Glassy dynamics and aging in colloidal hard spheres

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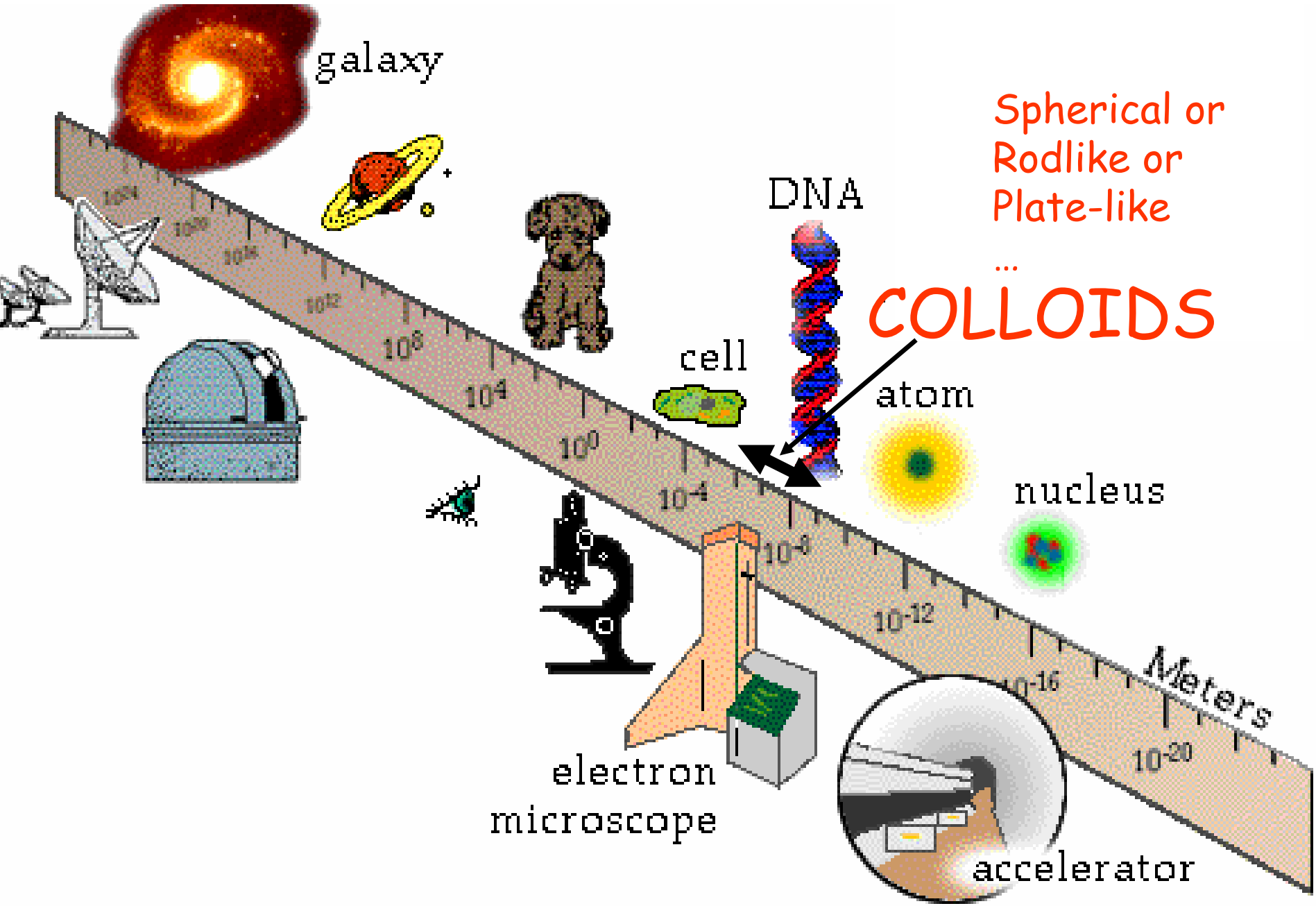


Spherical or
Rodlike or
Plate-like
…

COLLOIDS

Outline

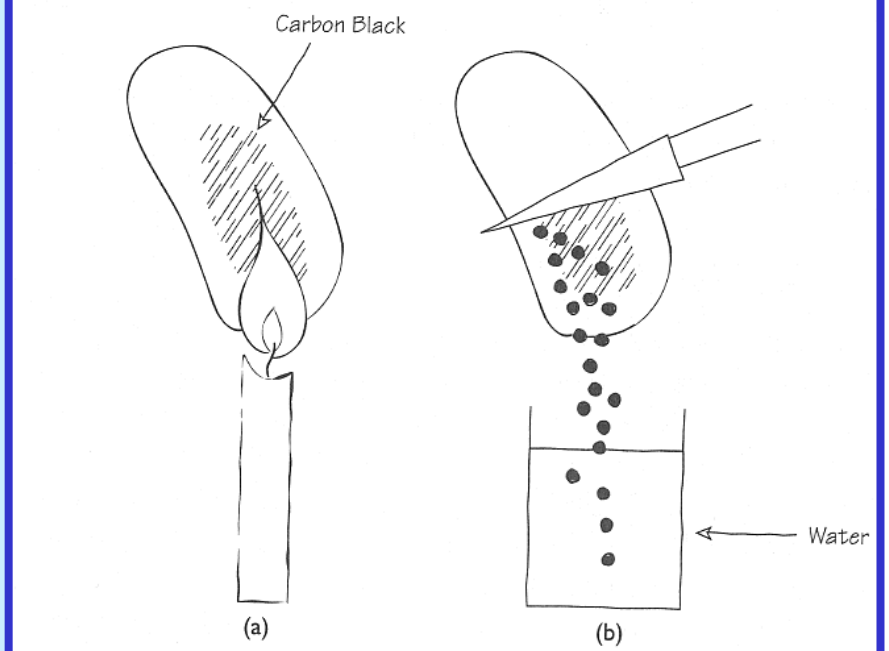
- Colloidal hard spheres, crystallization, & glass transition
- Displacement distribution in / near glasses – 'dynamic heterogeneity'
- Dynamics & aging in 'glasses' – influence of gravity
- Conclusions/ open questions

Colloids usually STICK ('aggregate').

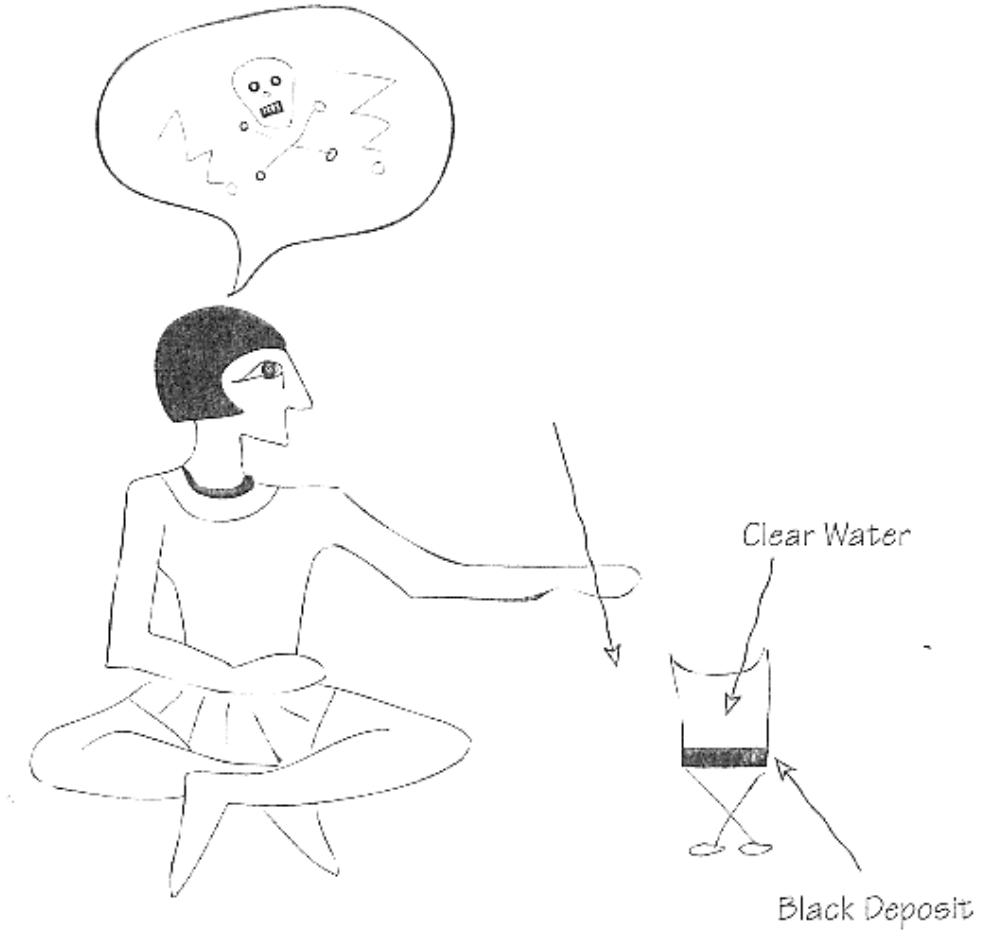
Why? -> Van der Waals forces!

E.g: Gecko setae & glass [PNAS ***99***, 12252, (2002)]

Steric repulsion



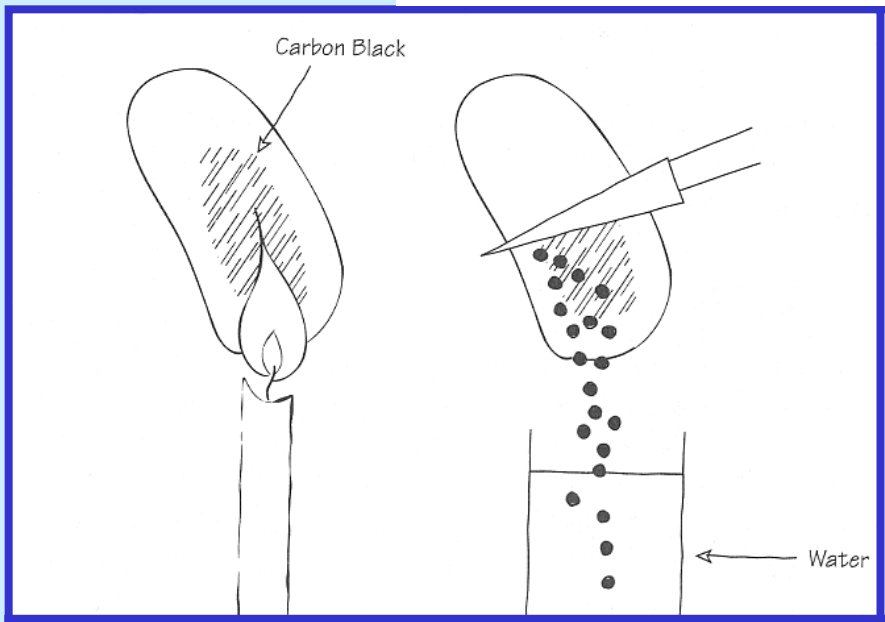
A primitive recipe for black ink.

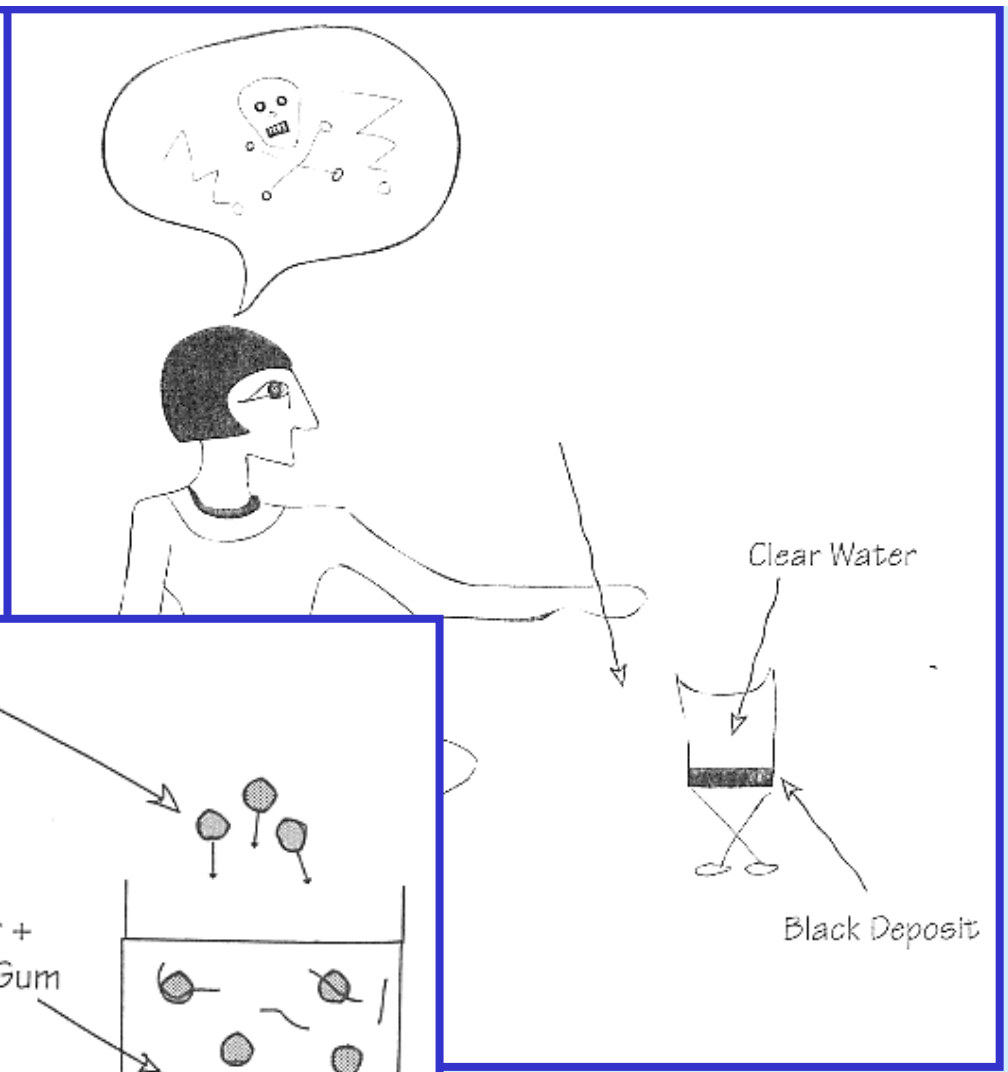


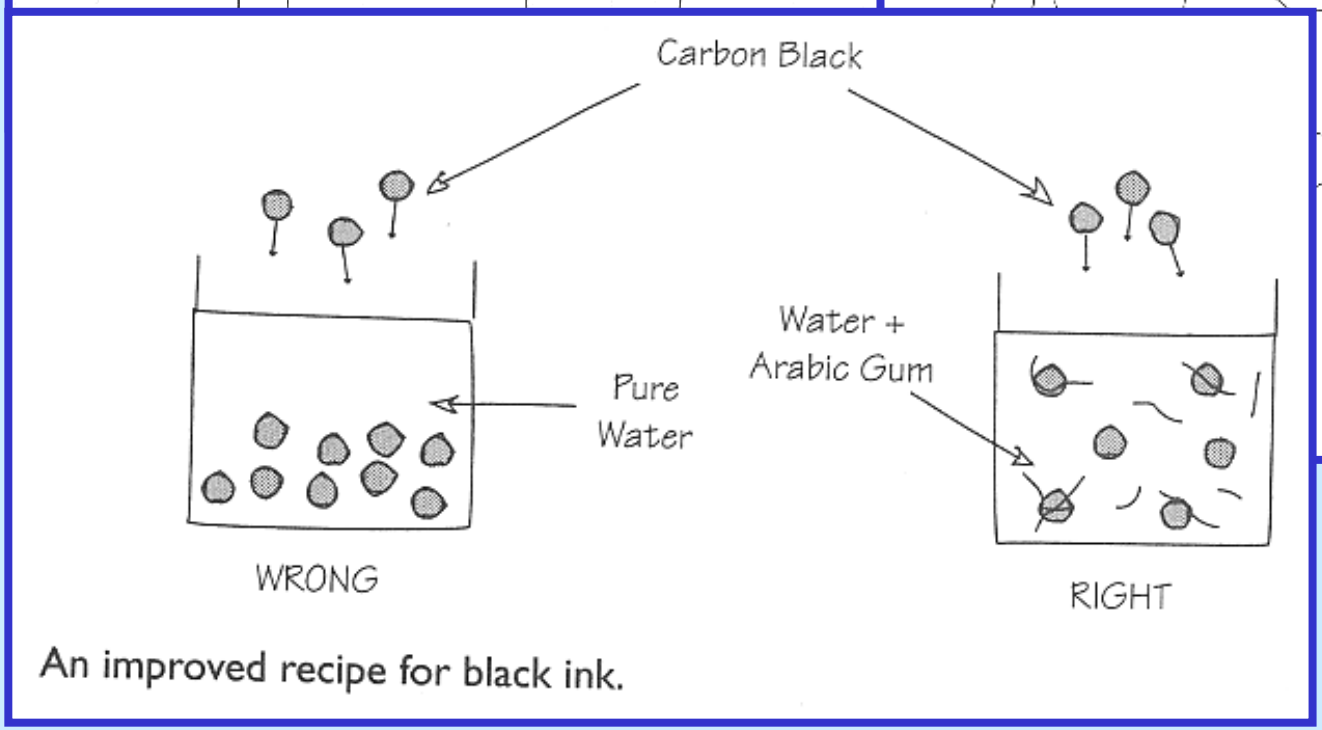
Nature does not always cooperate.

de Gennes & Badoz, "Fragile Objects", (Springer-Verlag, New York, 1996).

