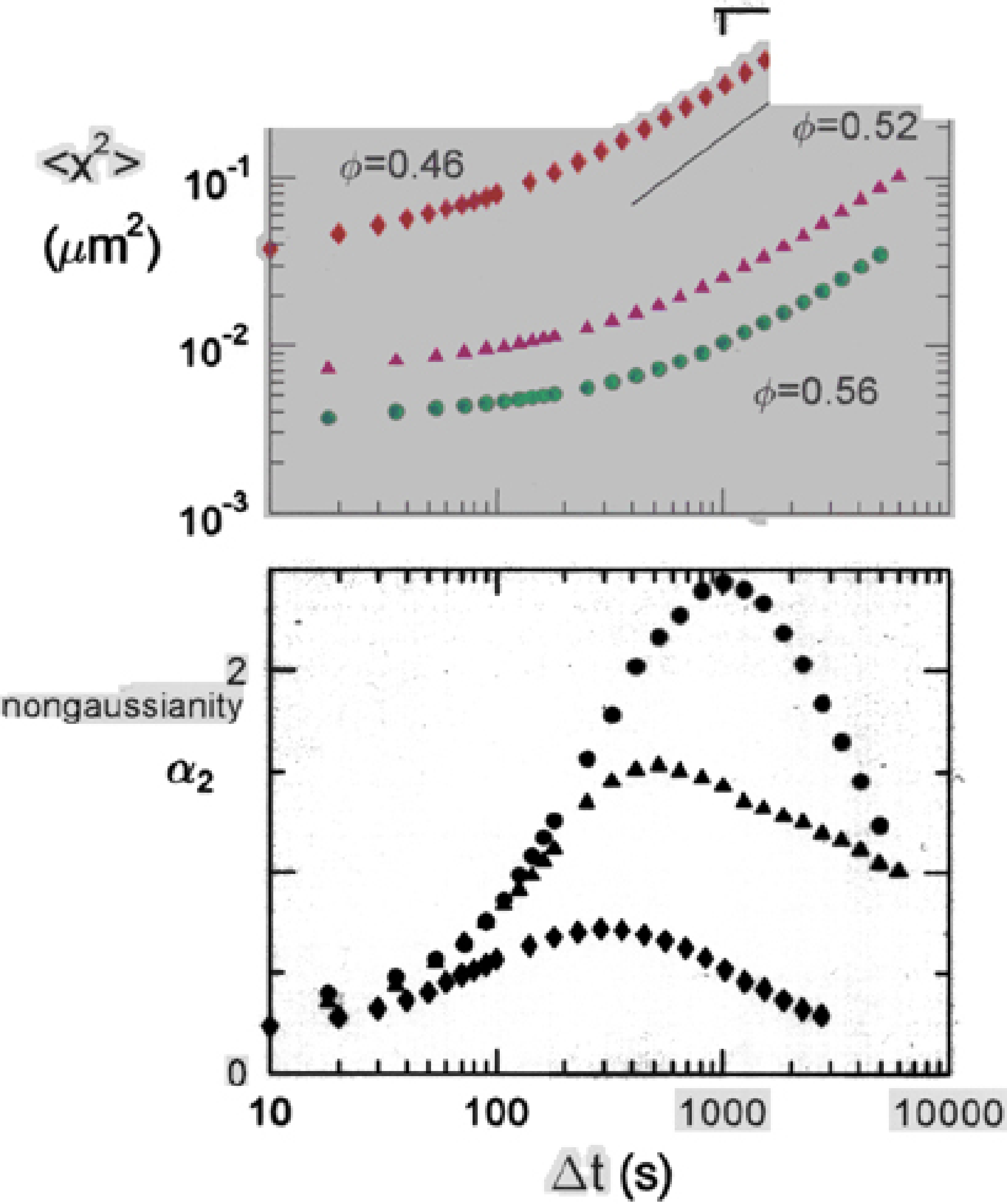
Nongaussian Parameter α_2

Rahman, 1964

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

Gaussian: $\alpha_2 = 0$

Exponential: $\alpha_2 = 1$



<x^2>
(μm^2)
10^-1
10^-2
10^-3
φ=0.46
φ=0.52
φ=0.56
2
nongaussianity
α2
0
10
100
1000
10000
Δt (s)

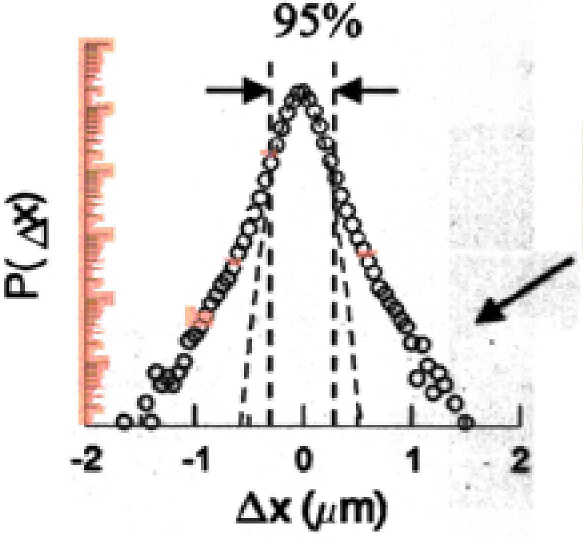
Time scale:

Δt^* when nongaussian parameter α_2 largest

Length scale:

Δr^* on average, 5% of particles have $\Delta r(\Delta t^*) > \Delta r^*$

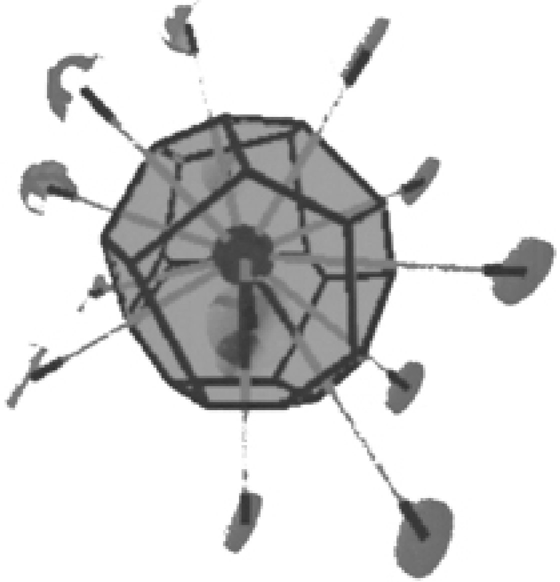
$\boxed{\approx \text{cage rearrangements}}$



top 5% = tails of Δx distribution

(ϕ=0.53, supercooled fluid)

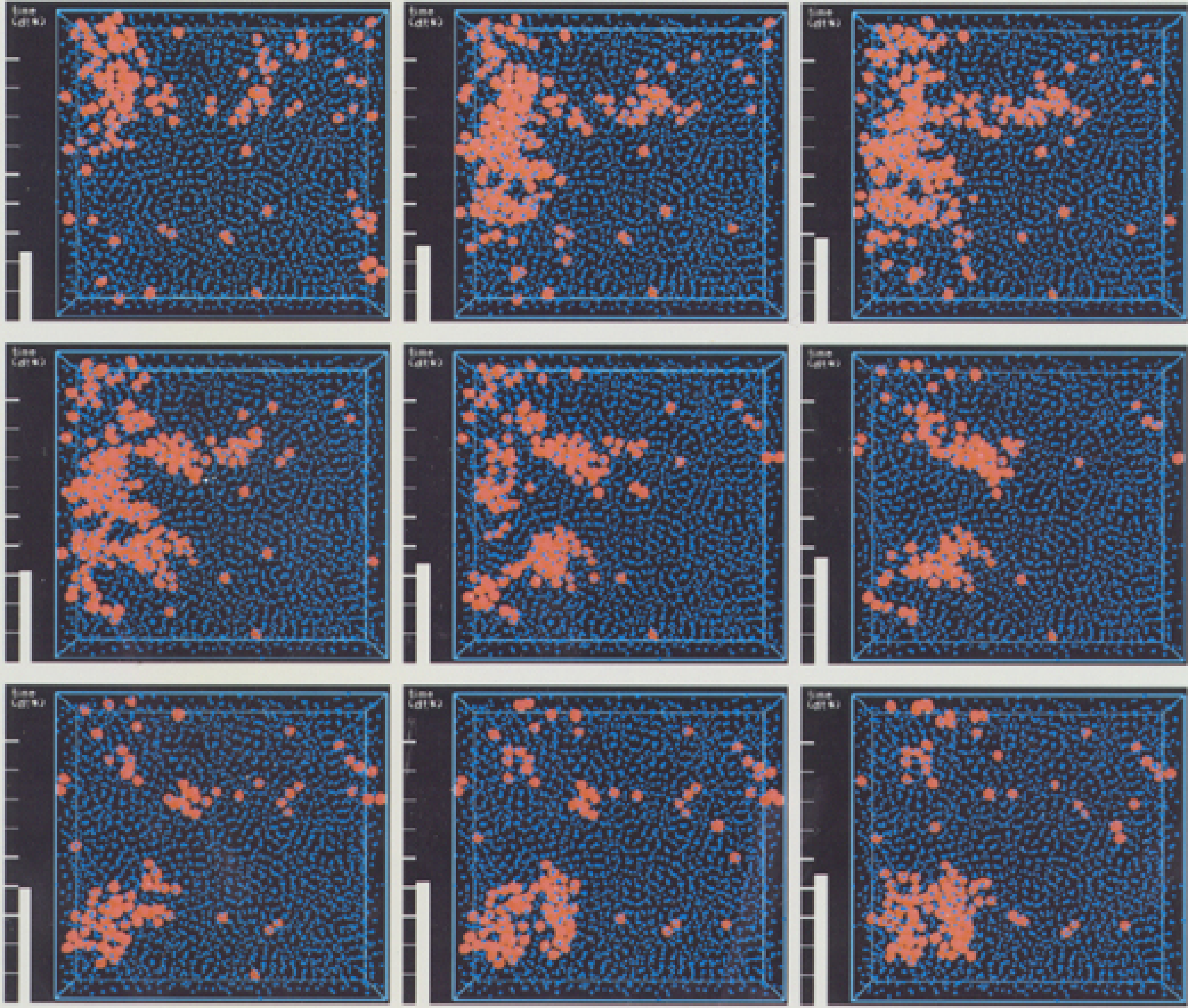
Voronoi polyhedra -- Delaunay triangulation



