Studying the glass transition with confocal microscopy

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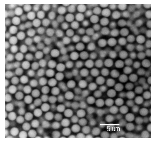
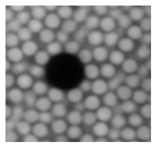
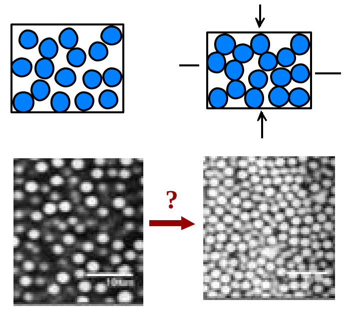
Funding by NSF-CAREER, NASA/PECASE
Colloidal particles from Andrew Schofield, University of Edinburgh

http://www.physics.emory.edu/~weeks/lab/





Basic idea: increasing density causes a glass transition. What do colloidal suspensions teach us about glass transitions?



Why study the glass transition?

" The nature of glass transition is one of the oldest unsolved questions in condensed matter physics."

A.J. Liu and S.R. Nagel, Jamming and Rheology (2001)

" The deepest and most interesting unsolved problem in solid state theory is probably the nature of glass and the glass transition. This could be the next breakthrough in the coming decade." P.W. Anderson, Science **267**, 1615 (1995)

GLASS TRANSITION:
The viscosity of the liquid is 10^{13} larger than that of water - arbitrary

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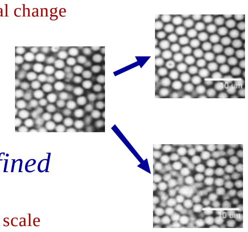
Regular phase transitions

- Obvious microscopic structural change *(symmetry, order parameter)*



Glass transition: *ill-defined*

- Viscosity grows *(diverges?)*
- No divergent structural length scale *(structure unchanged at transition)*
- Theories incomplete & conflicting *(mode coupling describes colloids!)*

Glass transition: *is there a secret length scale?*

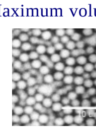
- No divergent structural length scale *(structure unchanged at transition)*

What other ways can we see a length scale?

1. Dynamical heterogeneities
2. Confinement
3. Stirring with magnetic beads
4. Poking with magnetic beads *(if time)*

Colloidal glass transition

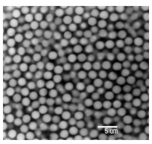
- Control parameter is volume fraction ϕ
- Glass exists when $\phi > \phi_g \approx 0.58$ (agrees with simulations with slight polydispersity)
- Diffusion constant → 0
- See aging behavior (Courtland & Weeks '03; Cianci, Courtland, Weeks '06)
- Maximum volume fraction $\phi_{RCP} \approx 0.64$



Experimental Details

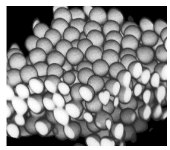
- 2.3 µm diameter PMMA colloids
- density matched solvent (cyclohexylbromide + decalin)
- slightly charged hard spheres

- confocal microscopy to take 3D pictures
- look > 30 µm from sample chamber walls



single 2D image

3D reconstruction from many 2D slices



Brownian Motion in dilute samples

Leads to normal diffusion:

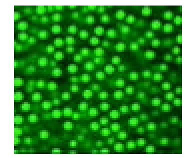
$\langle \Delta x^2 \rangle = 2Dt$

$$D = \frac{k_B T}{6\pi\eta a}$$

viscosity η

particle size *a*

2 µm dia particles



5 µm

Stokes-Einstein-Sutherland equation

$$D = \frac{k_B T}{6\pi\eta a}$$

Derived in 1905:
A. Einstein, *Ann. der Physik*, 17, 549.
W. Sutherland, *Phil. Mag.*, 9. 781.

Willian Sutherland in his twentieth year.

www.aapps.org/archive/bulletin/vol15/15_1/15_1_p35p36.pdf
antwrp.gsfc.nasa.gov/ apod/ap000108.html

Stokes-Einstein-Sutherland equation

$$D = \frac{k_B T}{6\pi\eta a}$$

On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat
Einstein, *Annalen der Physik*, 17(1905), pp. 549-560.

Implication: Avagadro's number

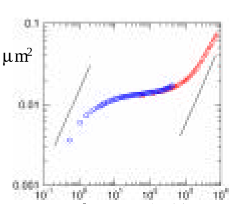
A dynamical theory of diffusion for non-electrolytes and the molecular mass of albumin
Sutherland, *Philosophical Magazine*, S.6, 9 (1905), 781-785.

