Colloids

1 nm - 10 μm solid particles in a solvent

Ubiquitous

ink, paint, milk, butter, mayonnaise, toothpaste, blood

Suspensions can act like both liquid and solid

Modify flow properties

Model System

- Slower dynamics:
  - $\tau \sim 10^{-5}$ to 10^{-1} sec
- Larger scale

Use light scattering methods

Control: Size, uniformity, interactions

→ ENTROPY IMPORTANT !

→ T → ϕ : NEW THERMODYNAMIC VARIABLES.

COLLOIDS ARE

① "BIG"

~1 μm. (10 nm → 10 μm)

- CAN "SEE" THEM

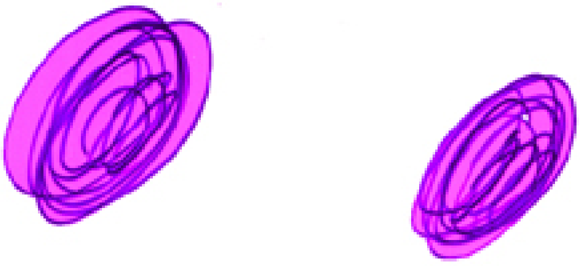
② SLOW

$\tau \sim \frac{a^2}{D}$ > ms → sec.

→ WATCH INDIVIDUAL PARTICLES MOVE.

→ MODEL : EACH COLLOID → LIKE AN ATOM.

INTERACTIONS



COLLOIDS ARE THERMALIZED

$E \sim k_B T.$

THERMAL HEIGHT

$$\Delta m g h = kT$$

$$h = \frac{kT}{\frac{4\pi}{3} a^2 \Delta\rho\, g}$$

THERMAL MOTION

→ COLLISIONS

∴ COLLISION RATE

$R_c \sim a\,C\,D$

PHYSICS: – DIFFUSIVE FLUX ONTO A SPHERE

– TIME TO EXPLORE MEAN INTERPARTICLE <u>VOLUME</u>

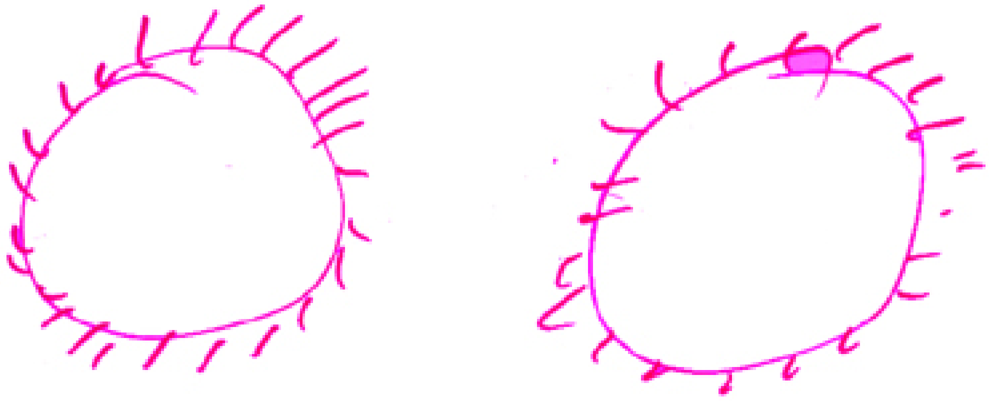
MUST BE <u>STABILIZED</u>

→ SHORT RANGE REPULSION

→ KEY TO COLLOID STABILITY.

SIMPLEST STABILITY

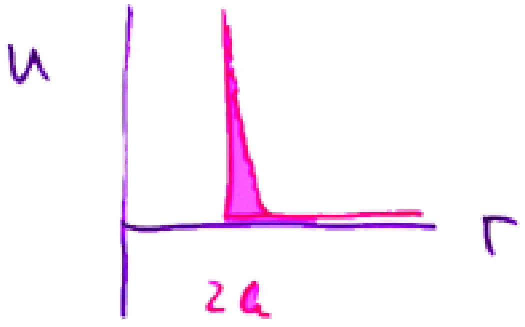
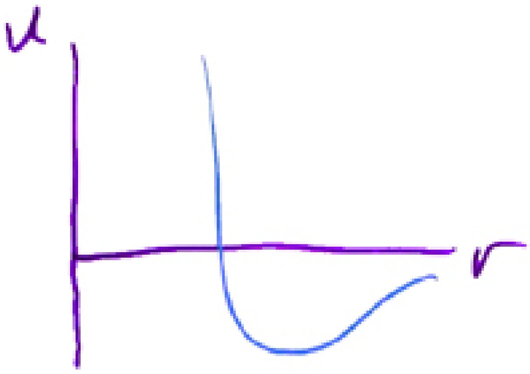
→ VERY SHORT RANGE REPULSION



STERIC STABILITY.

MANY OTHERS POSSIBLE

SOFT SOLIDS

COLLOIDS	ATOMIC SOLIDS
	
HARD SPHERES	LEONARD-JONES
OSMOTIC PRESSURE	ATTRACTION
CENTRO-SYMETRIC	CENTRO-SYMETRIC
THERMALIZED $k_B T$	THERMALIZED

GAS, LIQUID, SOLID } DENSITY { GAS, LIQUID, SOLID

PHASE BEHAVIOR IS <u>SAME</u>

Soft Solids

Elastic Constant: $\frac{\text{Energy}}{\text{Volume}}$

Colloids: $\frac{k_B T}{\mu m^3}$ **~Pa**

Atoms: $\frac{eV}{\text{Å}^3}$ ~GPa

Colloidal Particles:
- Slow speed
- Large size (microns)