Steric repulsion: often polymer is added as stabilizer





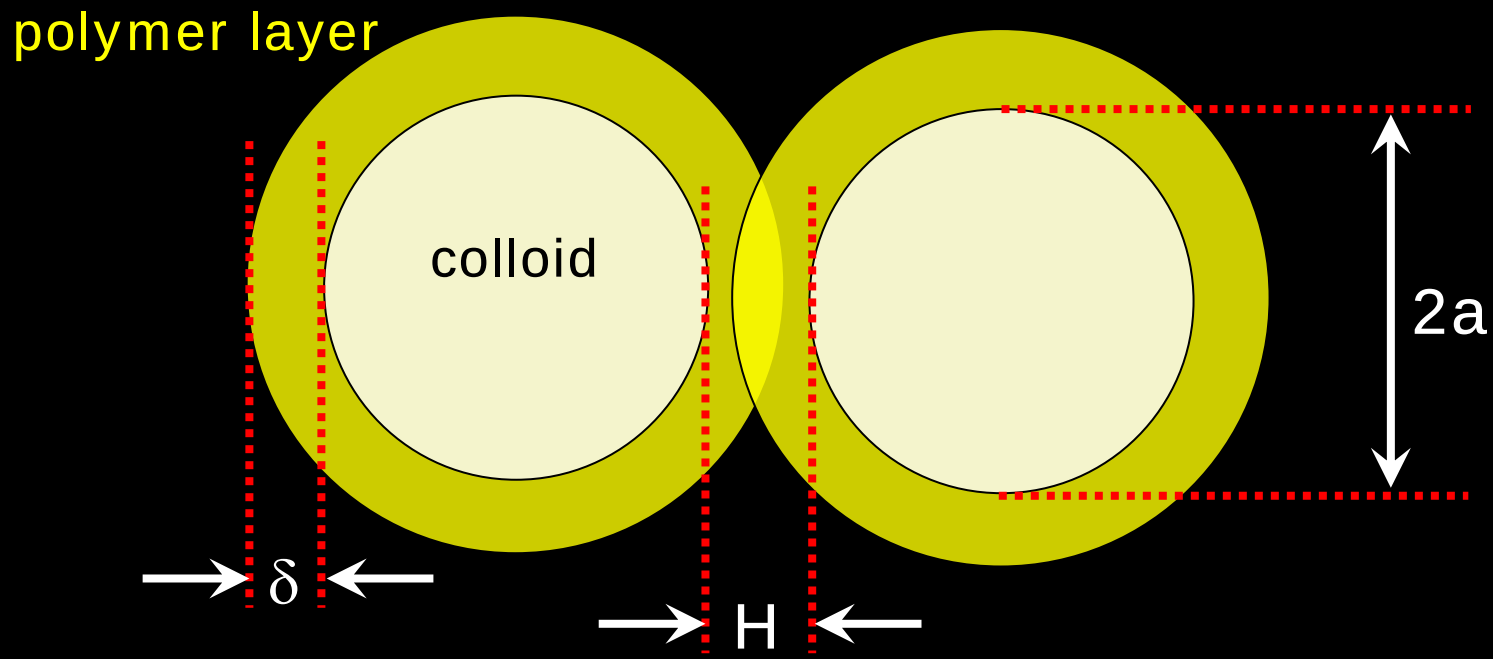


An improved recipe for black ink.

de Gennes & Badoz, "Fragile Objects", (Springer-Verlag, New York, 1996).

Steric repulsion

E.W. Fischer, *Kolloid Z.* 160, 120 (1958).



$$\frac{V_{steric}}{k_B T} = 4\pi a \Gamma^2 N_{Av} \frac{\bar{v}_2}{\bar{v}_1} \left(\frac{1}{2} - \chi\right) \left(1 - \frac{H}{2\delta}\right)^2$$

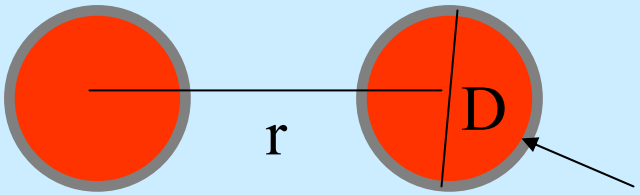
polymers adsorbed per surface area

molar volumes

χ must be <0.5 for repulsion!

overlap volume

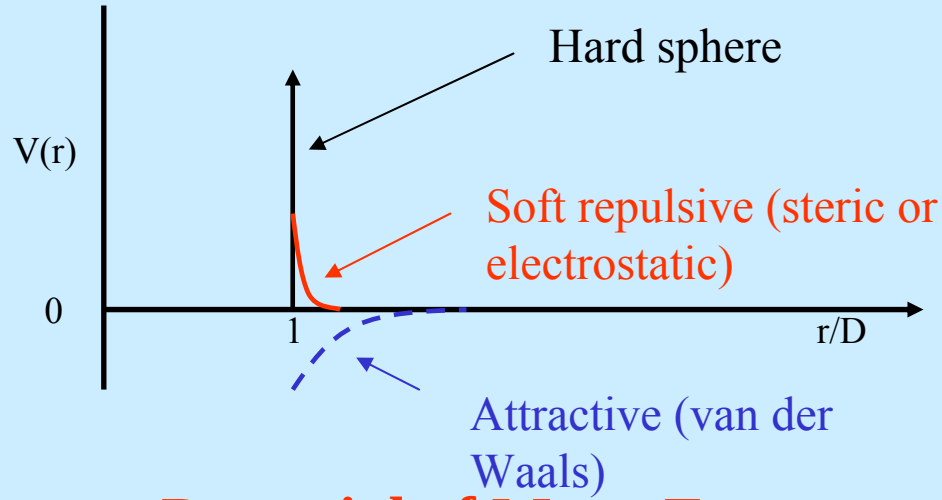
Colloids as atoms



$D=O(10^{-9}\text{-}10^{-6})m$

Stabilizing (polymer) layer or charged groups

Sample phase space by BROWNIAN MOTION



V(r) = **Potential of Mean Force**

- depends on (macroscopic) solvent properties
- If $n_{solvent} = n_{colloids}$ => V(r)≈ hard sphere potential

Generalization / formalization

Potential of mean force $-\nabla_1 v(r) = kT\nabla \ln Z'$

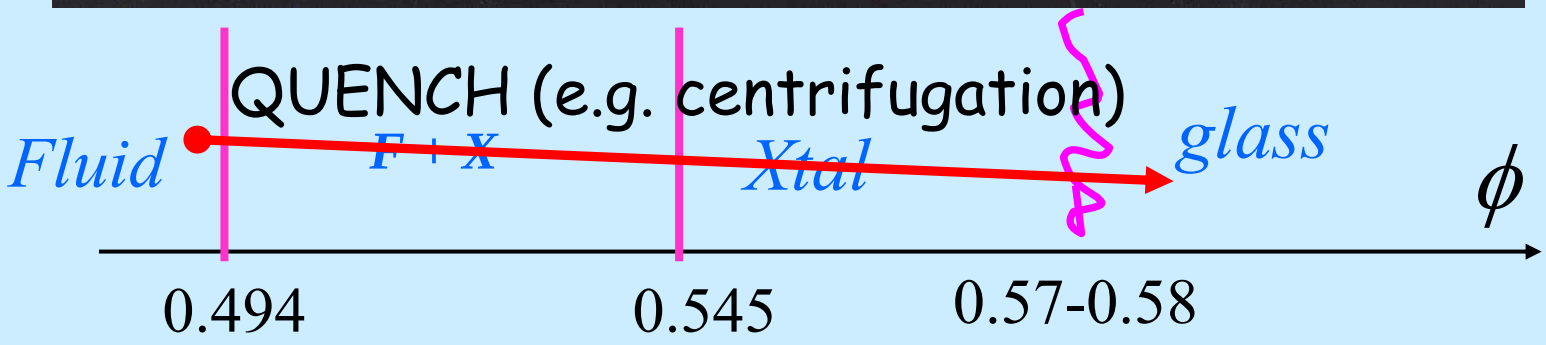
Constraint: positions 1,2 FIXED

or:

$$-\nabla_1 v(r) = \left\langle -\nabla_1 U(r^N) \right\rangle = \frac{\int .. \int d\vec{r}_3 .. d\vec{r}_N (-\nabla U(r^N)) e^{-U(r^N)/kT}}{\int .. \int d\vec{r}_3 .. d\vec{r}_N e^{-U(r^N)/kT}}$$

Work changing distance 1,2: $\delta W_{rev} = (dF)_{T,V,N} = -\nabla_1 v(r) \bullet d\vec{r}_{12}$

Colloidal Hard spheres: Pusey & van Megen, *Nature* 1986

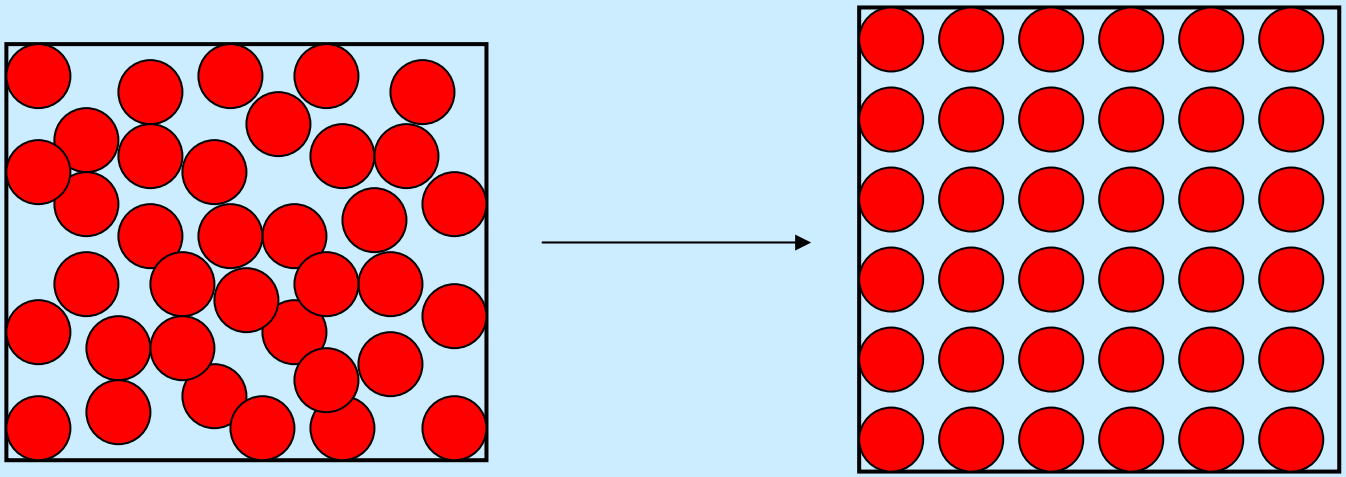


Crystallization in hard spheres is entropy driven

First indications by computer simulation:

W.W. Wood & J.D. Jacobsen, J. Chem. Phys. **27**, 1207, (1957)
B.J. Alder & T.E. Wainwright, J. Chem. Phys. **27**, 1208, (1957)

Entropy-increase without increase of 'disorder'



entropy ~ Log(available volume)

MECHANISM of freezing & melting?

Challenge: Theory of order – disorder transitions.


ENTROPY
I DON'T ACCEPT
FUNDAMENTAL
TENETS OF SCIENCE
AND I VOTE

'The Onion'

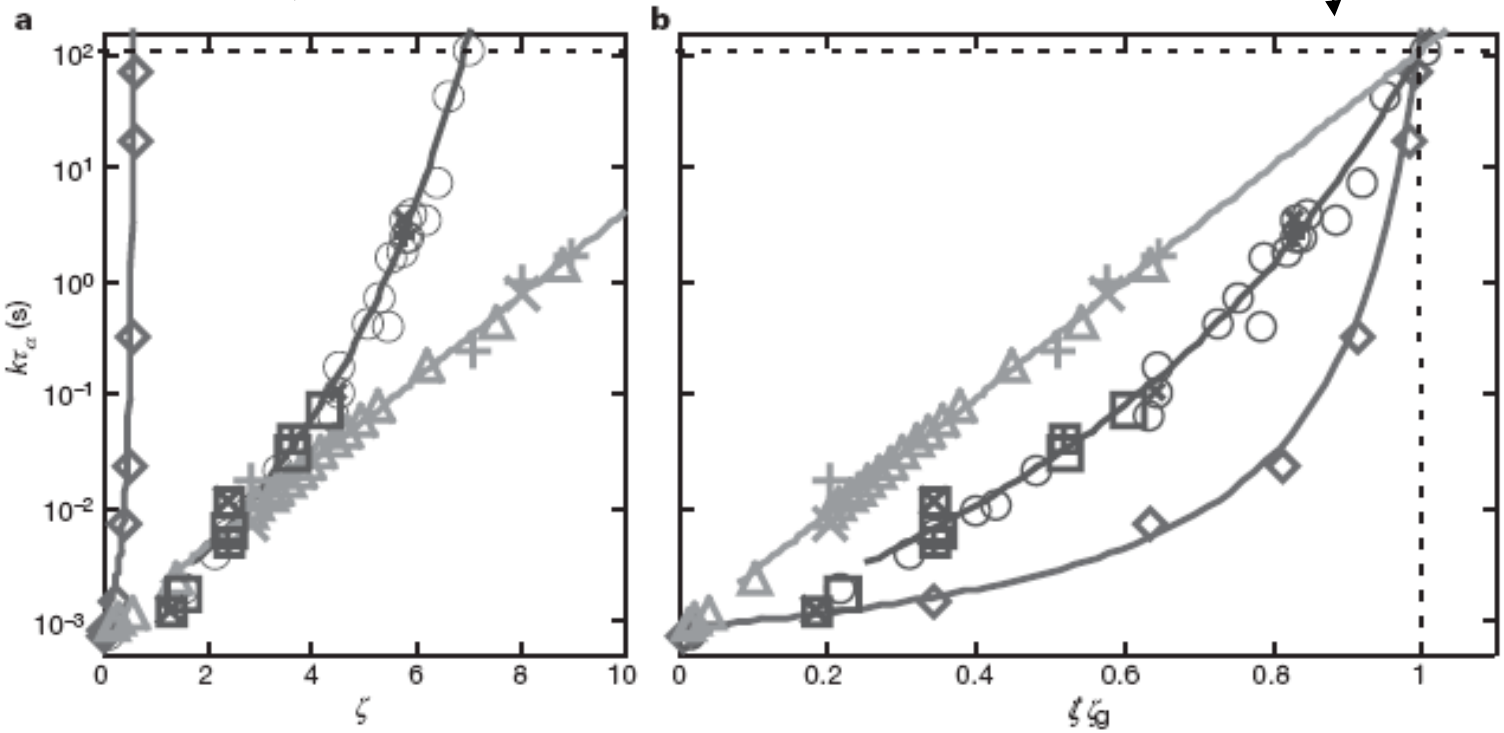
Xtal: Stacks of hexagonal layers (FCC or HCP); close packing $\phi_{CP} = \frac{\pi}{3\sqrt{2}} \approx 0.74$

Challenge: theoretical treatment of crystallization WITHOUT inserting order parameters of coexisting phases in advance

Glass: metastable; no (spontaneous) crystallization; (random) close packing ϕ_{rcp}=0.64

Surprise: glass transition at $\phi < \phi_{rcp}$!