Implication: size of albumin

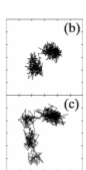
See: www.aapps.org/archive/ bulletin/vol15/15_1/15_1_p35p36.pdf

Mean square displacement– dense samples

$\langle x^2 \rangle$ µm^2



lag time Δt (s)



0.5 µm

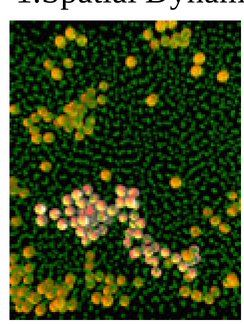
Short times:
particles stuck in "cages"

Long times:
cages rearrange

($\phi \approx 0.52$, 2 hours)

Weeks & Weitz, *Chemical Physics* **284**, 361 (2002)
Weeks & Weitz, *Phys. Rev. Lett.* **89**, 095704 (2002)

1.Spatial Dynamical Heterogeneity



Large particles = most mobile at this time
Small particles = less mobile

$\phi = 0.56$, $\Delta t = 1000$ s,
$\Delta r > 0.5$ µm

Weeks et al., *Science* **287**, 627 (2000)

Dynamical Heterogeneity: possible *dynamic* length scale

Molecular Experiments:

- Schmidt-Rohr & Spiess (1991, NMR of polymers)
- Tang, Johnson, et al (1998, NMR of metallic glasses)
- Sillescu et al (1992, NMR of o-terphenyl)
- Cicerone & Ediger (1995, photobleaching of OTP)
- Russell & Israeloff (2000, AFM study of polymers)
- Deschenes & Vanden Bout (2001, tracers in polymers)

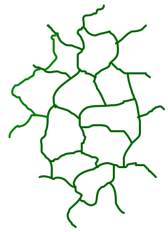
Colloidal Experiments:

- Marcus, Schofield & Rice (1999, 2D colloids)
- Kegel & van Blaaderen (2000, 3D hard spheres)
- Weeks et al (2000+, 3D charged spheres)

Simulations:

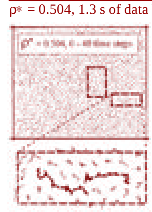
- Harrowell, Hurley, Perera (1996+, 2D soft disks)
- Glotzer, Kob, Donati, et al (1997+, Lennard-Jones)
- Yamamoto & Onuki (1997+, soft spheres)
- Doliwa & Heuer (1998+, hard spheres)

Adam & Gibbs, '65: "**cooperatively rearranging regions**"



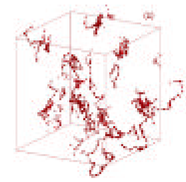
Particles follow neighbors

AH Marcus et al
PRE '99
2D Colloidal hard spheres, 0.93 μm diameter
ρ* = 0.504, 1.3 s of data below



C Donati et al., PRL '98
Binary Lennard-Jones mixture

R Yamamoto & A Onuki
JPhys:Cond Mat '00
Binary soft sphere mixture



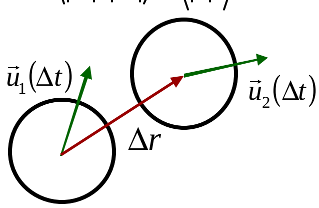
Correlation Functions

ER Weeks, JC Crocker, DA Weitz – in preparation
based on Doliwa & Heuer, PRE (2000)

Avoid defining "special" particles

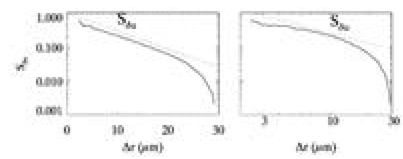
➢ "Mobility" correlation function:

$$S_{du}(\Delta r, \Delta t) \approx \langle |u_1| \cdot |u_2| \rangle - \langle |u| \rangle^2$$

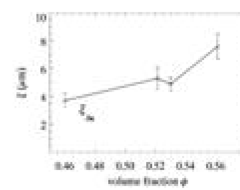


Larger separation: exponential decay

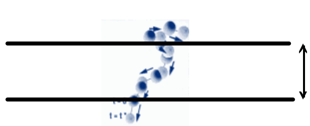
E. R. Weeks, J. C. Crocker, D. A. Weitz (in preparation)



slight growth in decay length as $\phi \rightarrow \phi_g$



2. Confine samples to influence mobile clusters



~ few particle diameters

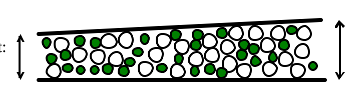
Use thin sample chamber, different way to probe length scale