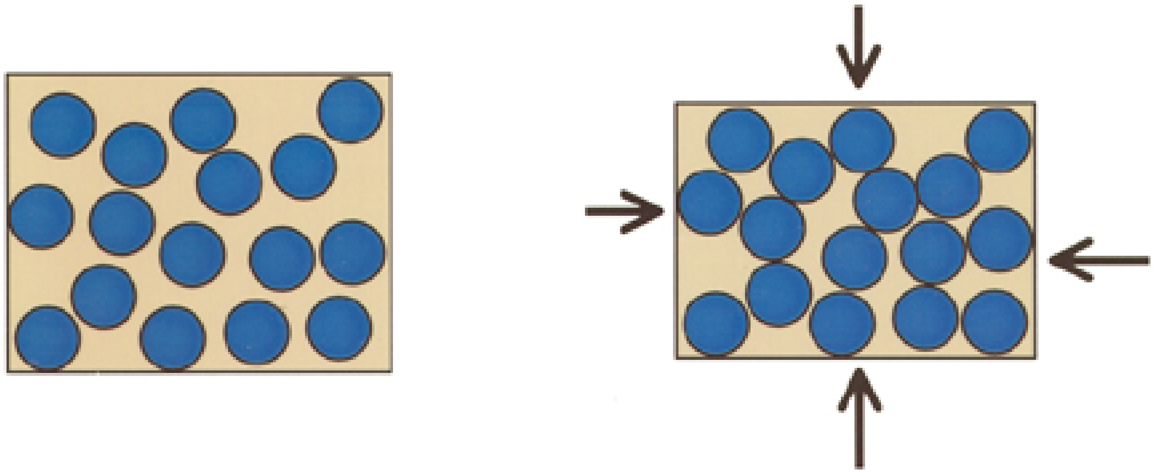
$\tau \sim \frac{k_B T}{\eta a^3}$

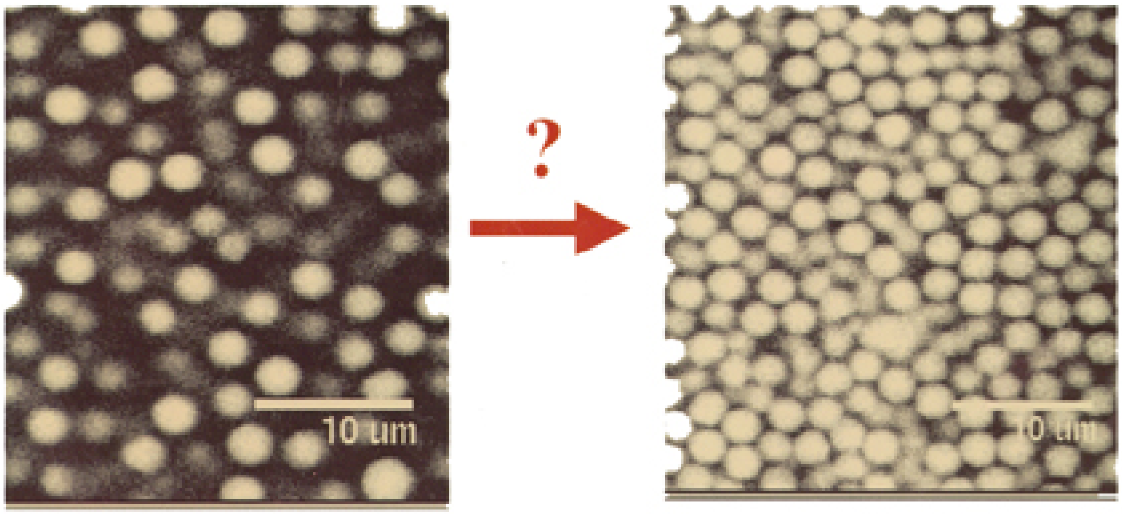
Colloidal Particle => Atom
Watch each atom

Volume Fraction Controls Phase Behavior

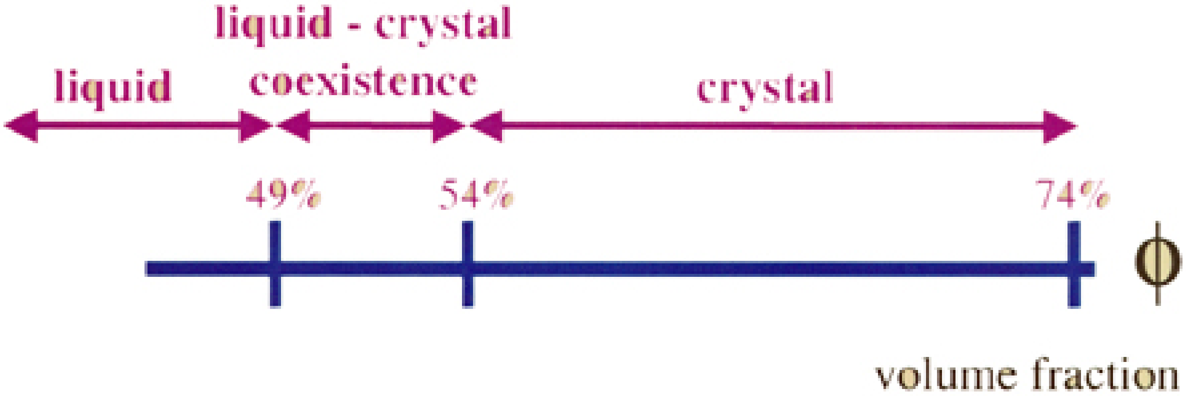
$$F = \cancel{U}^{\,0} - TS$$

Increase ϕ => Decrease Tempreature



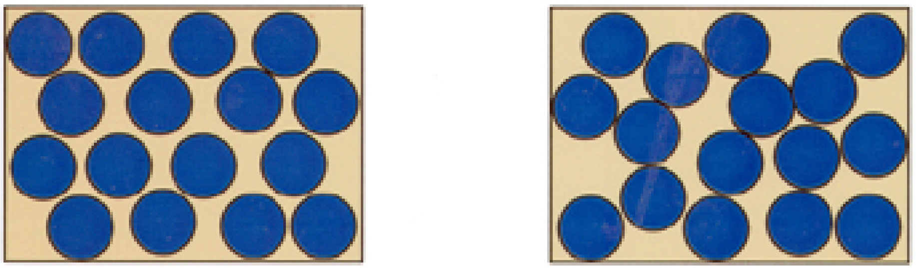


(1-D) Phase Diagram for Hard Spheres:



Theory predicts phase diagram for hard spheres *(entropy)*

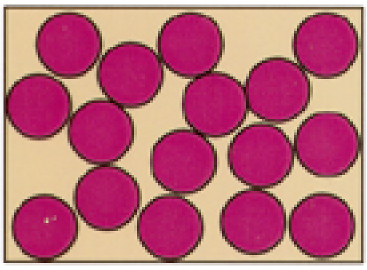
$$F = \overset{0}{\cancel{U}} - TS$$



Entropy Drives Crystallization

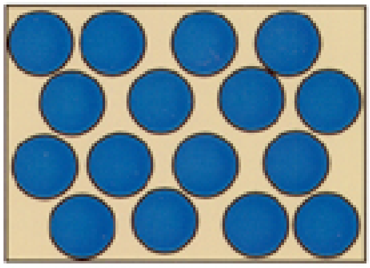
$$F = \cancelto{0}{U} - TS$$

Entropy => Free Volume



Disordered:
Higher configurational entropy
Lower local entropy
Higher Energy

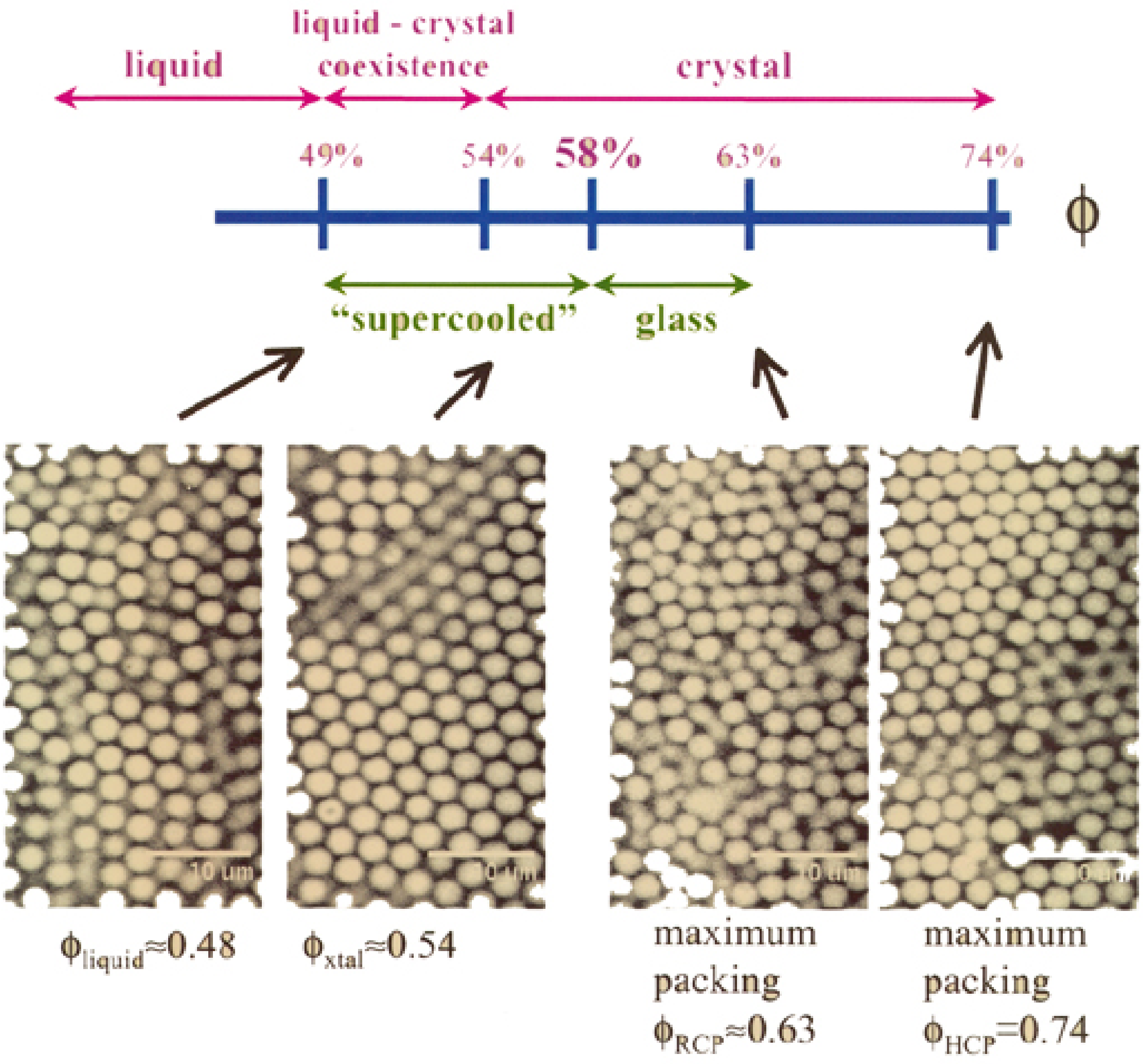
maximum packing
$\phi_{RCP} \approx 0.63$