Hard spheres: 'fragile' glass; soft spheres: strong glass

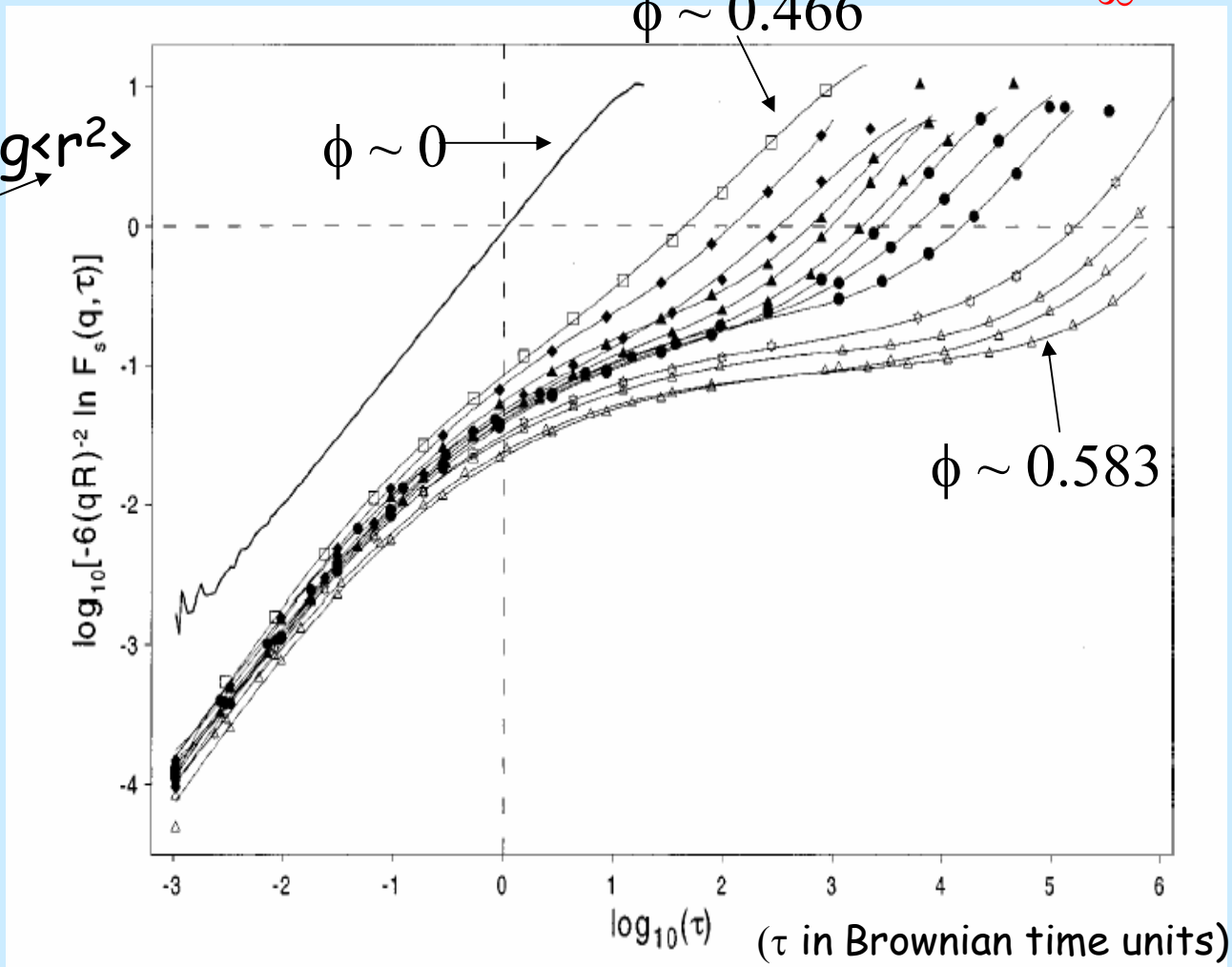


Mattson ea Nature 2009

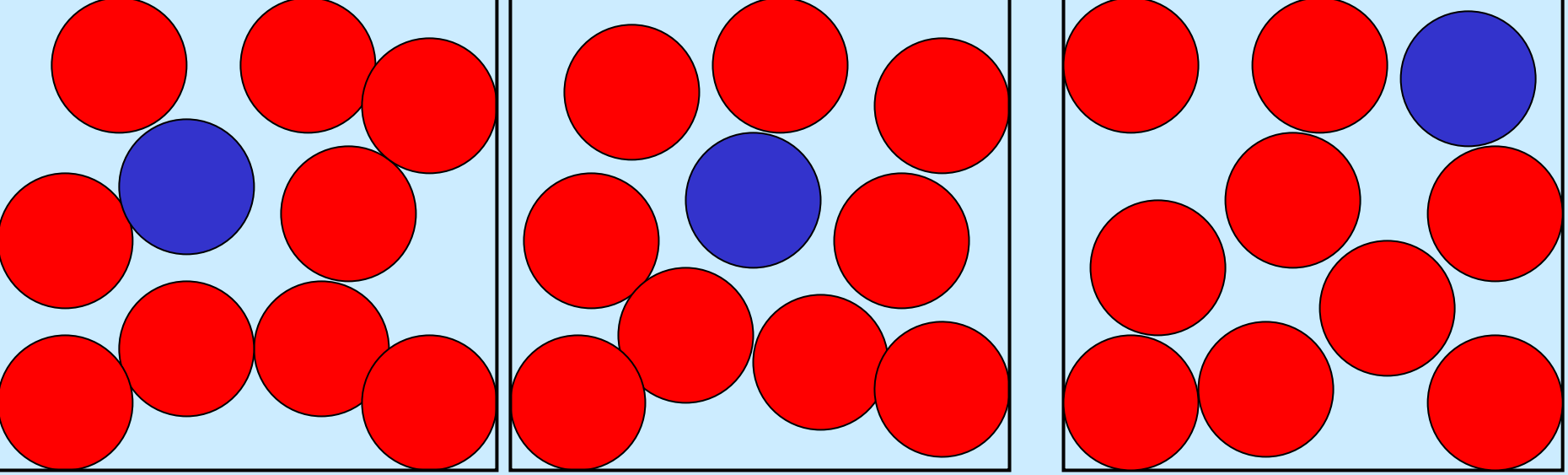
Mean squared displacements from self-intermediate scattering functions [Van Megen ea PRE 1998]

"Diffusive" iff mean squared displacements

$$<r^2>=\int_{-\infty}^{+\infty} r^2 G_s dr = 6D_s t$$



($\tau_B=R^2/6D$)



dense fluid

$\langle r^2 \rangle = 6D_L t$

$\log\langle r^2 \rangle$

"glass"

$\langle r^2 \rangle = 6D_S t$

Log(time)

Short-time self diffusion

Long-time self diffusion

At colloidal glass transition:

- crystallization is suppressed;
- AT THE SAME TIME long-time self diffusion is not reached within experimental time window

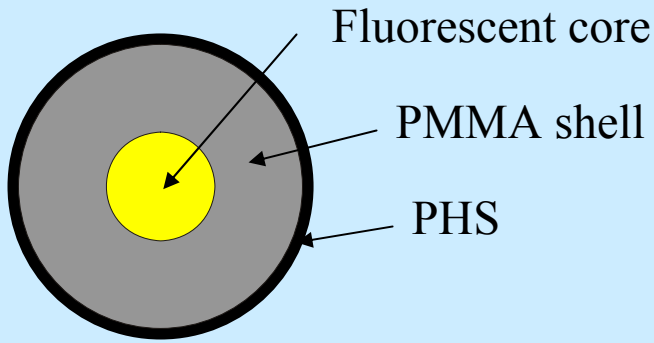
Time window can be quite long

Stained-glass window;
Sint Janskerk, Gouda

Colloidal model system: Core shell particles

R_{core} = 235 nm (fluorescent)

R_{total} = 650 nm, polydispersity σ = 7 %



- (mass) Density matched: milli-gravity
- Volume fractions: 0.44 – 0.64
- Refractive index matched
- Steric stabilization

  thickness PHS ~ 0.01 R_{total}

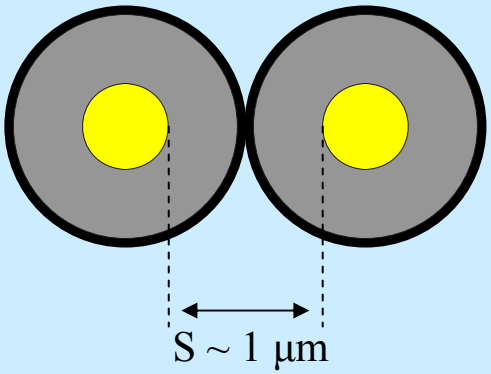
Hard sphere interactions

[Bosma ea J. Coll. Interface Sci. 2002; Dullens ea Langmuir 2004]

Confocal Microscopy

Refractive index matching:

• only fluorescent core is visible



High resolving power:

• analysis on single particle level

• even in 3D if S ≥ z-resolution CSLM

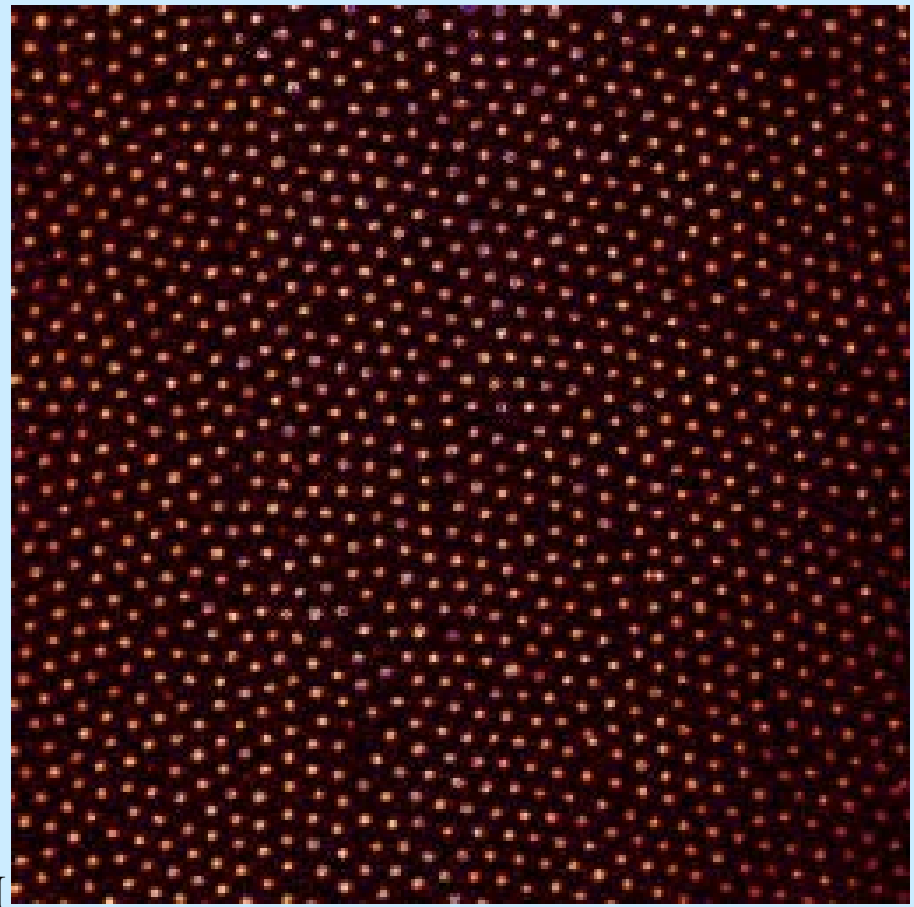
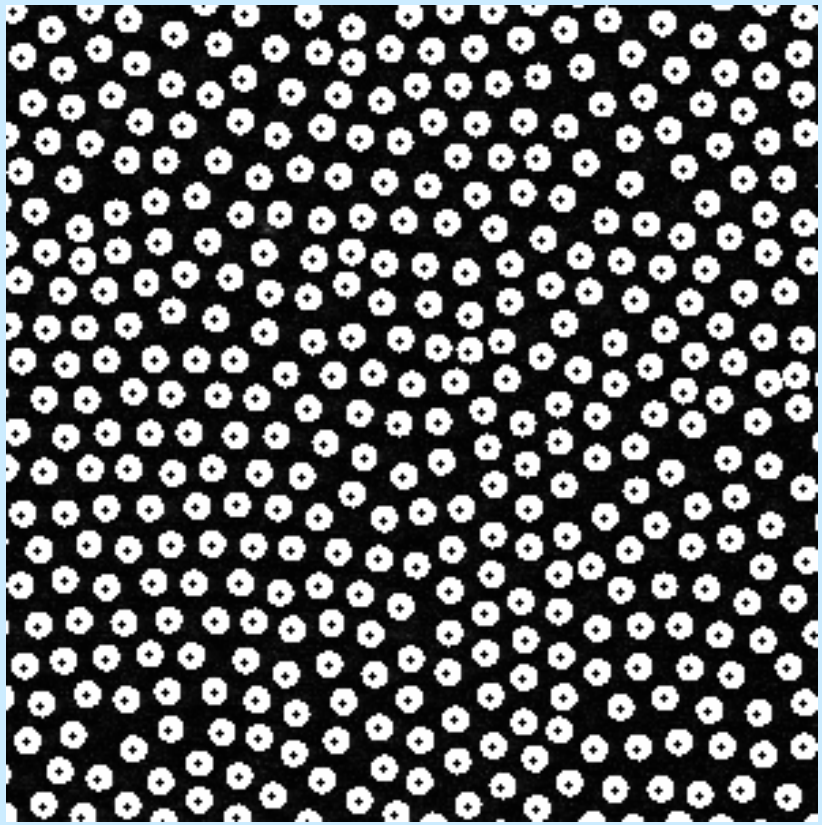


Image processing

Particle coordinates
in time series



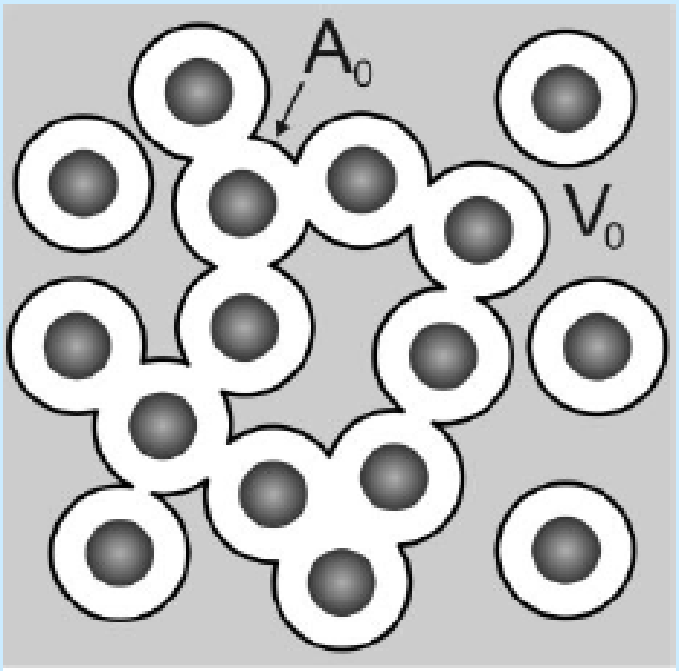
- **Dynamics**: correlation between the particles in subsequent (time) frames
- **Structure**: correlation between the particles in one frame