Previous work: T_g can increase or decrease!
Excellent review: GB McKenna, *J. Phys.:Cond. Mat.*, 2005

Examine confined samples

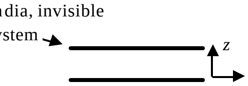
Carrie Nugent, Kazem Edmond, Hetal Patel, Eric Weeks
cond-mat/0601648

Thinnest: ~ 4 μm

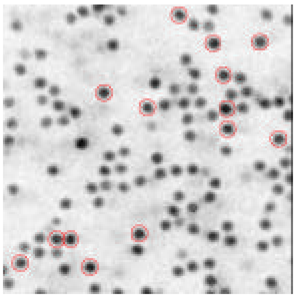


Thickest: > 60 μm

- Wedge-shaped sample chambers (~ 0.5° angle)
- Two particle sizes ("binary" sample)
  - ➢ small: 2.2 μm dia, fluorescent
  - ➢ large: 3.1 μm dia, invisible
- Note coordinate system



Boundary conditions: some particles stuck to surfaces



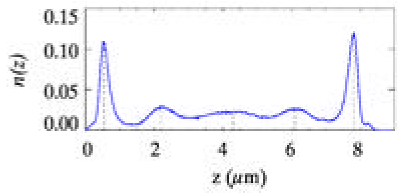
50 µm

Image of particles at coverslip. Circled ones are stuck.

Also some invisible particles present: some stuck and some mobile.

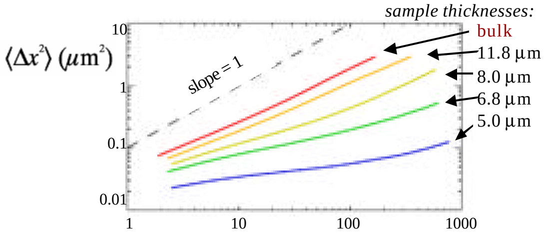
Walls induce layering

(like Mark Robbins showed yesterday)



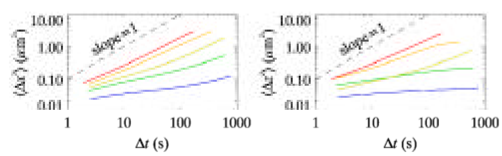
thickness = 8.02 µm measured center-to-center of stuck particle layers; add 2.1 µm for diameter of stuck particles

Confinement slows motion parallel to walls



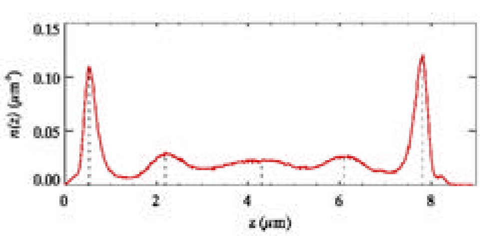
Onset of slowing = 12 µm ≈ 6 small diameters ≈ 4 large diameters

Confinement greatly slows motion perpendicular to walls



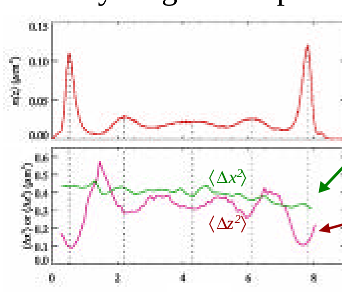
thicknesses: bulk, 11.8, 8.0, 6.8, 5.0 µm

Walls induce layering



thickness = 8.02 µm measured center-to-center of stuck particle layers; add 2.3 µm for diameter of stuck particles

Layering affects particle motion



Motion parallel to walls unaffected by proximity to walls

Motion perpendicular to walls slows near walls, slows in layers

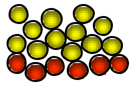
Dt = 100 s

Boundary conditions important

Simulations (Kob '02, Löwen '99) and experiments suggest:

? rough walls = slow motion, $T_g \uparrow$

? smooth walls = fast motion, $T_g \downarrow$



simulated rough wall

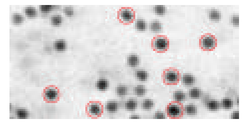
Our experiments have "rough" walls…

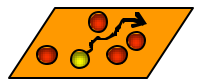
Boundary conditions important

Simulations (Kob '02, Löwen '99) and experiments suggest:

? rough walls = slow motion, $T_g \uparrow$

? smooth walls = fast motion, $T_g \downarrow$





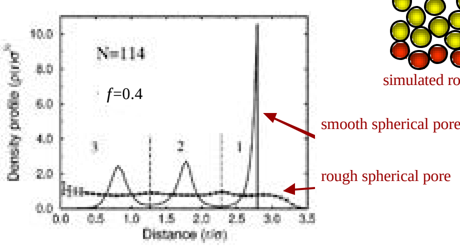
Our "rough" walls formed by stuck particles: hinder motion in x

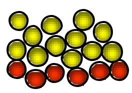
But: at walls we see x motion same as interior, whereas z slowed

Boundary conditions important

Simulations show rough walls frustrate layering:

ZT Németh & H Löwen, *Phys Rev E* 59, 6824 (1999)





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Boundary conditions important

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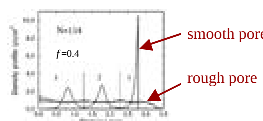
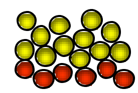
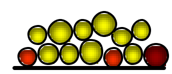
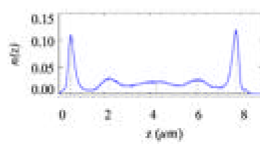




simulated rough wall



experimental rough wall



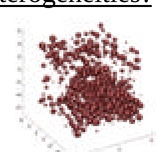
Our work: roughness broadens 1^{st} layers: but binary sample frustrates layering already

Boundary conditions important

Another idea: "rough" ≈ "strong interaction" (to slow down motion of particles near surface)

Perhaps in our experiment, hydrodynamic interaction with wall is important. Our future work will examine completely smooth walls.

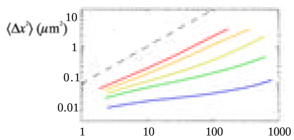
What about dynamical heterogeneities?



- Bulk sample: no large mobile clusters
- Slowing shows confinement length scale ~6 particle diameters

- Agrees with simulations of Kob et al ('02): length scale for confinement is 3× larger than size of mobile clusters

Summary of part 2: Confinement slows dynamics



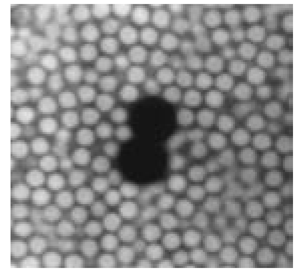
- Bulk sample too dilute for mobile clusters
- Slowing indicates confinement length scale 12 μm
- Motion perpendicular to walls slowed even more

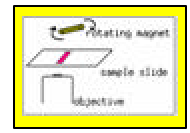
see cond-mat/0601648 for more details

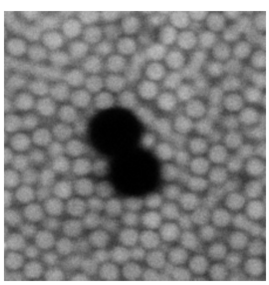
3. Rotational perturbations

Piotr Habdas & Eric Weeks, Emory University

Add 5 μm diameter superparamagnetic particles. Some form dimers: rotate them!



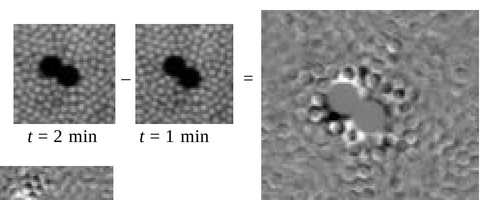




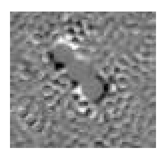
Local response to perturbations

Rotation rate = 1.25 rev/hr
(rotates 10° between pictures)