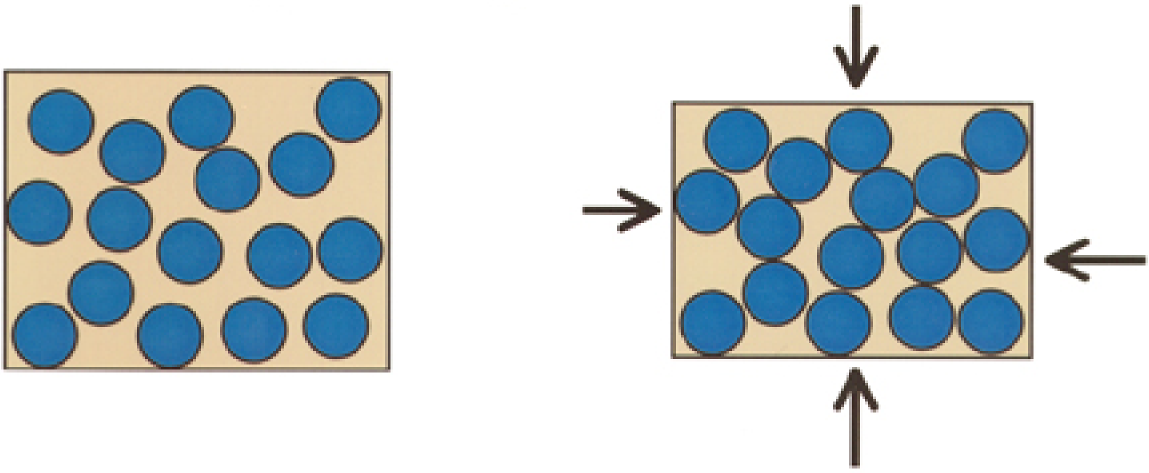
Ordered:
Lower configurational entropy
Higher local entropy
Lower Energy

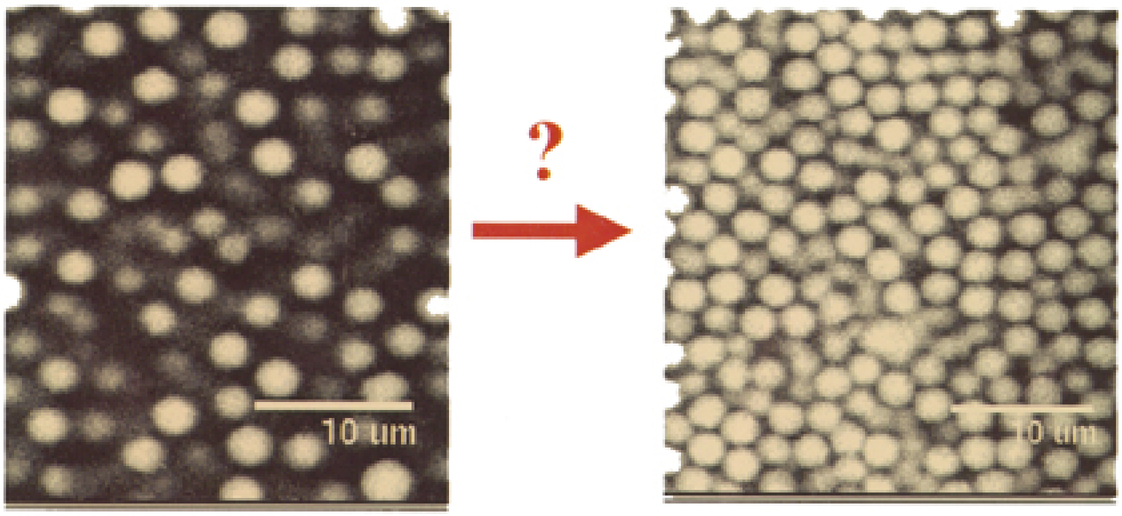
maximum packing
$\phi_{HCP} = 0.74$

Metastable Hard Sphere Phases



Basic idea: increasing density causes a glass transition. How does motion of colloidal particles get constrained?





More about the Glass Transition

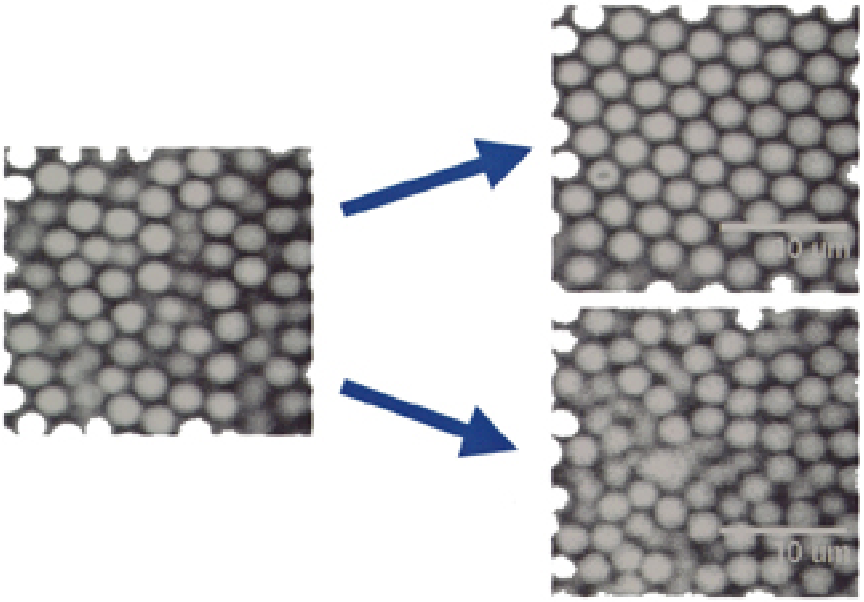
- Theories incomplete & conflicting:
  - is major factor density? entropy?
  - underlying thermodynamic transition?
  - underlying dynamic transition?