("Wigner-Seitz cell")

polyhedron face: *set of all points equidistant from two particles*

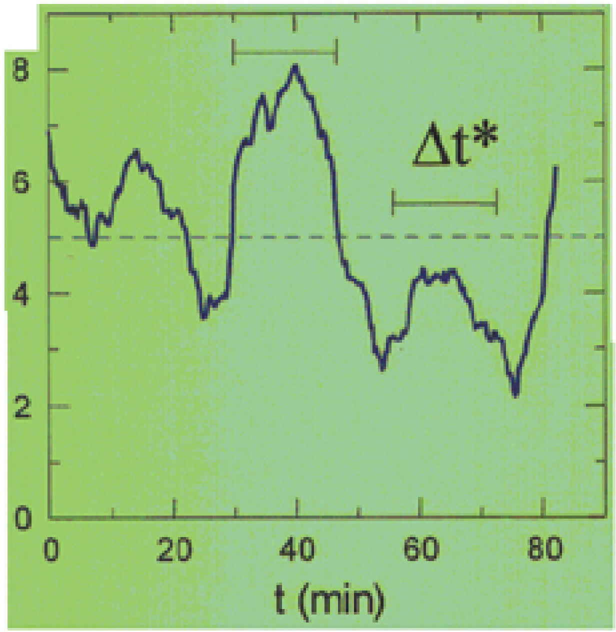
defines nearest neighbor particles



F of

Supercooled fluid

$\phi = 0.56$

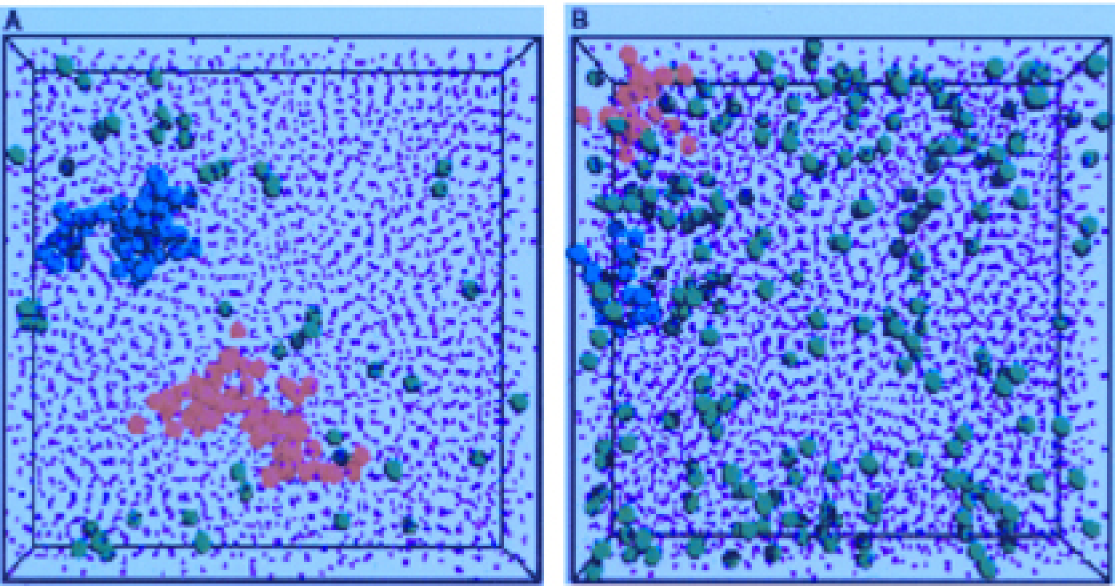


top 5%

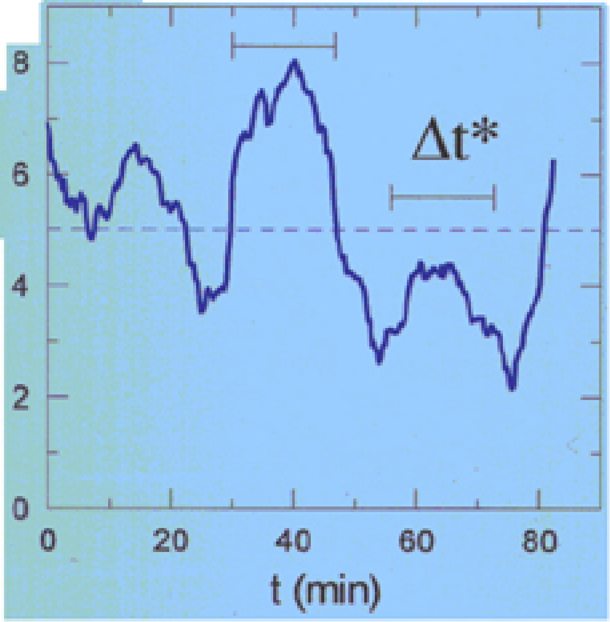
Very large fluctuations

- Sample is not ergodic

Glass Transition