Intermezzo: thermodynamics by microscopy

Direct measurement of the free energy by optical microscopy

Roel P. A. Dullens*†, Dirk G. A. L. Aarts*‡, and Willem K. Kegel

PNAS 2006

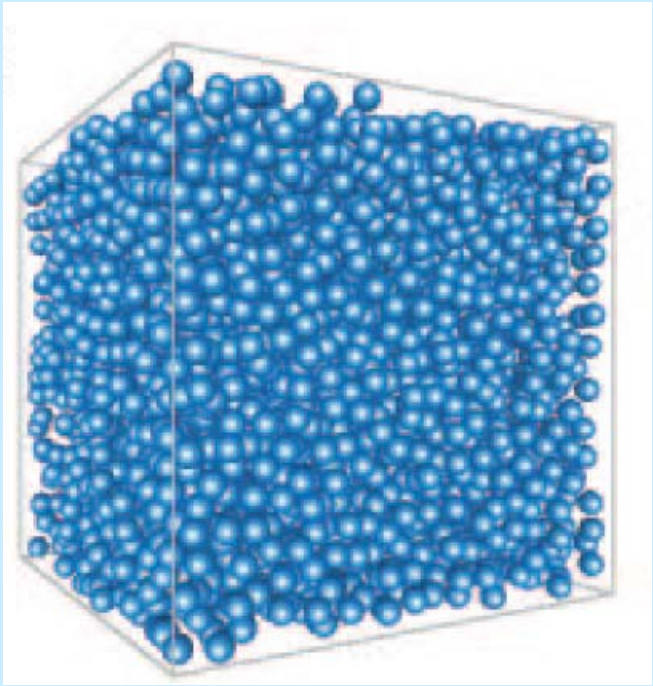


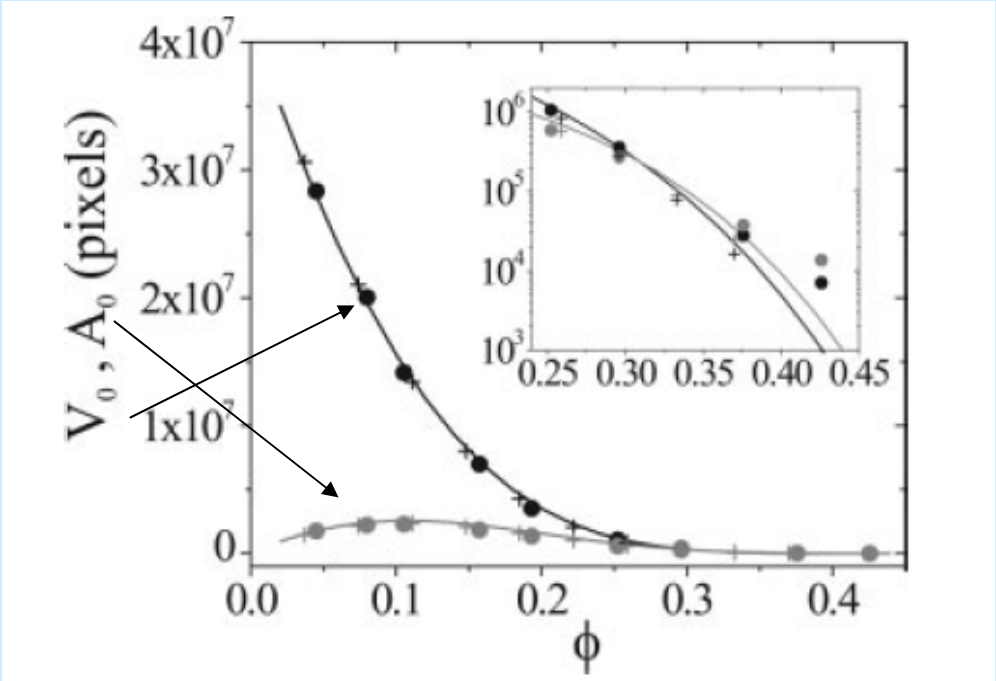
$$P = \rho k_B T \left(1 + \frac{\sigma A_0}{6 V_0} \right)$$

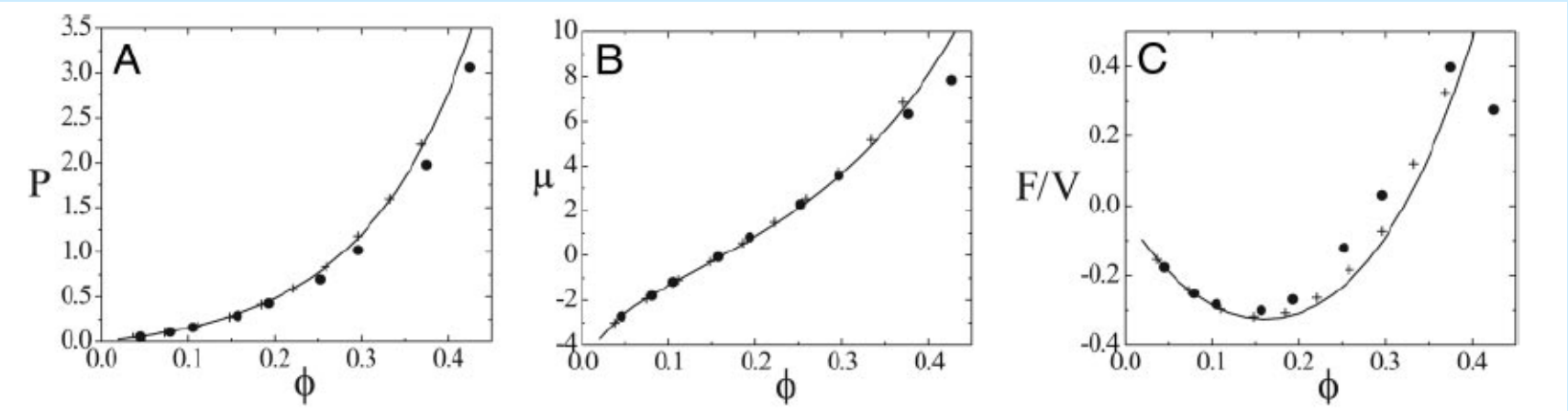
$$\mu = \mu^0 - k_B T \ln\left(\frac{V_0}{V} \right)$$

'statistical geometry'

$$F/V = -P + \mu\rho.$$



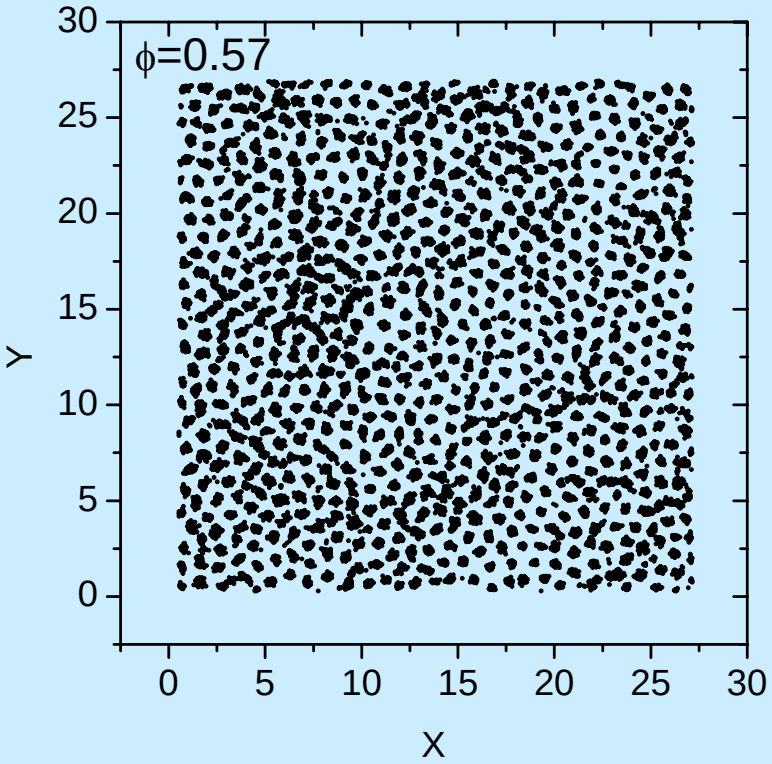


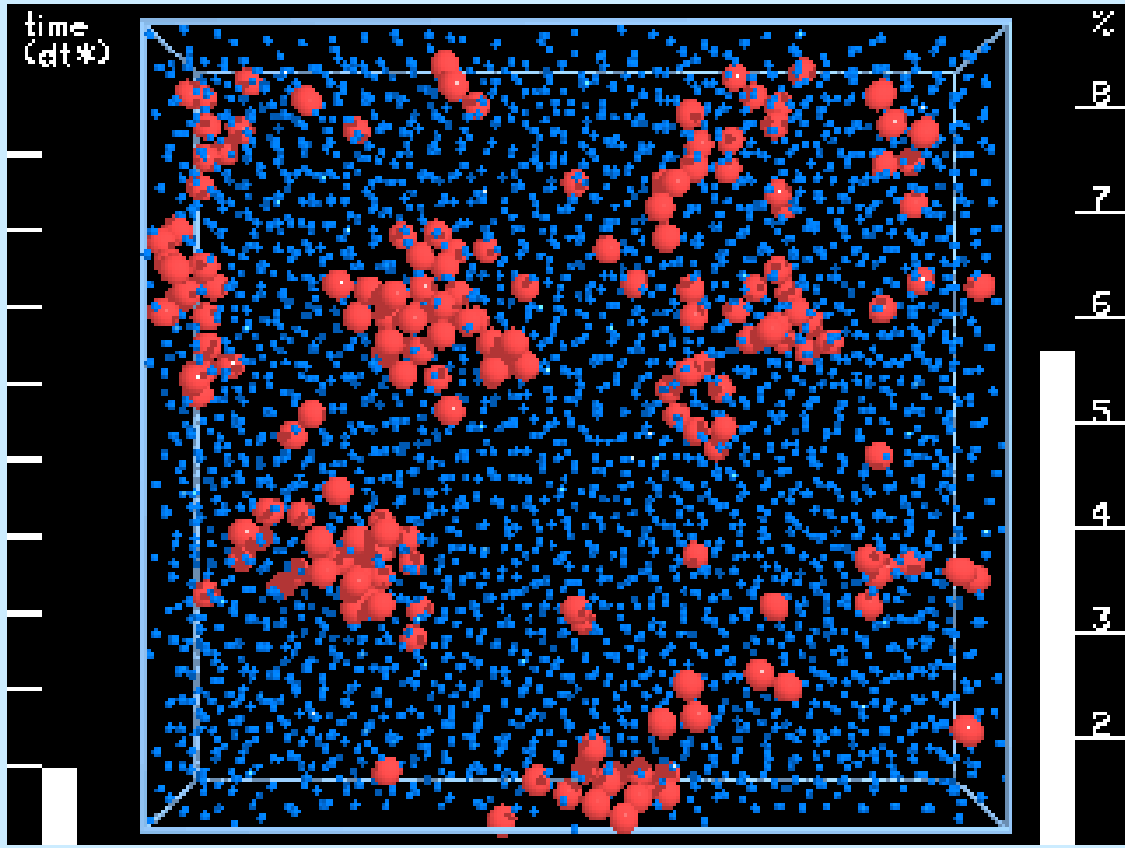


Excellent agreement with Carnahan – Starling (lines)

How to move in a crowd?

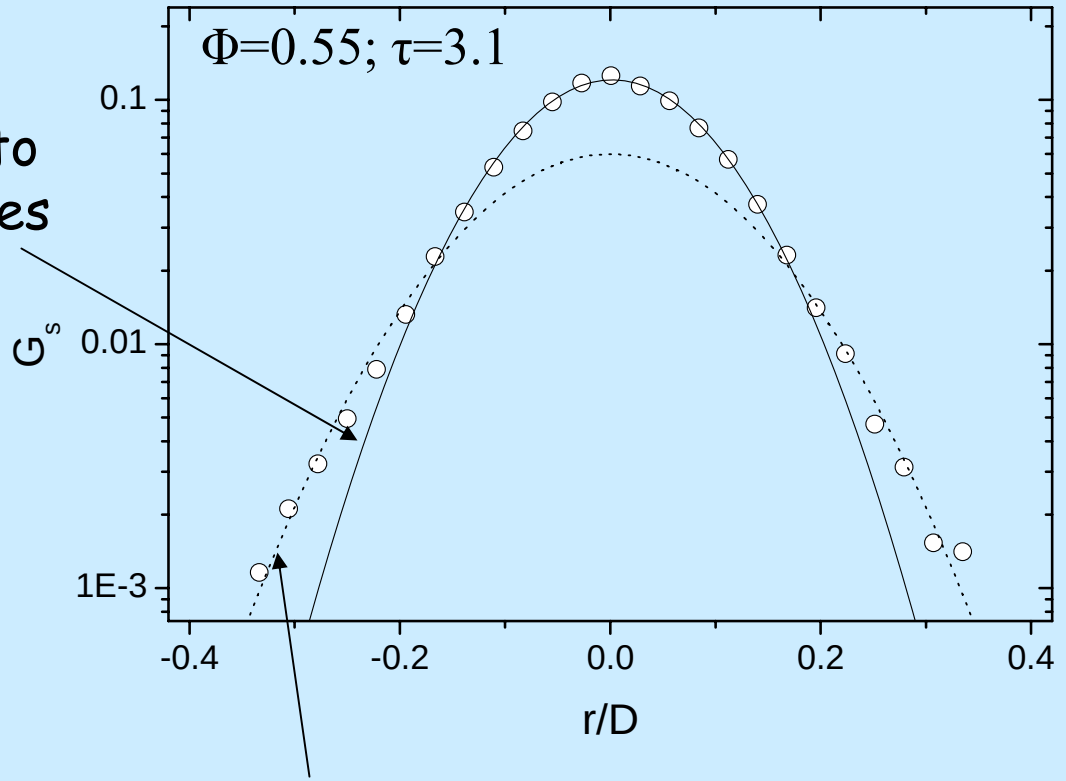
Displacement distributions - Dynamic heterogeneity





[WKK and A. van Blaaderen; E. Weeks ea, Science (2000)];

Consequence of dynamic heterogeneities: non-Gaussian displacement distribution ('Self – van Hove correlation function' G_s)

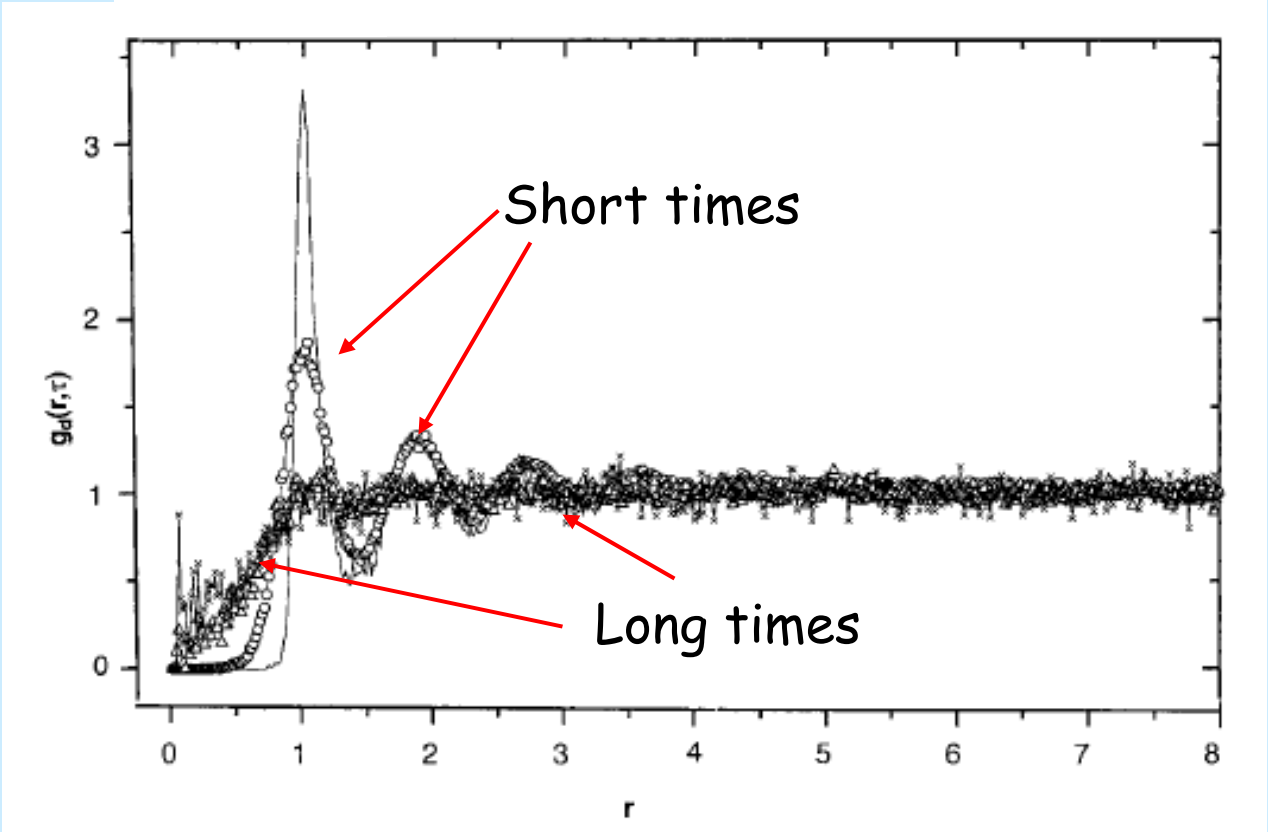


Gaussian fit to all trajectories

Gaussian fit to only fastest ones (> | ±0.175 |)

Distinct van Hove correlation function

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



WKK & AvB
Science 2000

Fig. 5. $g_d(r,\tau) = G_d(r,\tau)/\rho$, where $G_d(r,\tau)$ is the distinct part of the van Hove correlation function, versus r for $\phi = 0.52$, at $\tau = 9.3$ (○), 74.6 (△), and 121.2 (×). The solid line is the pair correlation function $g(r) = g_d(r,\tau = 0)$.