- Many glass-forming systems:
  - Molecular glasses (silica, glycerol, o-terphenyl,…)
  - polymers
  - metallic glasses
  - hard spheres
  - colloids & emulsions

- May be related to granular materials:
  - "jamming" (Cates '98, Liu & Nagel '98)

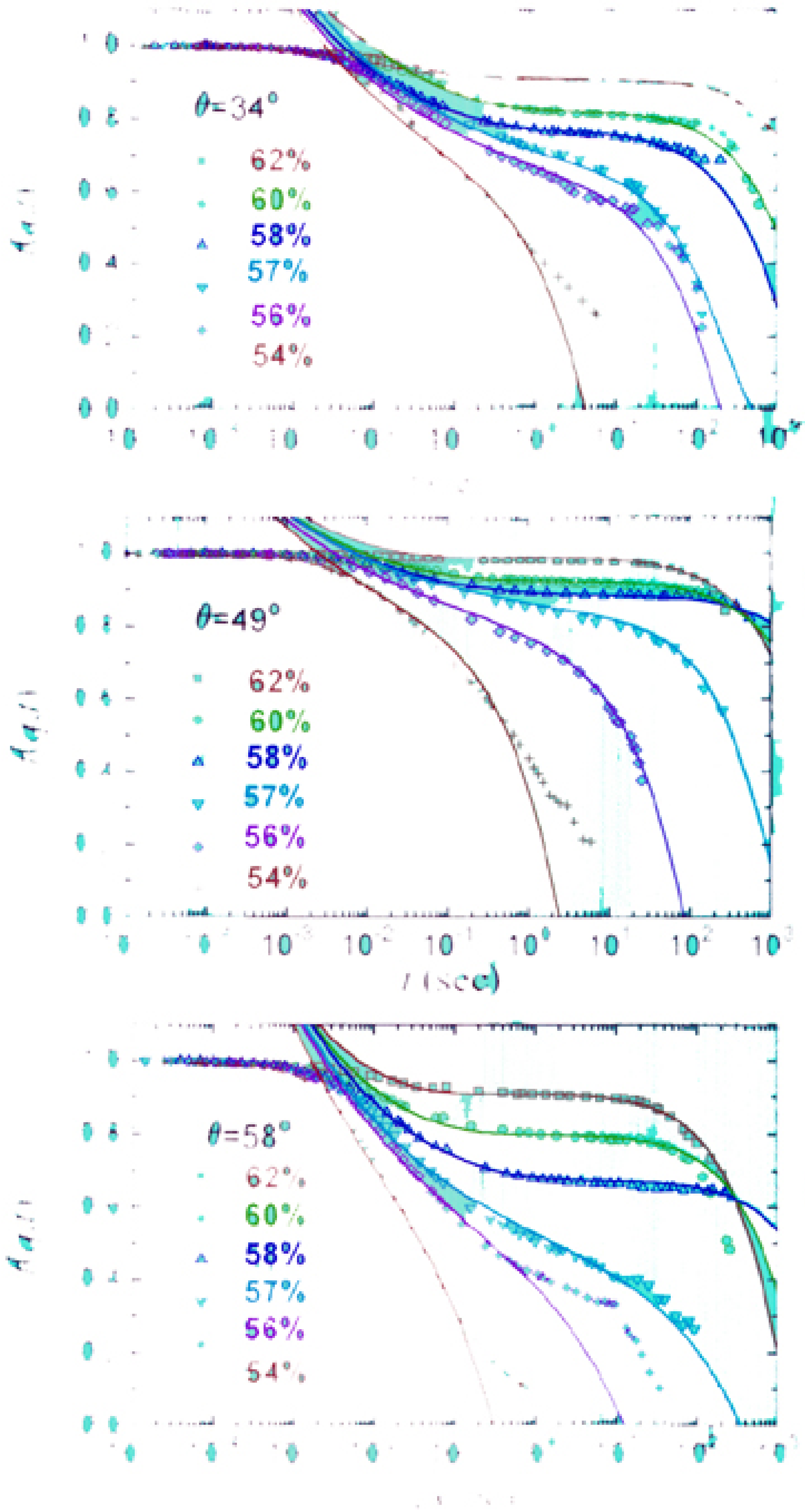
Regular phase transitions

- 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


θ=34°
62%