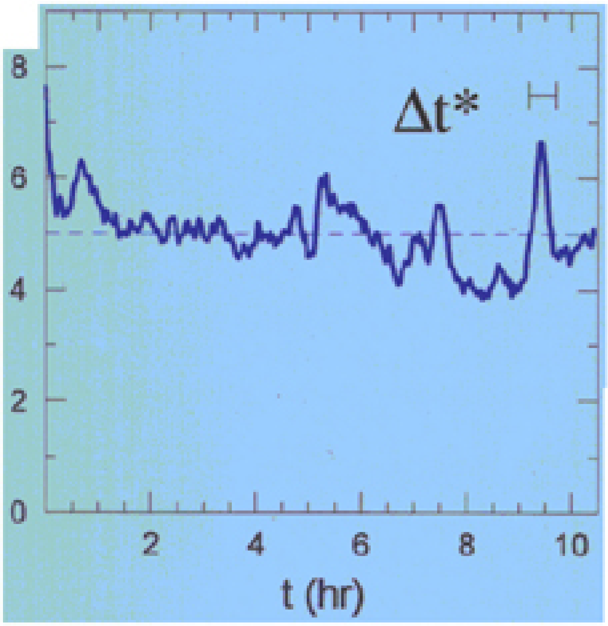


supercooled fluidφ=0.56



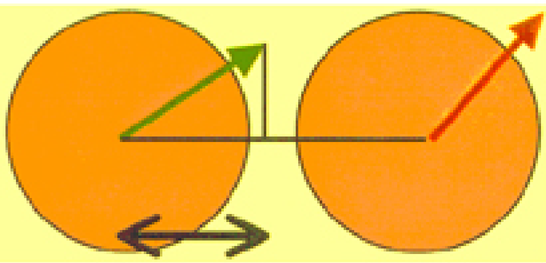
top 5%

glass
φ=0.61

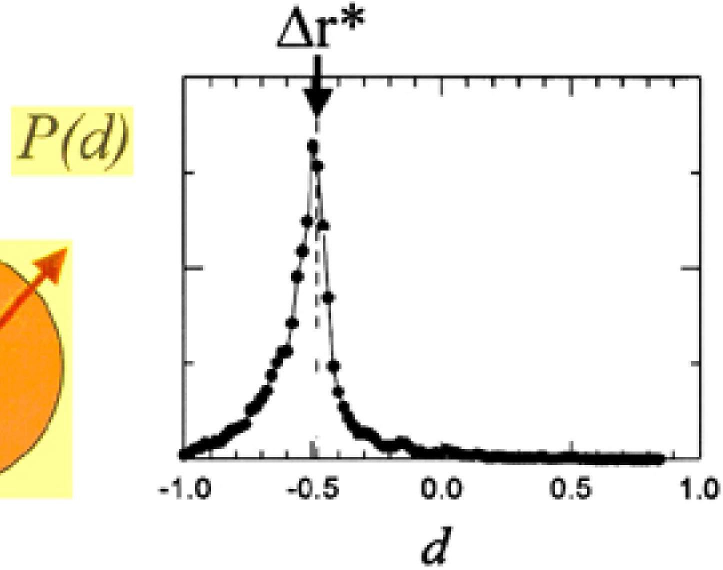


top 5%

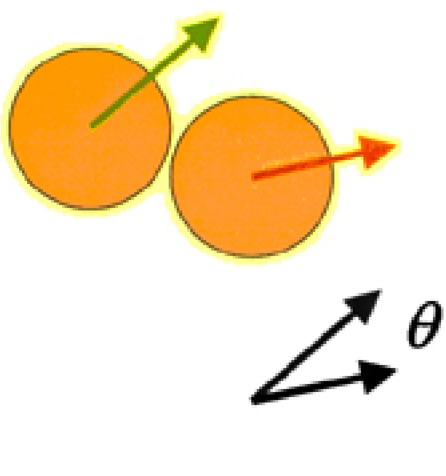
Particles move towards neighbors

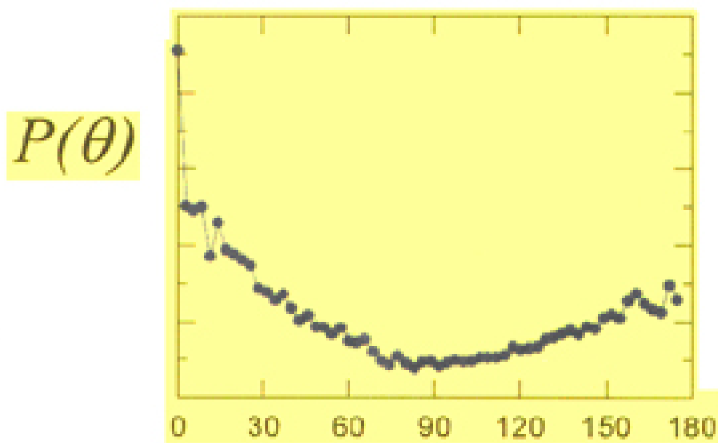


d



Particles move in same direction as neighbors

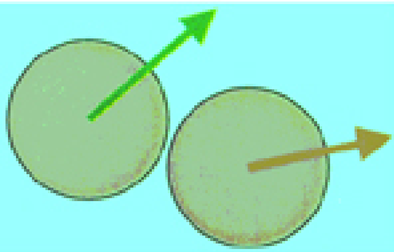