Compute non-Gaussian parameter

$$\alpha_2(\tau) = \frac{< r^4(\tau) >}{3 < r^2(\tau) >^2} - 1$$

for several fractions of particle population. Result:

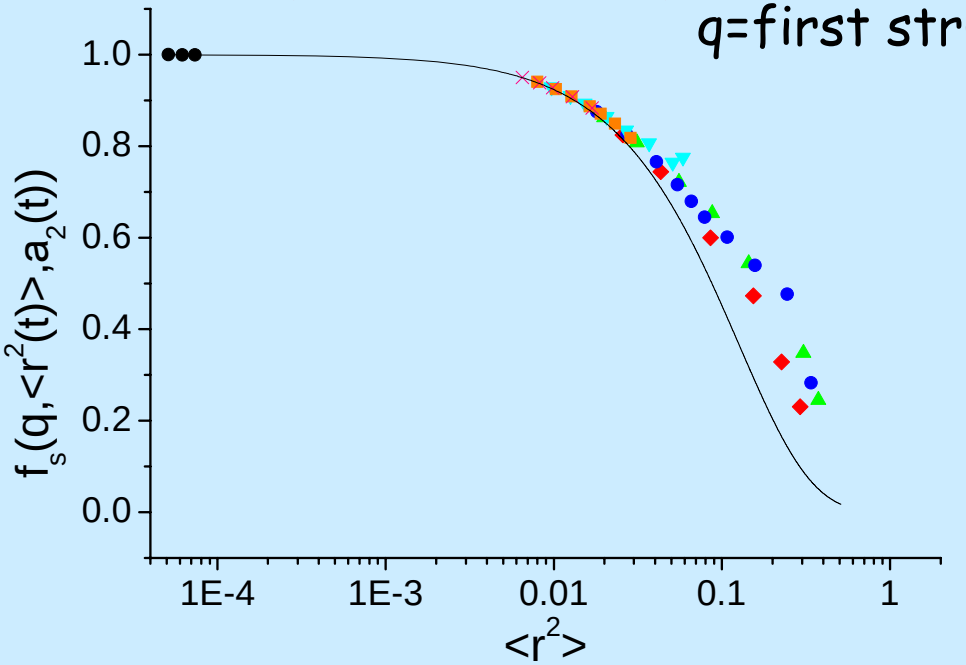
Fraction	α_2	$\sqrt{< r^2 >}$
All	1.14±0.23	0.099
50% slowest	0.31±0.09	0.054
10% slowest	0.17±0.07	0.020
50% fastest	0.58±0.17	0.118
10% fastest	0.00±0.10	0.175

⟶ Dynamical heterogeneities are reflected in a non-Gaussian $G_s(r,\tau)$.

Self-intermediate scattering function vs $\langle r^2 \rangle$

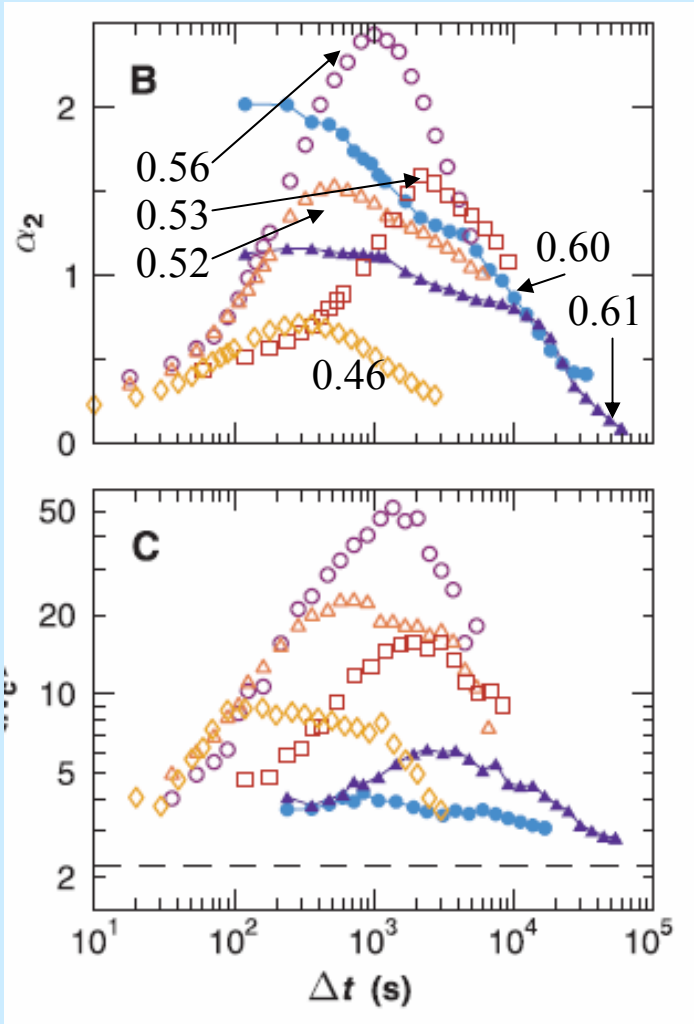
$$f_s(q, < r^2(\tau) >, \alpha_2(\tau)) = \exp\left(\frac{-q^2 < r^2(\tau) >}{6}\right) * \left[1 + \frac{\alpha_2(\tau)}{2}\left(\frac{q^2 < r^2(\tau) >}{6}\right)^2\right]$$

q=first structure factor peak



Deviation from exponential relaxation when particles move (appr.) 0.4R. Also found by [Perera & Harrowell, PRL (1998)] in 2D system. → General feature of glassy liquids?

Characterizing dynamical heterogeneity

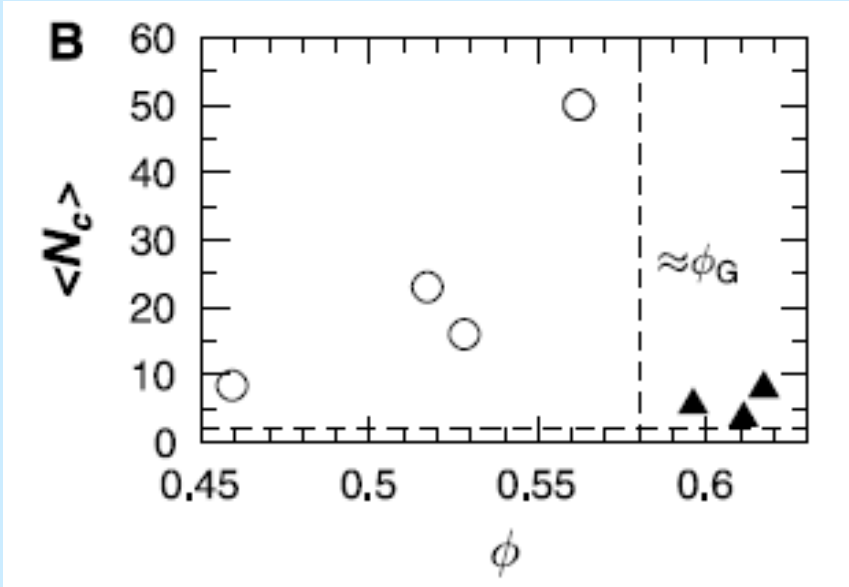


Average 'cluster' size

[E. Weeks ea, Science (2000)];

Average # of particles in fast 'clusters':

[E. Weeks ea, Science (2000)];



Growing 'dynamical length scale' upon approach of glass transition?

* First proposed by:

[G. Adam & J.H. Gibbs, J. Chem. Phys. **43**, 139, (1965)] *

Correlation function to characterize dynamic heterogeneity

Define 'order parameter' $Q(t) = \sum_{i=1}^{N} \sum_{j=1}^{N} w(|\vec{r}_i(0) - \vec{r}_j(t)|)$

w≡ overlap function

# of particles that have not moved
further than some distance a ~ vibrational amplitude

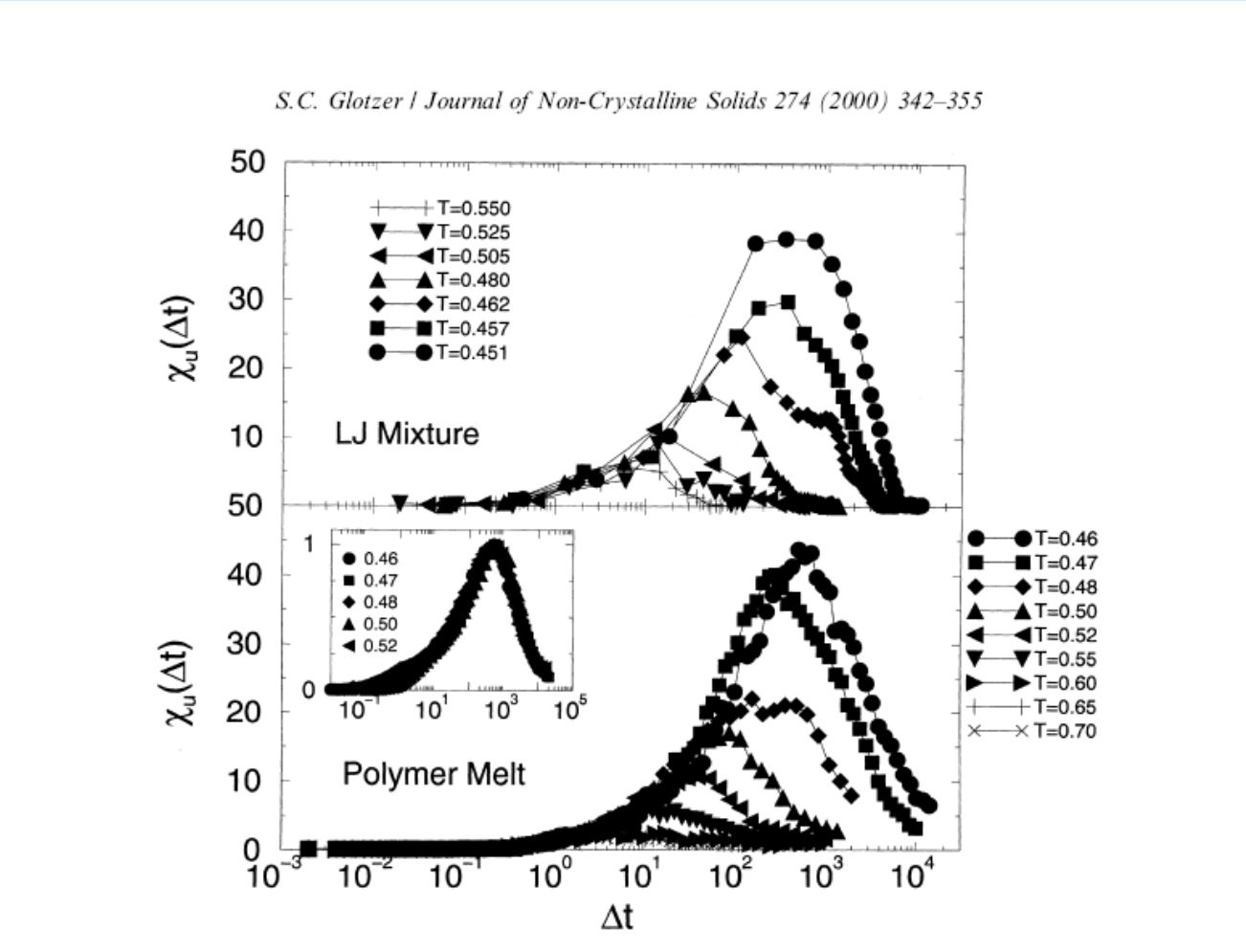
'Dynamic susceptibility' ≡ variance $\chi \sim \langle Q(t)^2 \rangle - \langle Q(t) \rangle^2$

$$\sim \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 G_4(\{\vec{r}_j\}, t)$$

$$G_4(\mathbf{r}_1, \mathbf{r}_2, t) = \langle \Delta\rho(\mathbf{r}_1, 0)\Delta\rho(\mathbf{r}_1, t)\Delta\rho(\mathbf{r}_2, 0)\Delta\rho(\mathbf{r}_2, t) \rangle - \langle \Delta\rho(\mathbf{r}_1, 0)\Delta\rho(\mathbf{r}_1, t) \rangle \langle \Delta\rho(\mathbf{r}_2, 0)\Delta\rho(\mathbf{r}_2, t) \rangle$$

4- point correlation function: lowest order that probes correlated motion

First used by [Dasgupta ea, Europhys. Lett. 15, 467, (1991)].
see, also, e.g, S.C. Glotzer, J. Non-Crystalline Solids **274**, 342, (2000)]



Relation with critical phenomena? –
'diverging susceptibility @ glass transition'
(in dispute)

Do hard sphere glasses really exist? (Y)

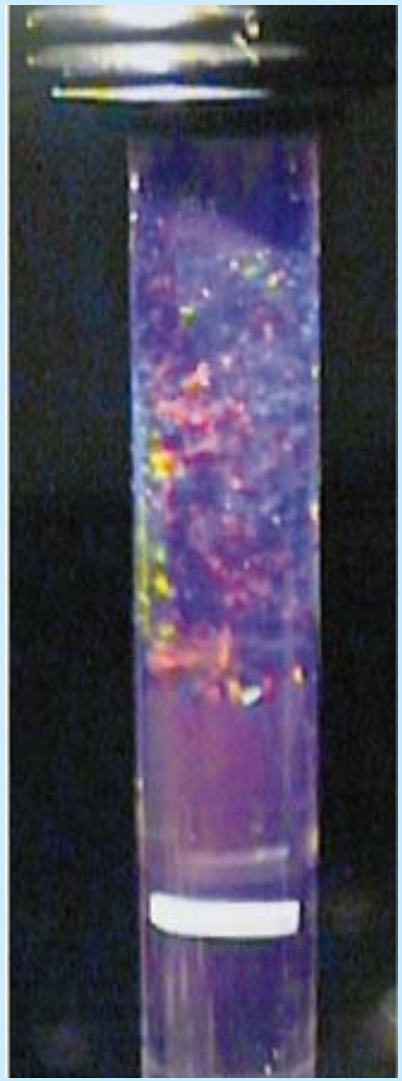
- Yes, experimentally [Pusey & van Megen, Nature 1986]

- Yes, *in computro* [Speedy 1988 ff]

- Yes, and the *glass transition* is well described by mode-coupling theory [Götze & Sjögren, Rep. Prog. Phys. 1992]

Do hard sphere glasses really exist? (N)

- Glass on earth crystallizes in microgravity [Zhu et al. Nature 1997]