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57%
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54%
θ=49°
62%
60%
58%
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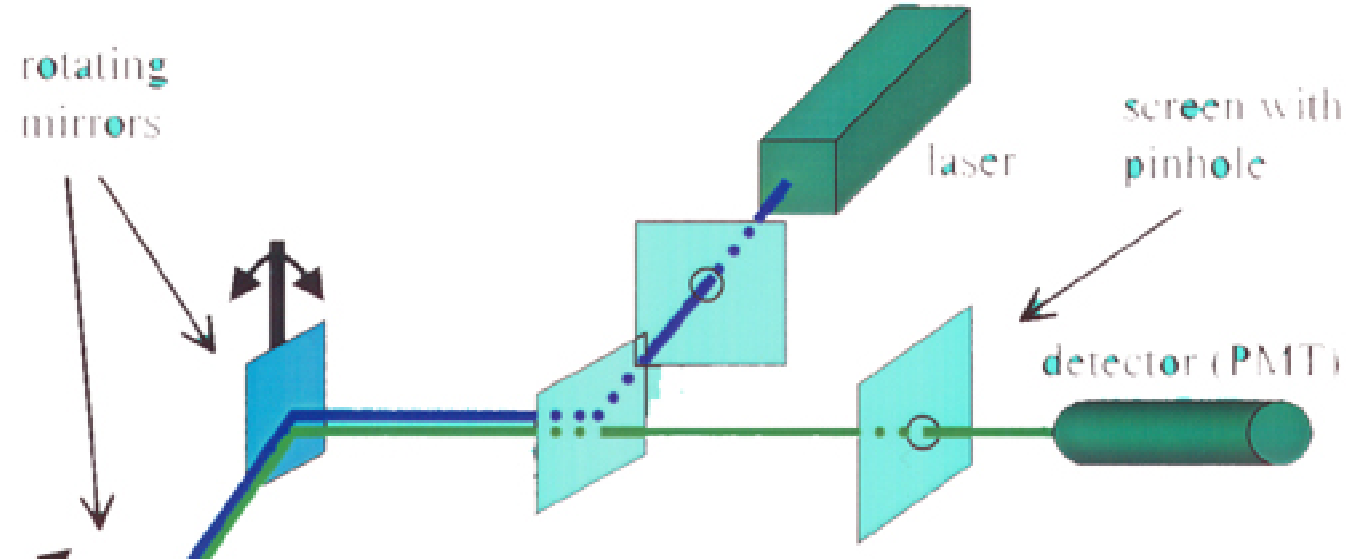
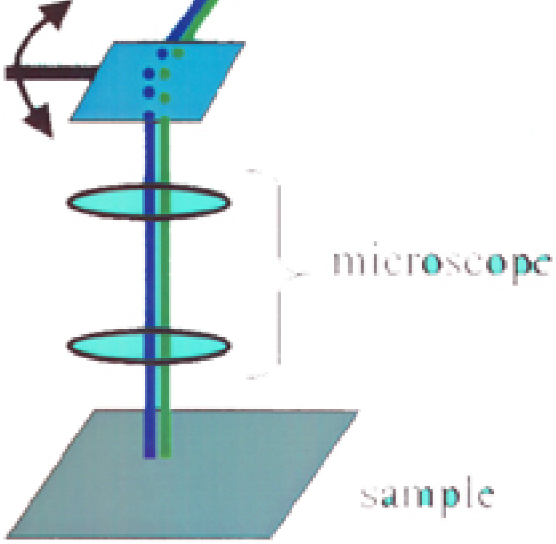
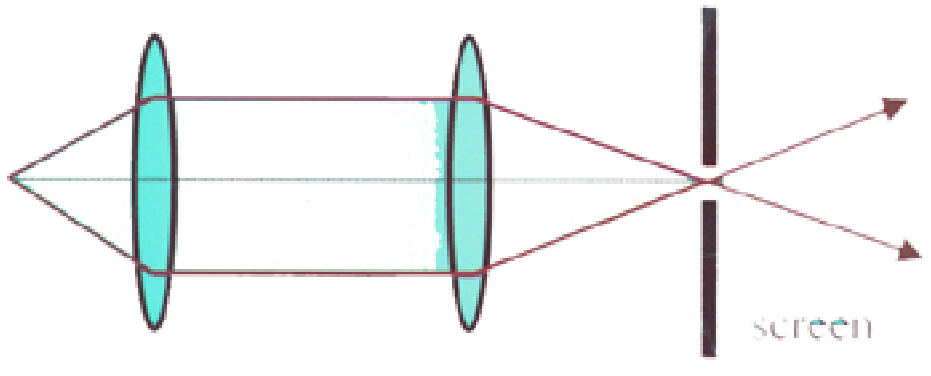
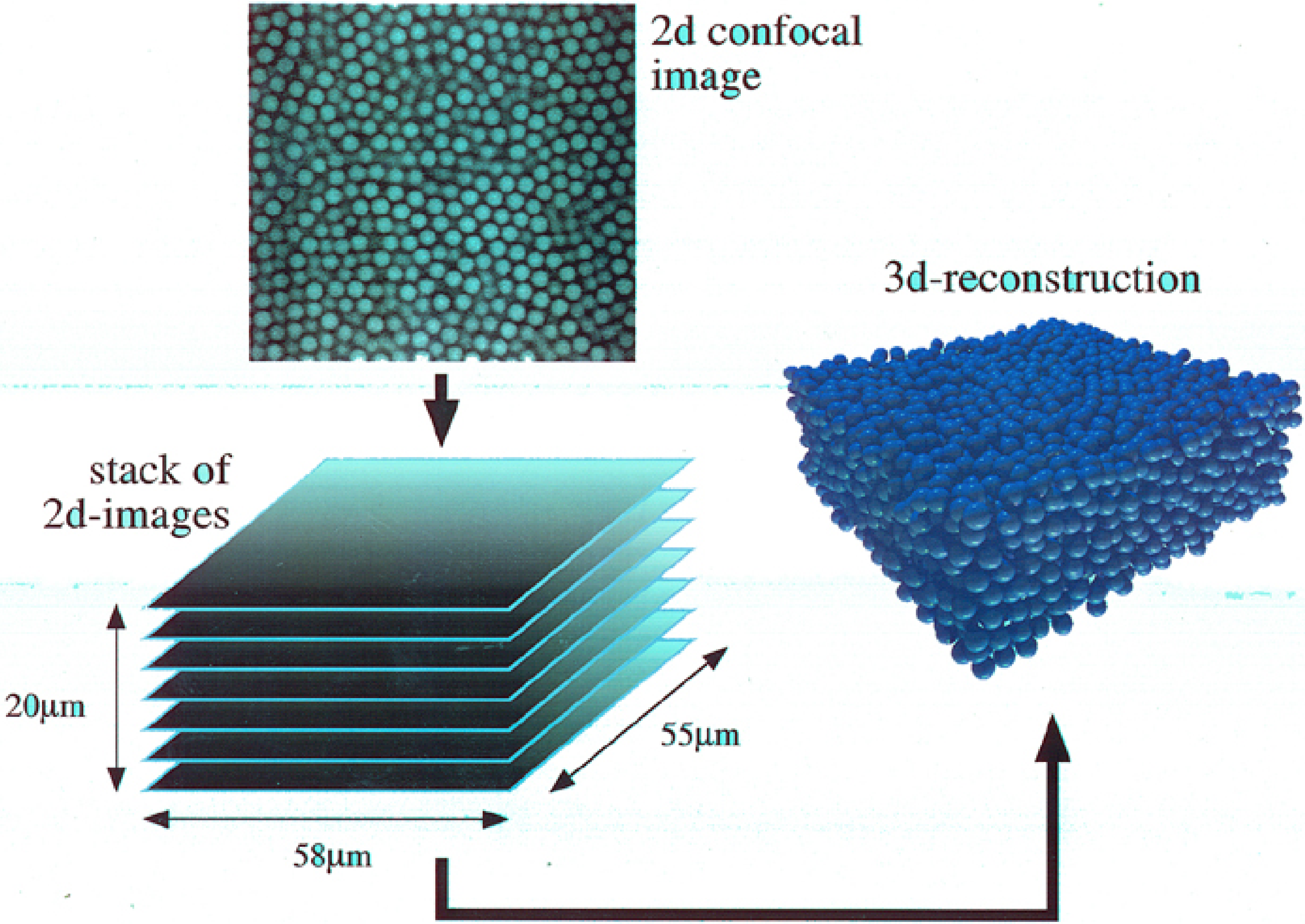
t (sec)
θ=58°
62%
60%
58%
57%
56%
54%