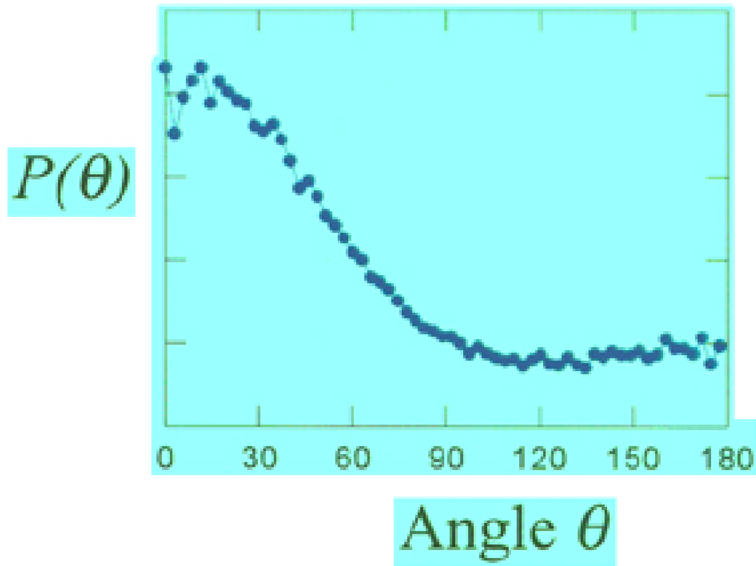


Angle θ

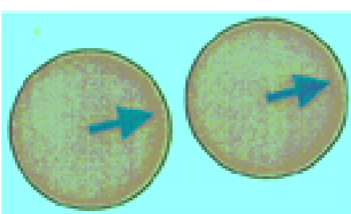
($P(\theta)$ corrected for spherical projection)

Particles follow neighbors



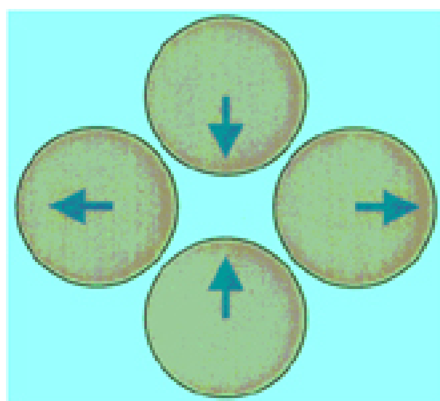


(P(θ) corrected for spherical projection)



θ≈0°

common



θ≈180°

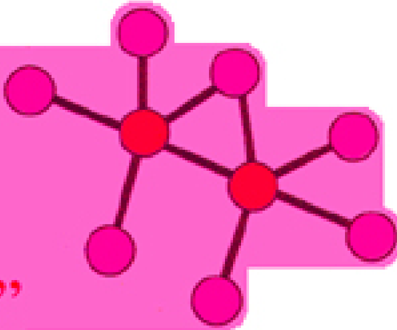
rare

Look for local orientational order:

[redacted]