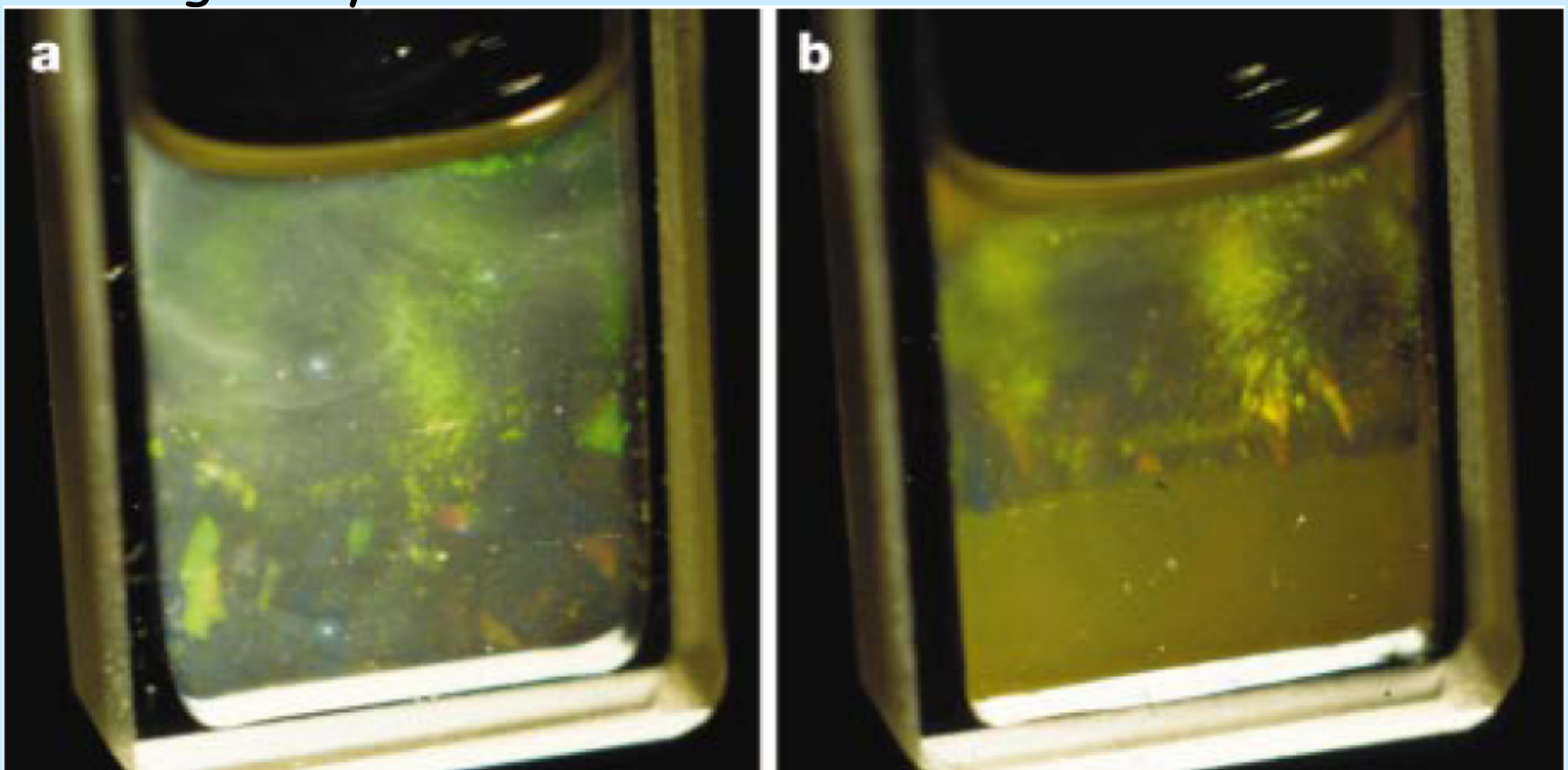
$\phi \sim 0.619$

Do hard sphere glasses really exist? (N)

- No glass *in computro* (large MD simulation; [Rintoul & Torquato, PRL 1996])

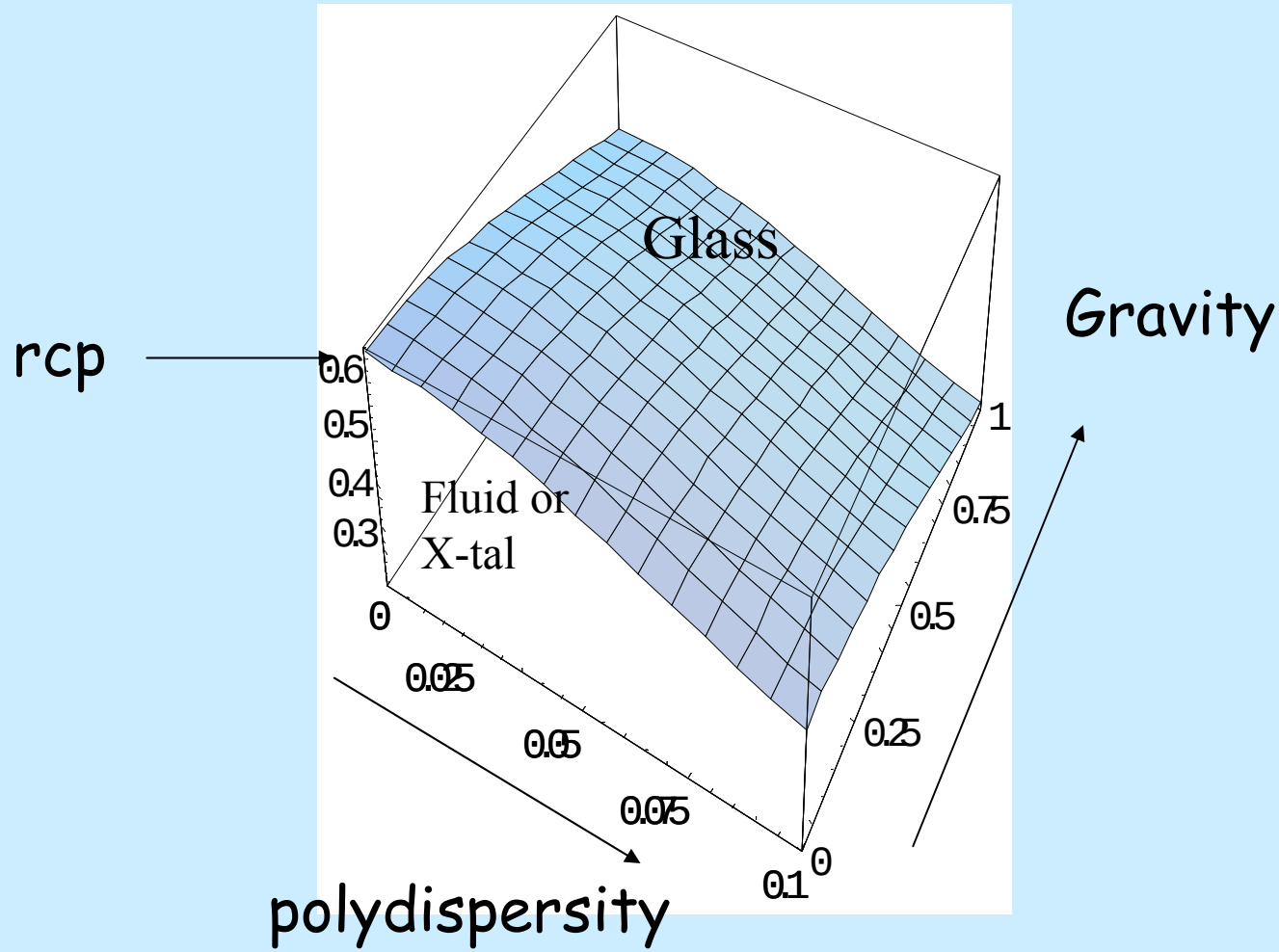
- No glass in milligravity, monodisperse colloids [wkk, Langmuir 2000]

milligravity $\phi \sim 0.63$ Uniaxial stress



Polydispersity and/ or gravity field induce glass in hard sphere colloids

Glass as 'dense metastable fluid':



Another surprise:

Gravity field is weak;

- Gravitational length h=O(10-100) particle diameters
- Displacements typically << particle diameter near GT

- **no qualitative influence of gravity field on (overall) dynamics expected**

Questions:

(How) does gravity influence real-space particle movements?

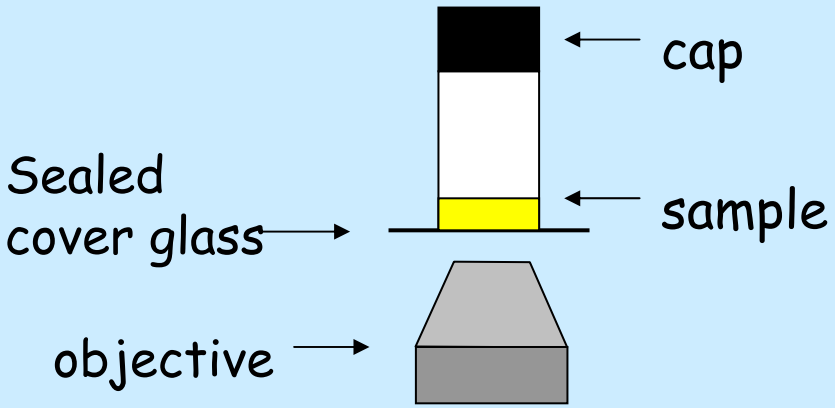
Connection with aging?

Experimental system

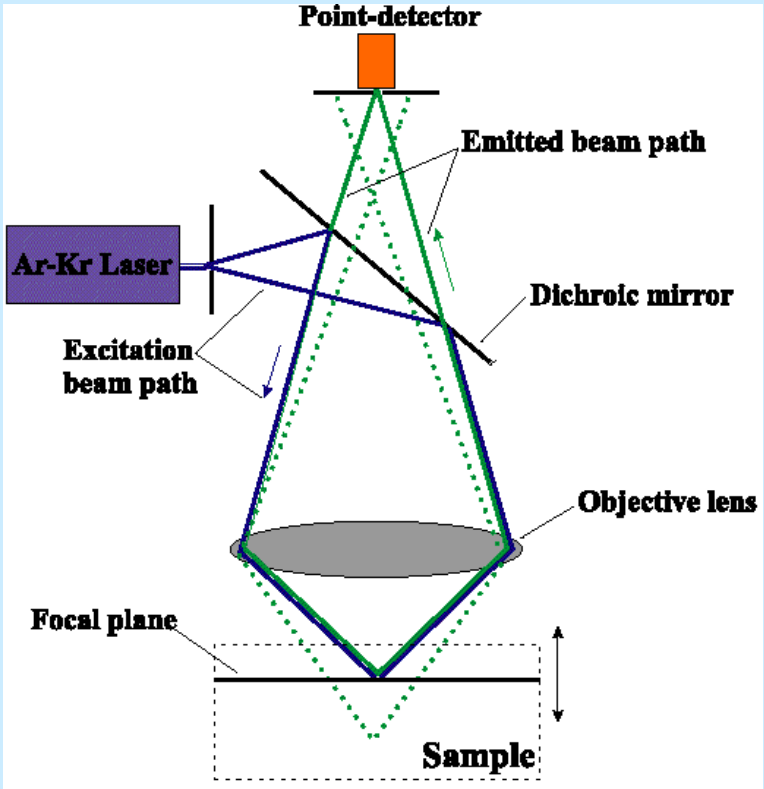
Model particles :
NBD labeled PMMA/ PHS
R≅0.2 μm, **polydispersity 7%** [**Avoids Xtallization**]

Solvents:
a) decalin/ tetralin/ CCl_4 - **density matched/milligravity** h= O(0.1mm)
b) decalin/ tetralin - **"conventional system"** h= O(10 μm)

Technique: CSLM –confocal scanning laser microscopy



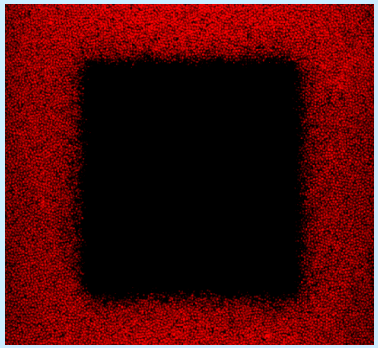
Confocal Scanning Laser Microscopy



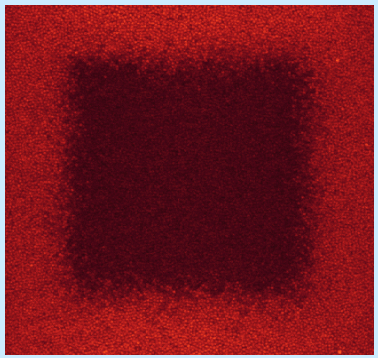
- Fluorescent colloidal particles
- Imaging: scan slices

Method: bleach cubes and monitor intensity profile

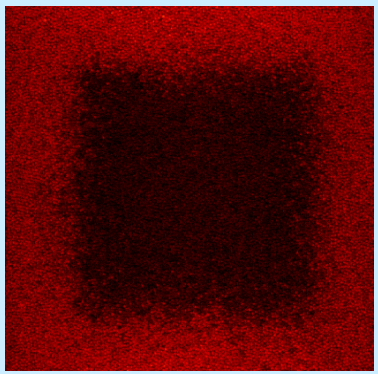
[N. Simeonova & WKK, Faraday Discuss. (2003); Phys. Rev. Lett. (2004)]



τ=4571
(2 min)

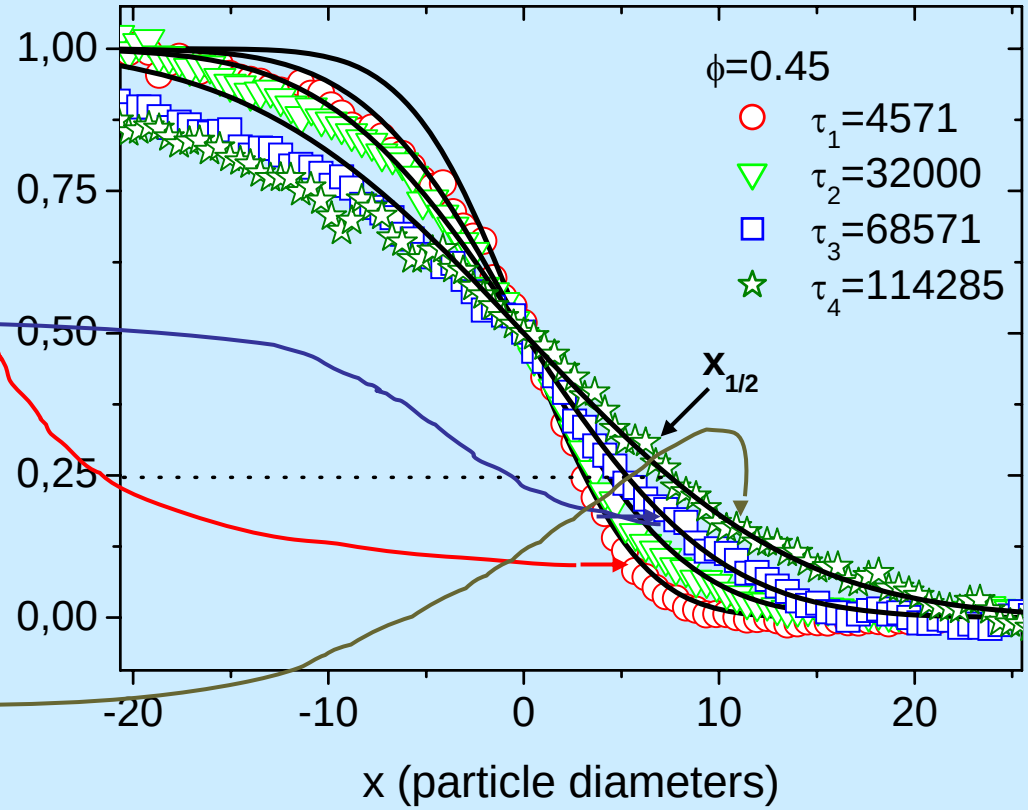


τ=68571
(30 min)



τ=114285
(50 min)

Normalized fluorescence intensity profiles, I(x), of the cubes



$$< x^2 > \approx 2.20 x_{1/2}^2$$

Get $< x^2 > \approx 2.20 x_{1/2}^2$ *via*

$$G_s(x, x_0, \tau) = \sqrt{\frac{1}{4\pi D\tau}} \exp\left(\frac{-(x - x_0)^2}{4D\tau}\right)$$

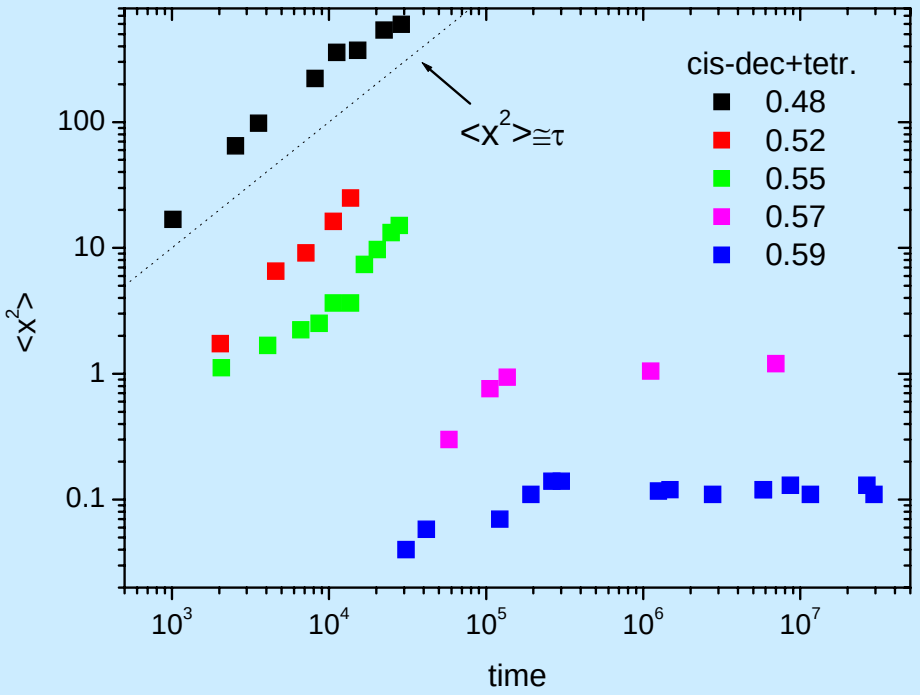
- Integrate over half-space
- Integral proportional to fluorescent intensity profile
- Solve numerivally for $x_{1/2}$
- Compare to $\langle x^2 \rangle = 2D\tau$