Confocal Microscopy








2d confocal image
stack of 2d-images
20μm
55μm
58μm
3d-reconstruction

Microscopy and Tracking

Confocal microscopy:

- 80 images x (512×480 pixels, 2D)
- ➡ one 3D "cube" per 6 s
- $67 \times 63 \times 10\ \mu m^3$
- 100× oil, 1.4 N.A. objective
- Identify particles within 0.03 μm (xy)
  0.05 μm (z)

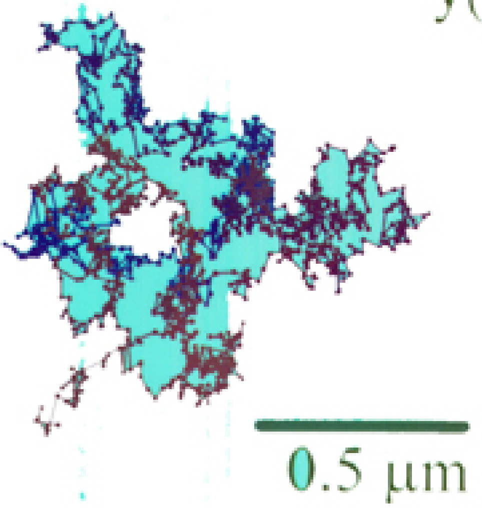
Particle tracking:

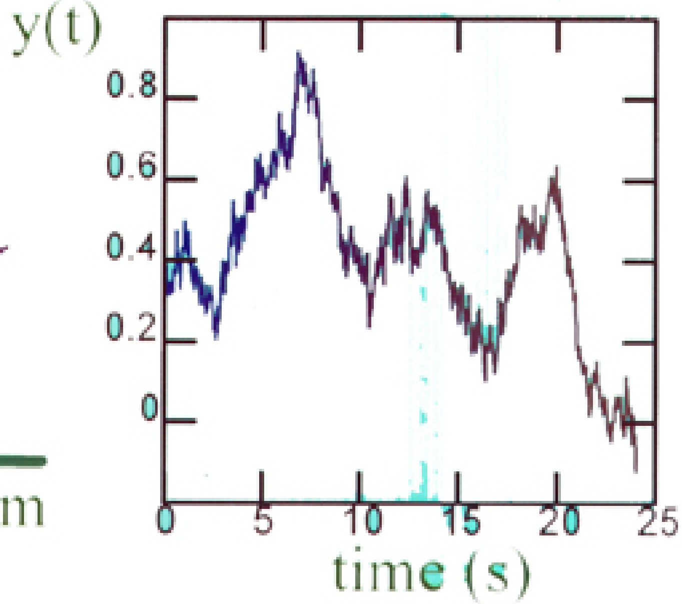
- Follow 3000-5000 particles in 3D
- 200-1000 time steps (hours to days)
- ~4 GB of images per experiment

First direct 3D observation of dynamics of crystallization

Brownian Motion

(2 μm particles, **dilute** sample)