- $q_{6m}(i)$ forms a 13-dimensional vector

- find unit vectors $q_{6m}(i)$

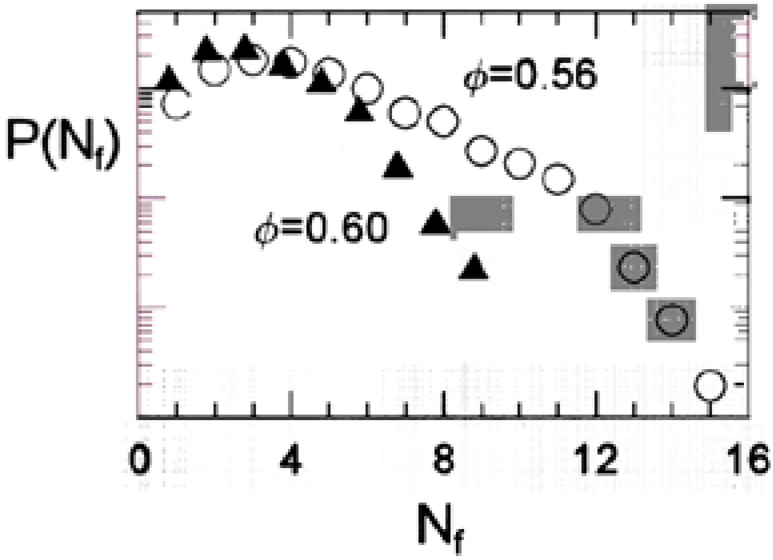


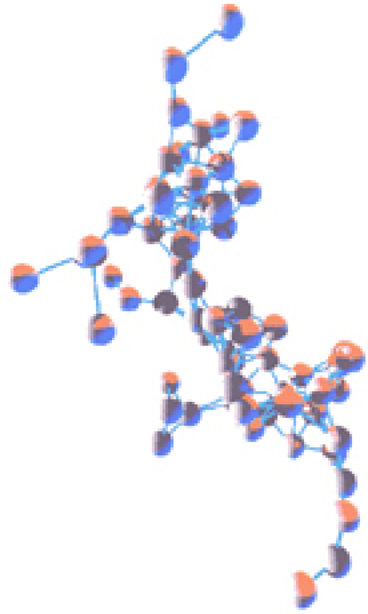
- if $q_{6m}(i) \cdot q_{6m}(j) > 0.5$,
  then bond (ij) is "crystal-like"

- if particle has ≥ 8 "crystal-like" bonds,
  it is a **<u>crystal-like particle</u>**

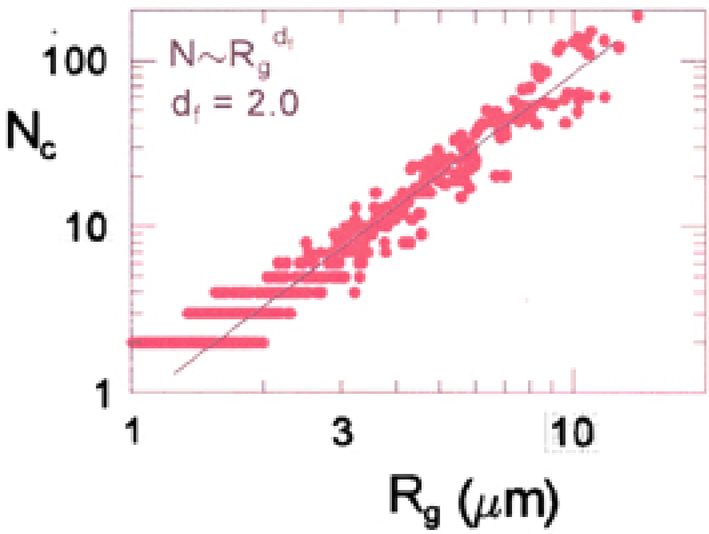
⇒ rotationally invariant, insensitive to type of crystal

Number N_f of fast neighbors to a fast particle:



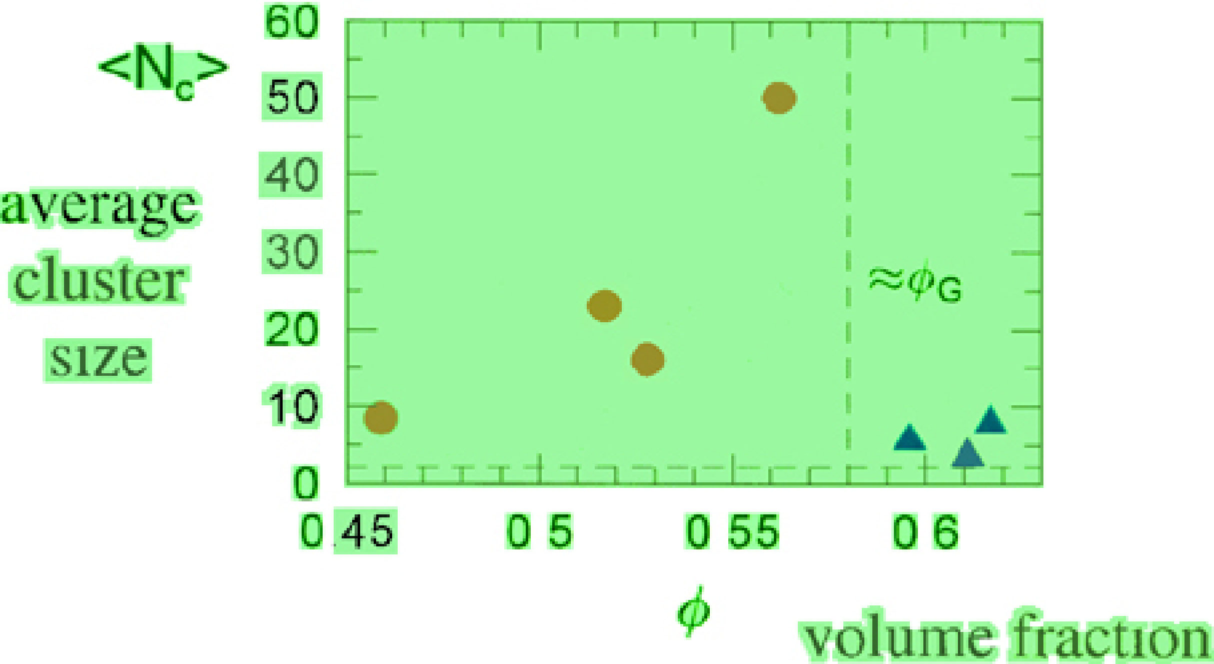


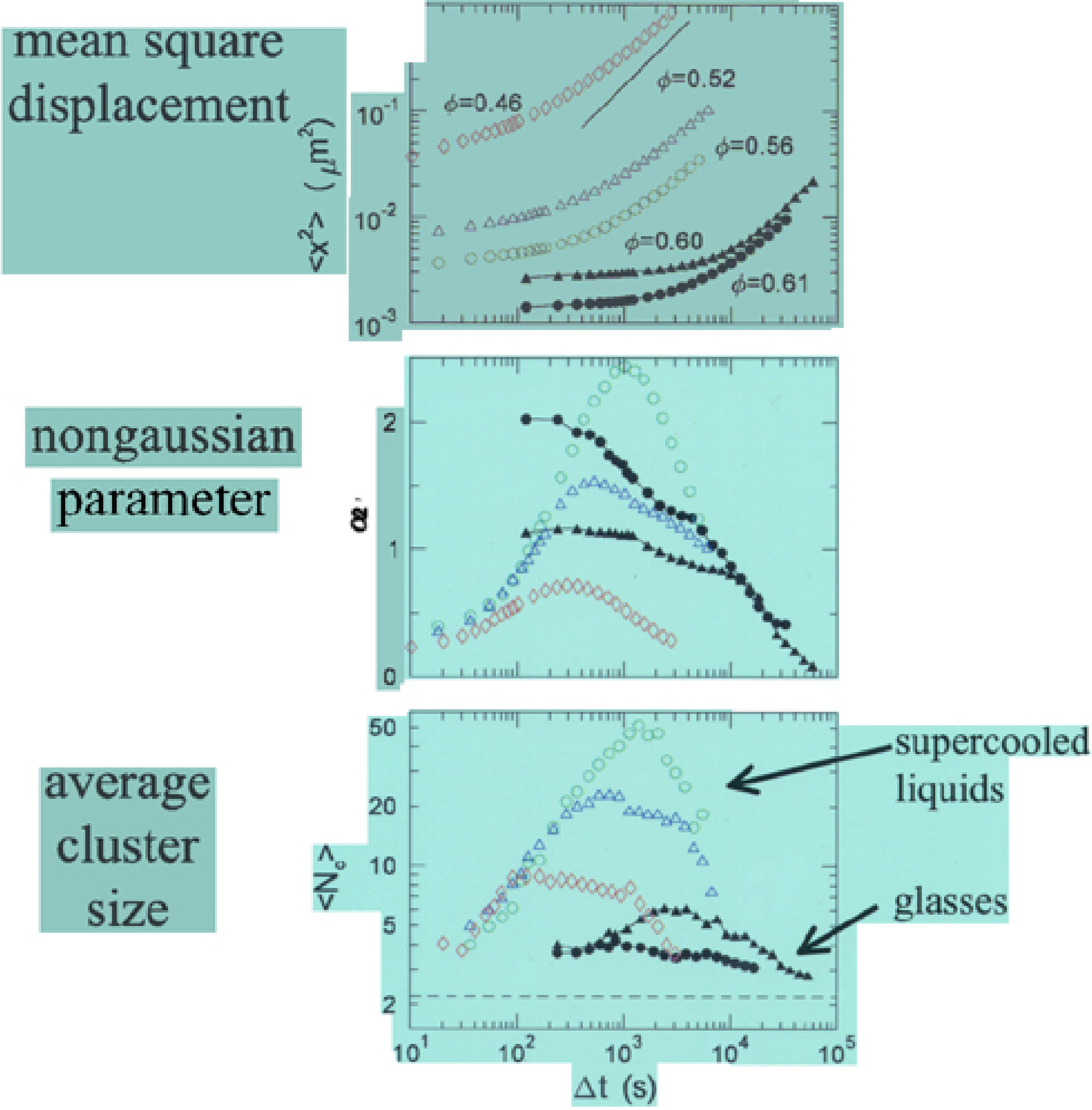
Fractal dimension:



φ=0.56
supercooled fluid

Cluster size grows as glass transition is approached





mean square displacement
nongaussian parameter
average cluster size
supercooled liquids
glasses
$\langle x^2 \rangle$ (μm^2)
ϕ=0.46
ϕ=0.52
ϕ=0.56
ϕ=0.60
ϕ=0.61
α_2
$\langle N_c \rangle$
Δt (s)

Relaxation modes of glasses & supercooled fluids

"α" and "β" relaxation processes:

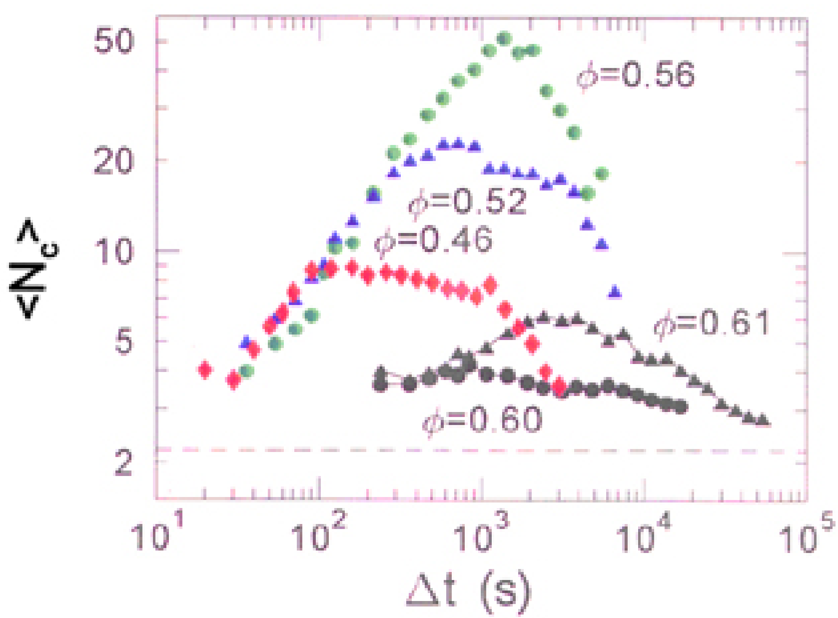
cage breakdown for fluids

short time scale relaxations, both fluids & glasses

Our results: cluster structure similar for

- Supercooled fluids, small Δt ("β")
- glasses, all Δt ("β")

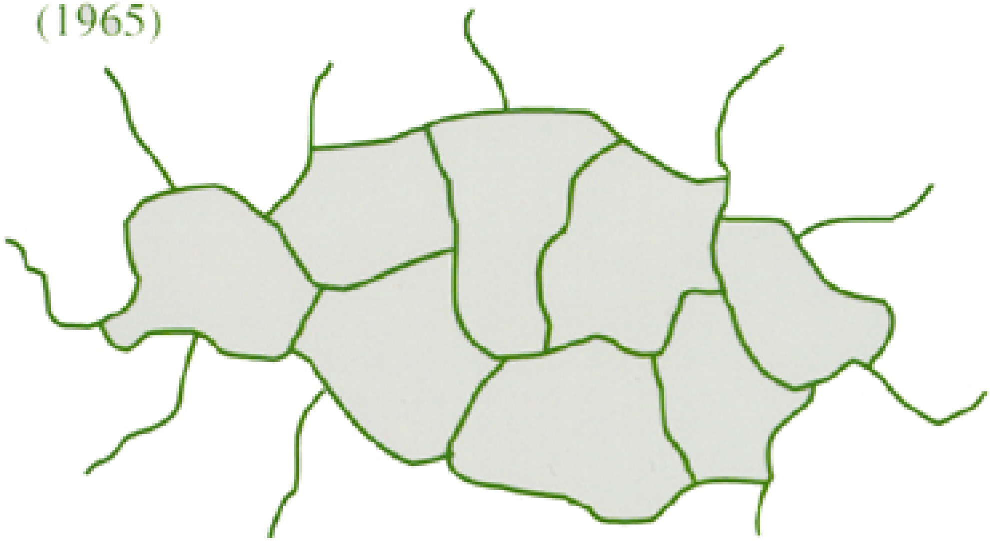
average cluster size



lag time

Dynamical Heterogeneity: possible *dynamic* length scale

Adam & Gibbs: "**cooperatively rearranging regions**"
(1965)



NMR experiments:

- Schmidt-Rohr & Spiess (1991, polymers)
- Tang, Johnson, et al (1998, metallic glasses)
- Sillescu et al (1992, o-terphenyl)

Photobleaching:

- Cicerone & Ediger (1995, o-terphenyl)

Simulations:

- Glotzer, Kob, Donati, et al (1997, Lennard-Jones)

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