N. Simeonova & WKK

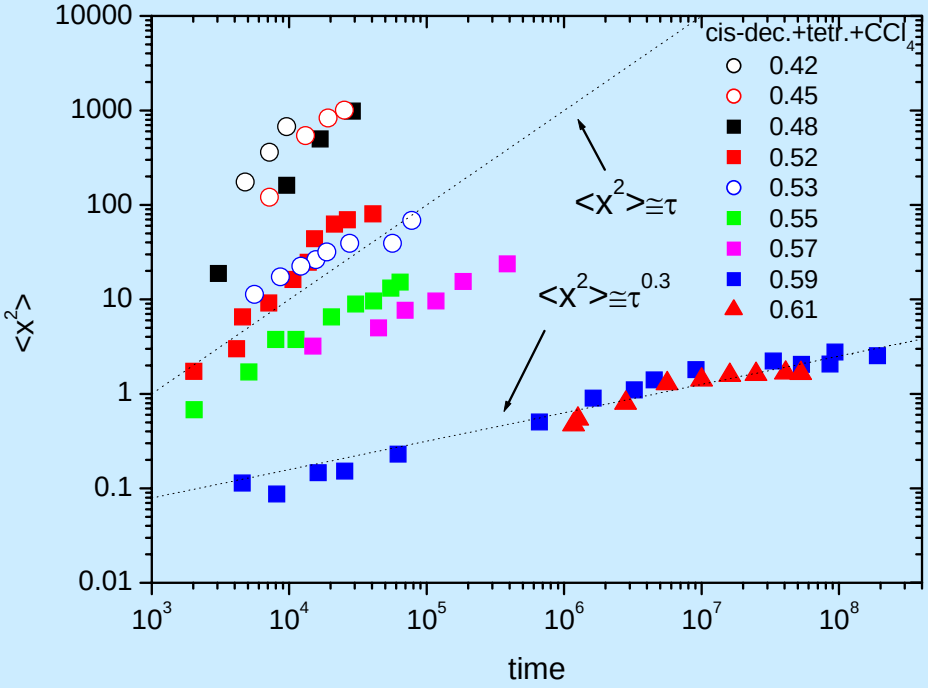
Faraday Discuss., 2003, **123**, 27–35

MSD for different volume fractions in two different solvents

gravity



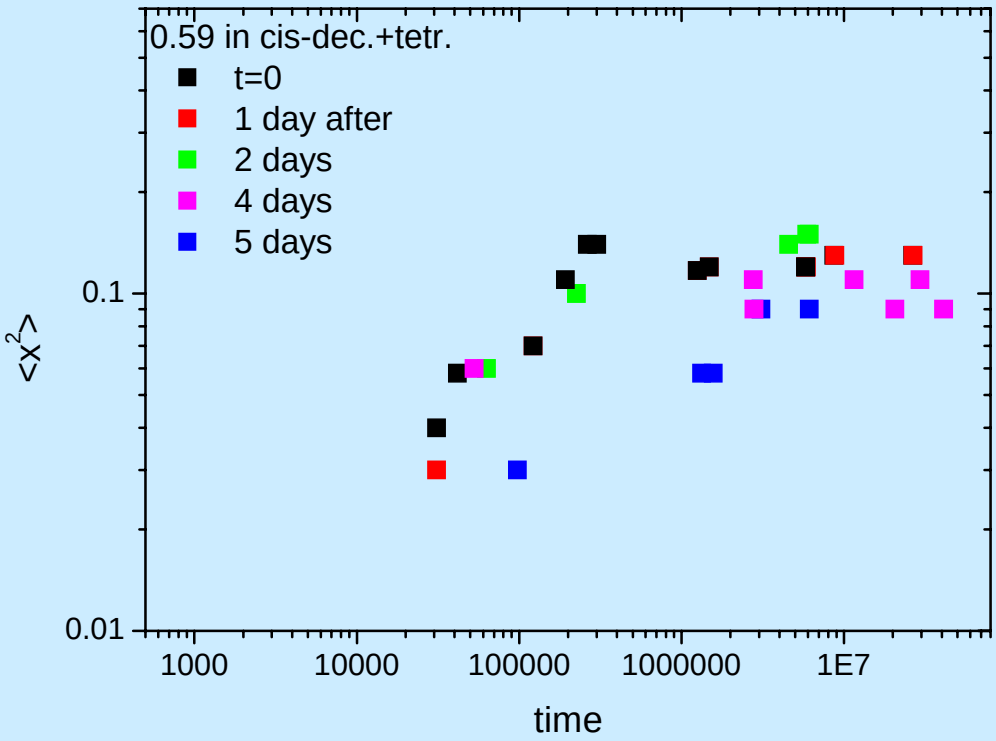
Milligravity



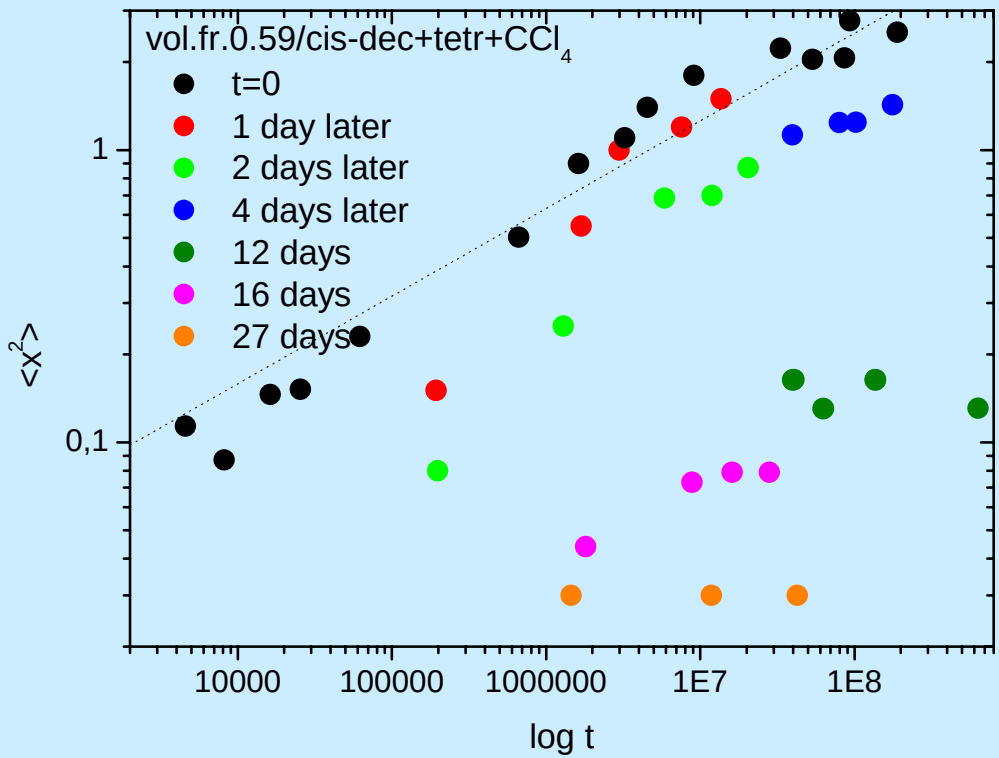
The effect of gravity is negligible for systems with low volume fractions of particles but **dramatic** for concentrated systems

Role of aging?

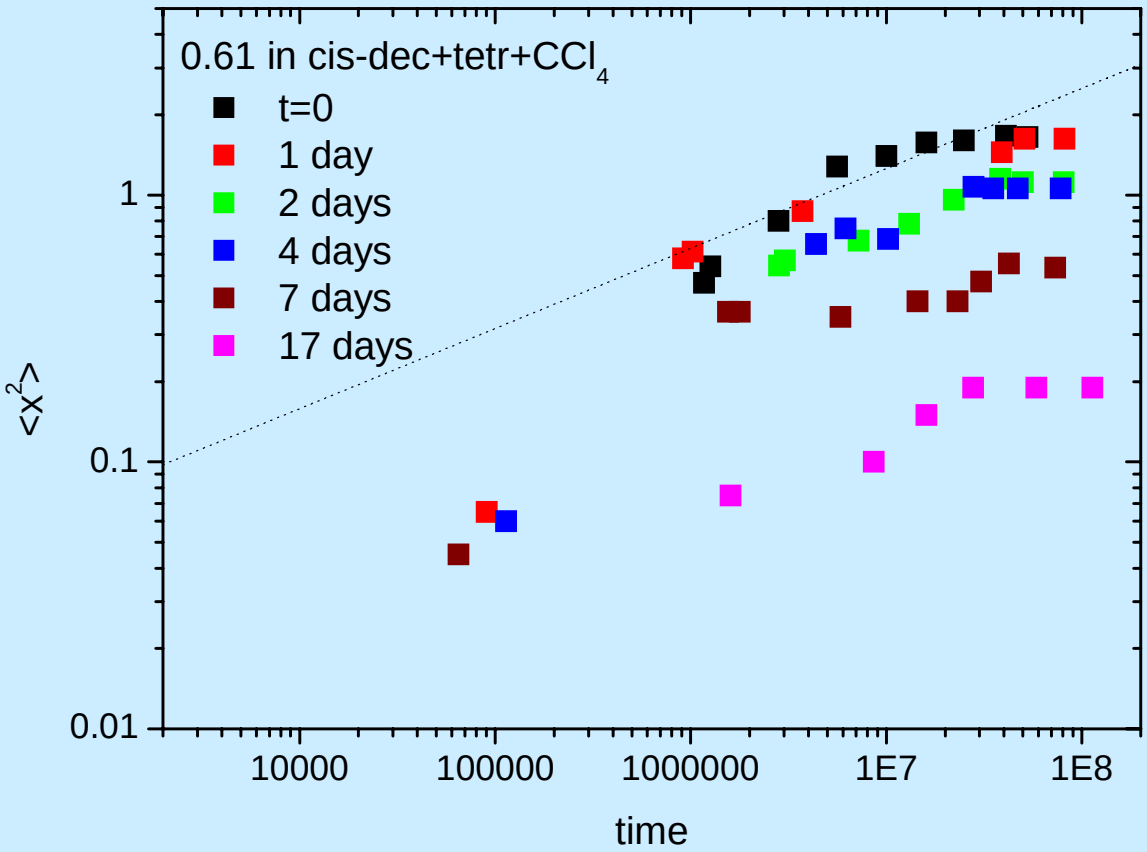
Different t_w for sample with ϕ =0.59 normal gravity



Different t_w for sample with ϕ =0.59 in milligravity



More concentrated system; milligravity



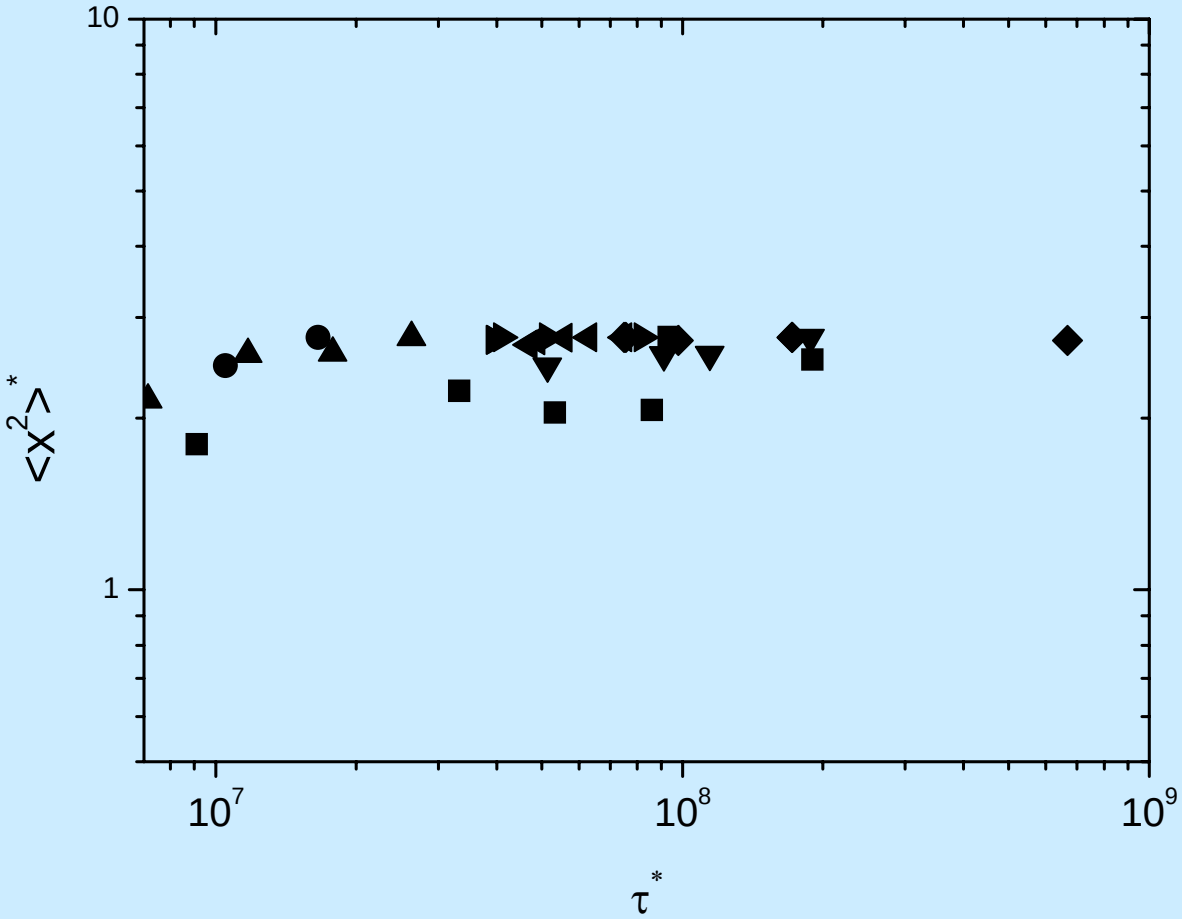
Gravity accelerates aging !