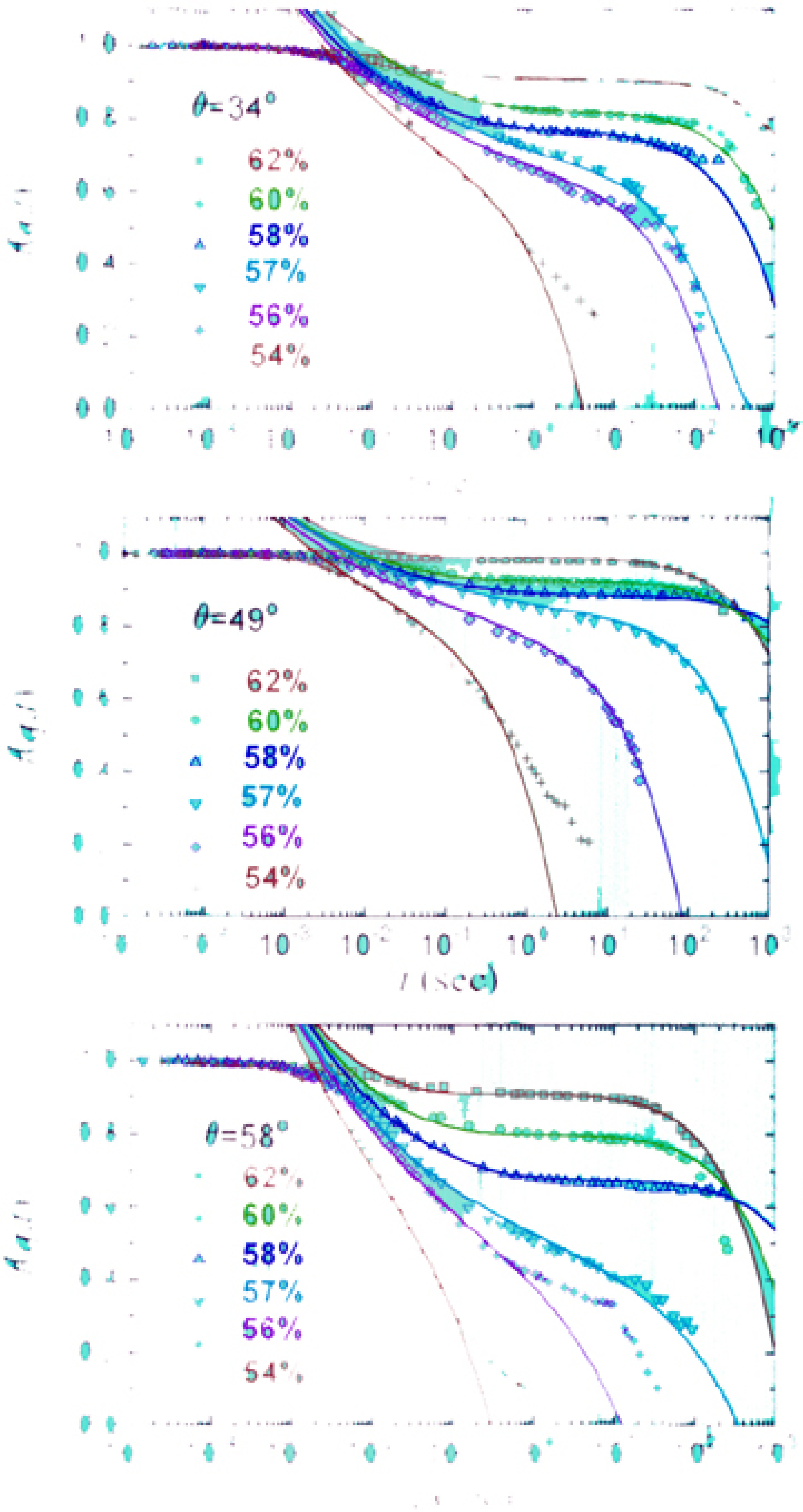
Leads to normal diffusion:

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

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

viscosity η

particle size *a*


θ=34°
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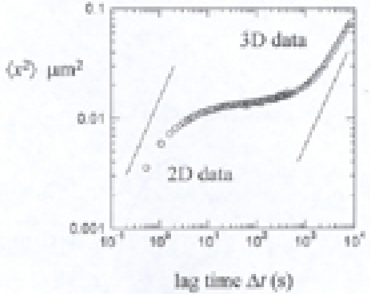
56%
54%
t (sec)
θ=58°
62%
60%
58%
57%
56%
54%

Mean square displacement

Volume fraction ϕ=0.53,
"supercooled fluid"

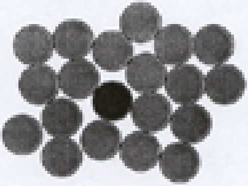


Slide missing

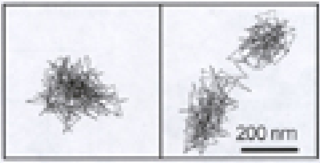
Slide missing

Slide missing

Cage trapping:



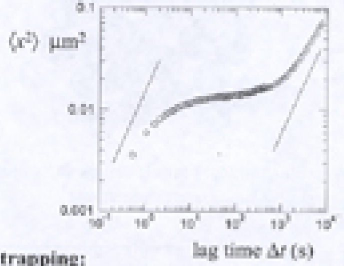
- Short times: particles stuck in "cages"
- Long times: cages rearrange



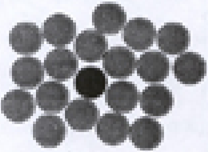
ϕ=0.56, 100 min (supercooled fluid)

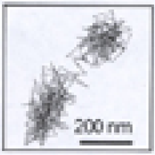
Mean square displacement

Volume fraction ϕ=0.53 -- "supercooled fluid"



Cage trapping:

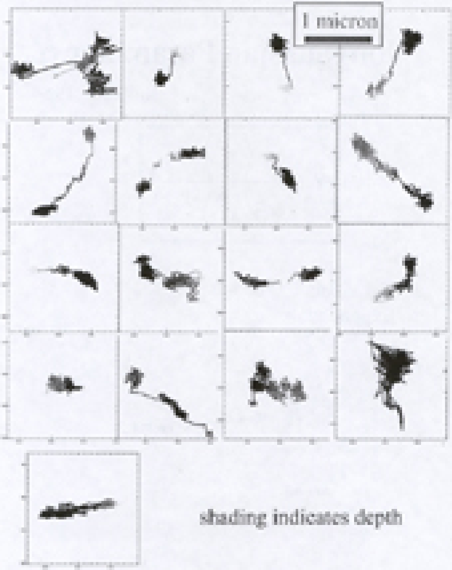




ϕ=0.56, 100 min (supercooled fluid)

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

Trajectories of "fast" particles, ϕ=0.56



shading indicates depth

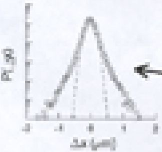
Nongaussian Parameter α_2

Rahman, 1964

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

Gaussian: $\alpha_2 = 0$

Exponential: $\alpha_2 = 1$



α_2=1.2