$\phi \approx 0.57$, $Pe^* \approx 6$

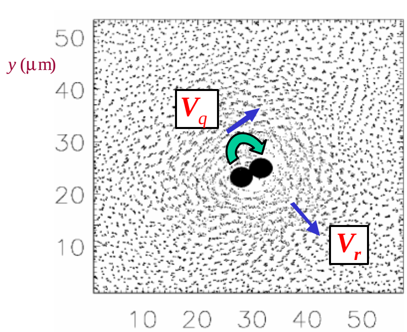


t = 2 min t = 1 min

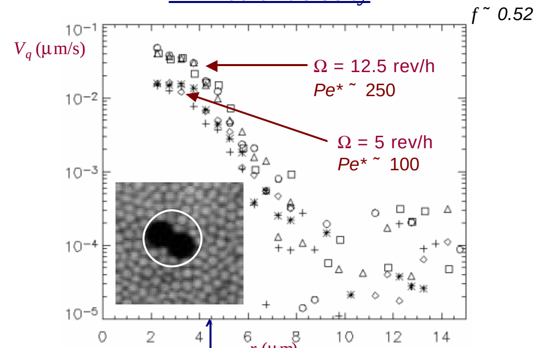


a trimer ←

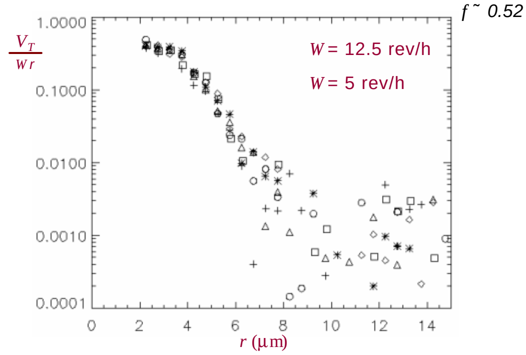
Azimuthal and Radial Velocity



Azimuthal Velocity

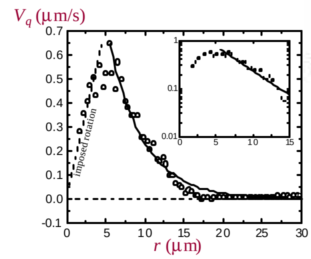


Normalized Azimuthal Velocity Profiles



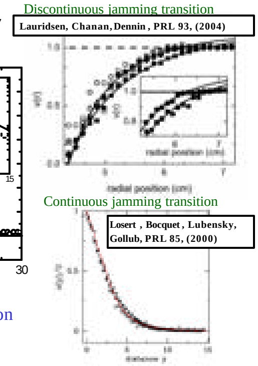
Azimuthal Velocity Profiles

Ω = 12.5 rev/h, φ ≈ 0.56, Pe* ≈ 17



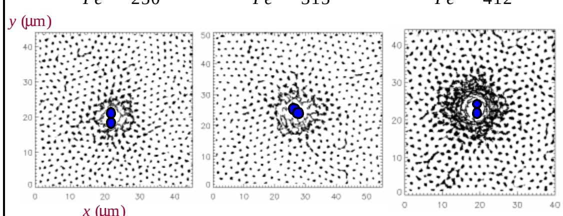
Discontinuous jamming transition

Habdas, Schaar, Levitt, Weeks, Europhys. Lett 67, (2004)



Local Response to Perturbations

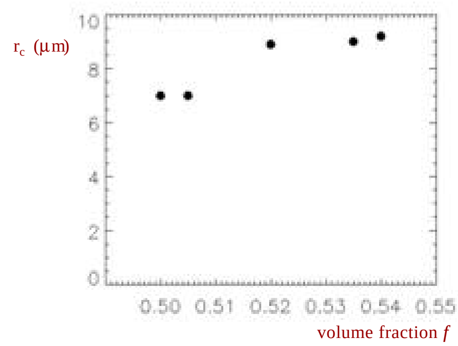
W = 12.5 rev/h one full rotation



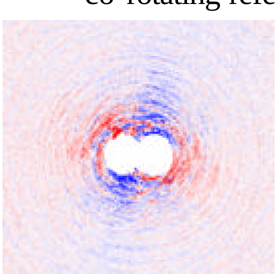
f ˜ 0.52 f ˜ 0.53 f ˜ 0.55

→ f

Decay length vs. volume fraction



Preliminary: looking at Dr in co-rotating reference frame



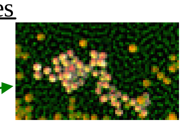
dimer rotating clockwise

blue = motion toward center
red = motion away from center

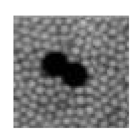
f ≈ 0.55
W = 12.5 rev/h

Summary: search for length scales

(Based on particle radius *a*)



* Dynamical heterogeneity: 4*a* – 8*a*
* Confinement: ~ 6*a*
* Rotating magnetic dimer: 7*a* – 10*a*



Weeks et al., Science **287**, 627 (2000) – dynamical heterogeneities
Nugent et al., cond-mat/0601648 – confinement
Habdas et al, Europhys Lett. **67**, 477 (2004) – magnetic beads

Movies, reprints, & free particle tracking software:
www.physics.emory.edu/~weeks/lab/