Brownian times >10^7: power-law behavior ambigious

Rescale data to t_w=0: $\tau^* = (\tau + t_w)$

$$\langle x^2 \rangle^* (\tau^*) = [\langle x^2 \rangle (t_w = 0, \tau) + \langle x^2 \rangle (t_w, \tau)]$$

Result:

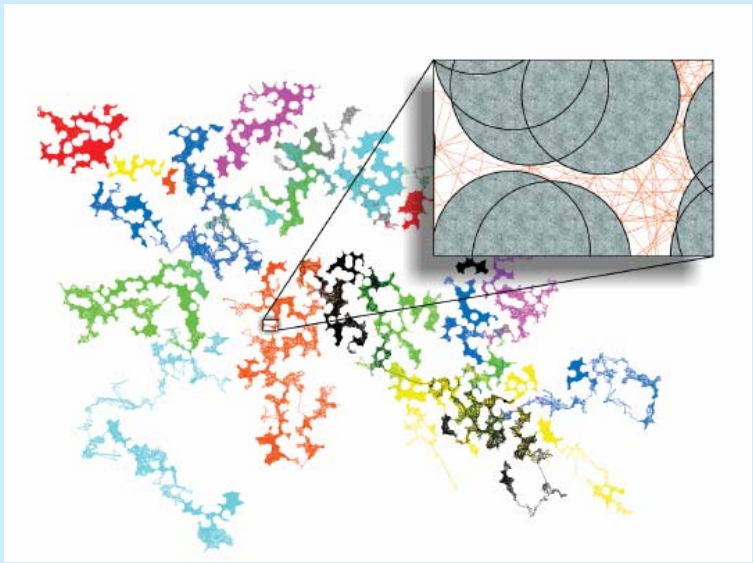


Limiting long time behavior in milligravity of hard sphere glasses:

STILL A PLATEAU in $\langle x^2 \rangle(t)$

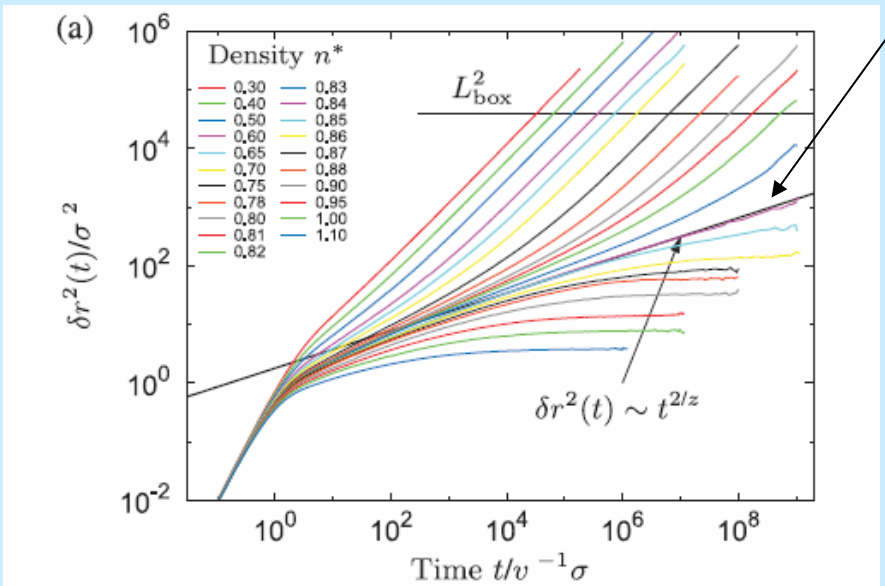
But plateau value of $\langle x^2 \rangle$ order of magnitude higher compared to normal gravity.

Is 'transient' power-law behavior universal?



(3D) Lorenz Model:
'diffusion' around fixed obstacles

Critical line ≡ percolation transition



Increasing obstacle density

z=6.25

[F. Hoffling, T. Franosch, E. Frey, PRL **96**, 165901, (2006)]

Y. Yu & S. Granick – unpublished

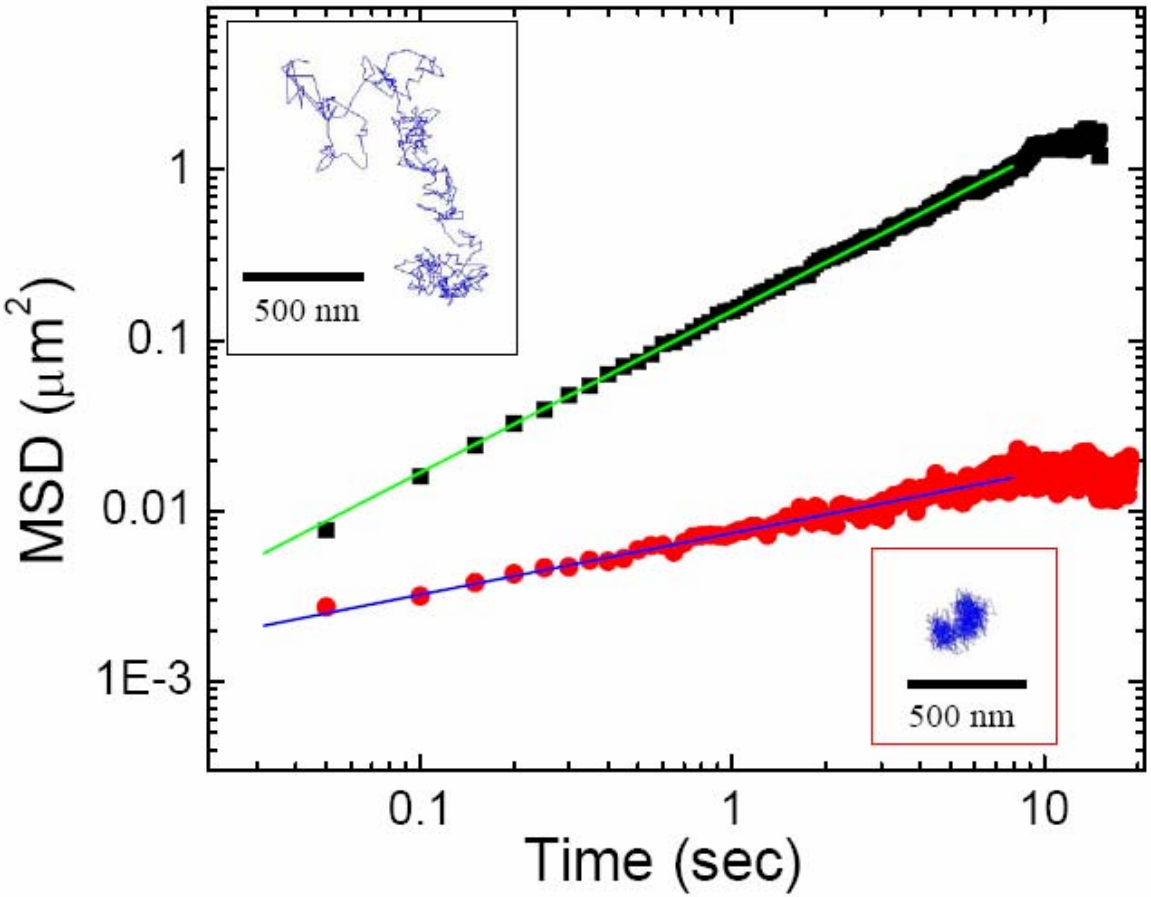
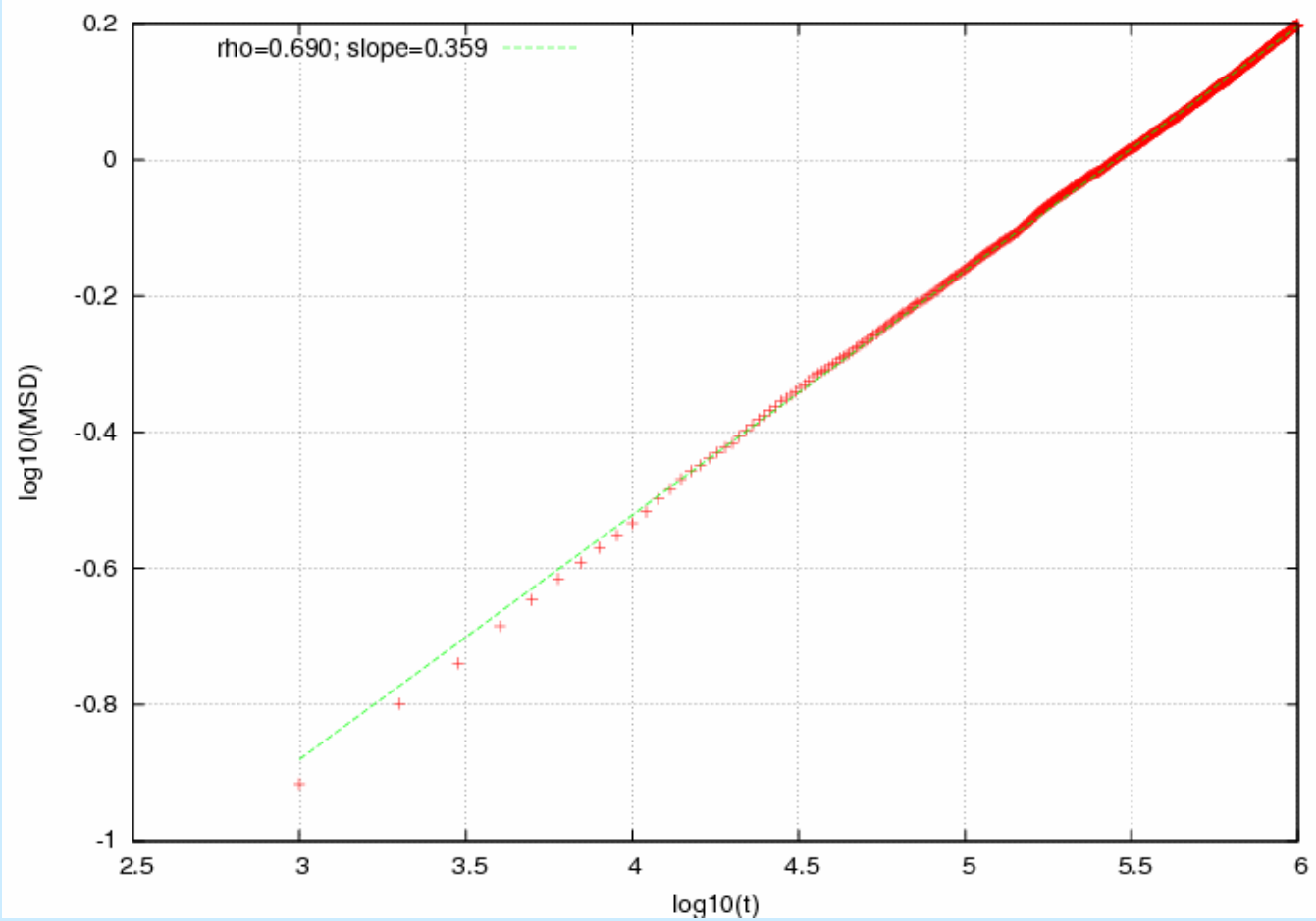


Fig 1. Ensemble MSD (t) of two populations in condensed liposome-nanoparticle complex. Volume fraction of liposomes and nanoparticles $\Phi = 63\%$. The slope is 0.95 for the linear fitting in green and 0.36 for the red one. Similar MSD (t) is observed for samples with volume fraction: 58%, 77% and 79%.

Lattice model

[D. Cellai, …, & K. Dawson] – to be published

See also: [PRL **89**, 245503, (2002)]



Conclusions / open questions

1. Gravity accelerates aging processes in glasses – relaxation of inhomogeneities over length scales > O(10 – 100) particle sizes (?)

2. TRANSIENT REGIME $\langle x^2 \rangle \propto \tau^{0.3}$ over several decades for concentrated colloidal systems in milligravity

…explains why glasses on earth crystallize in microgravity

…but long-time self diffusion is not reached even on Brownian times of $O(10^8)$!

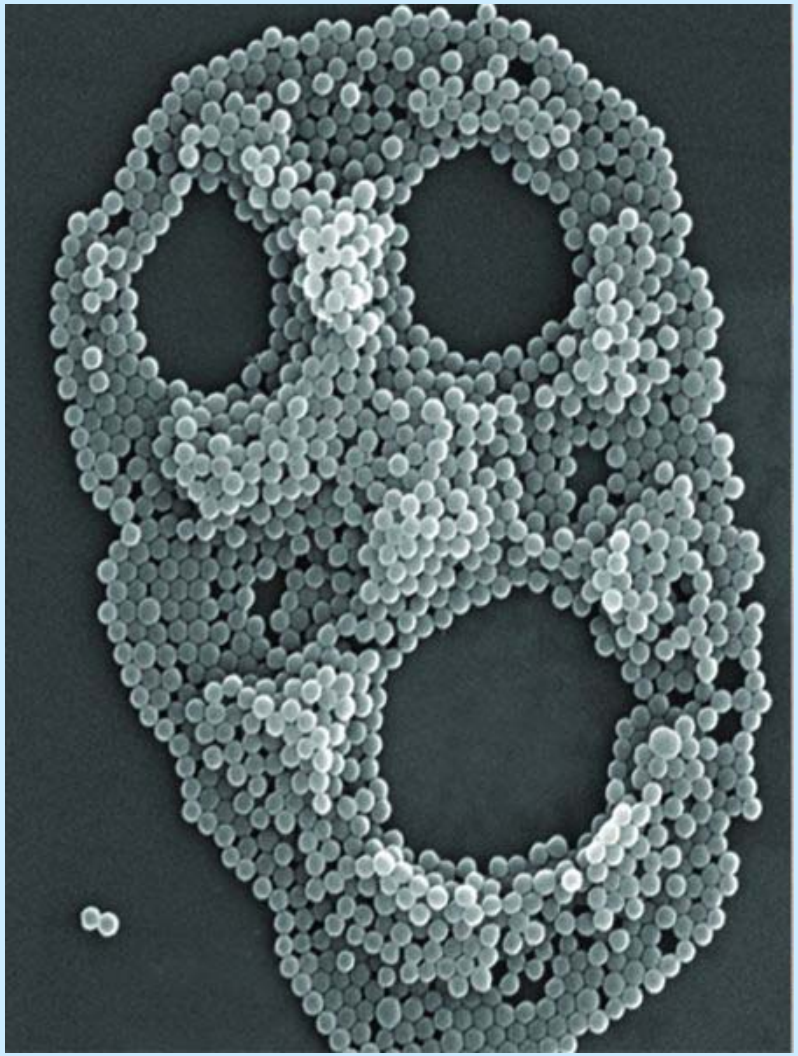
1. By what (microscopic) mechanism does gravity couple to aging in dense colloidal HS systems? Shear inhomogeneities? Dynamic heterogeneity?

2. What happens in zero (or micro) gravity? Still a plateau of $\langle x^2 \rangle$ vs. t ? Power law? Long-time self diffusion? Or something else? - answer from space / simulation

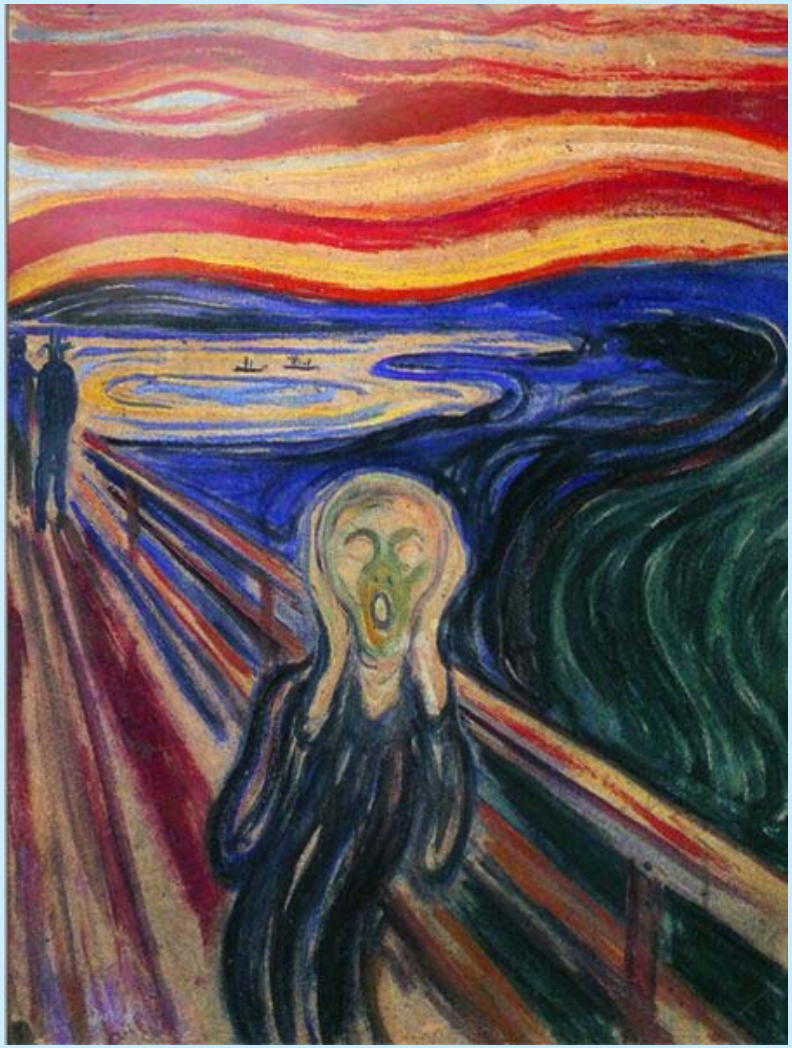
Thank you!

And:
Nikoleta Simeonova
Roel Dullens
Dirk Aarts
Gilles Bosma

FOM
NWO-CW



PMMA particles



Munch, (1893)

Colloidal art by Elise Beynon (2004)