The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

SMR/1845-5

Conference on Structure and Dynamics in Soft Matter and Biomolecules: From Single Molecules to Ensembles

4 - 8 June 2007

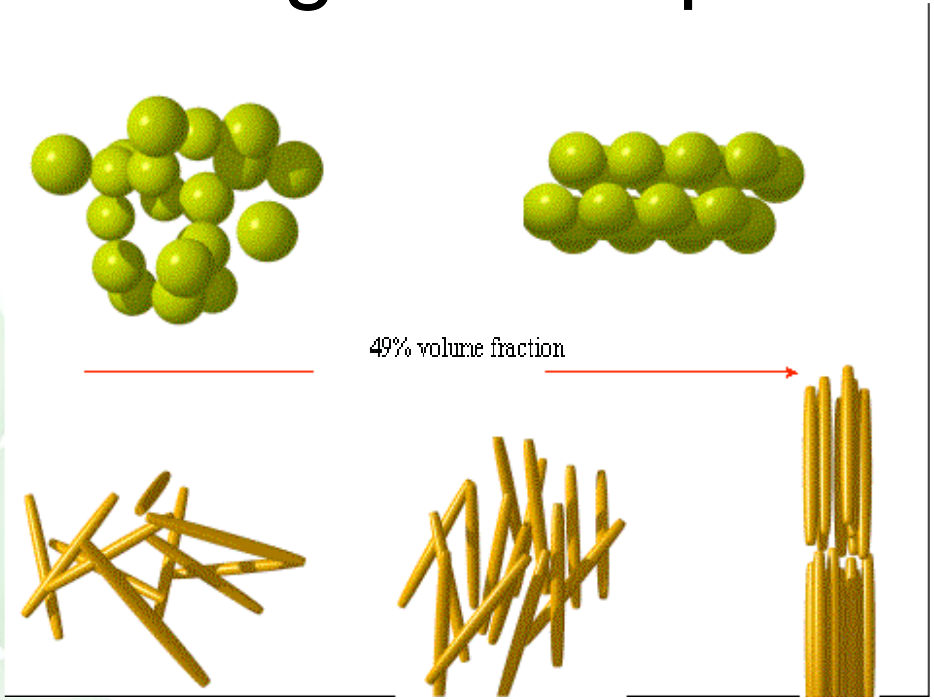
Packing in the Spheres

Maria KILFOIL

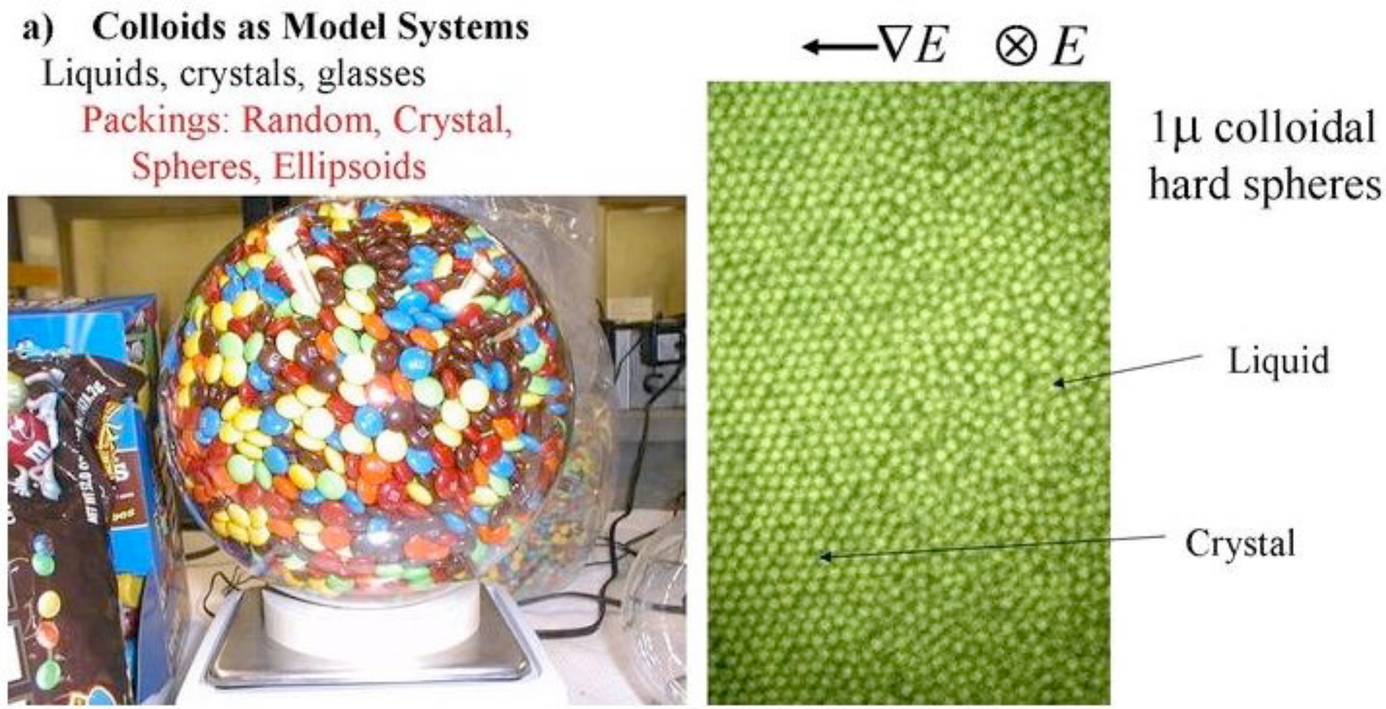
Ernest Rutherford Physics Building
McGill University
3600 Rue University
Montreal QC, H3A 2TB
CANADA

Maria Kilfoil

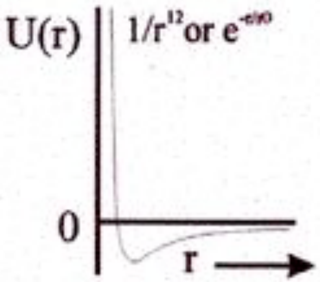
Packing in the Spheres



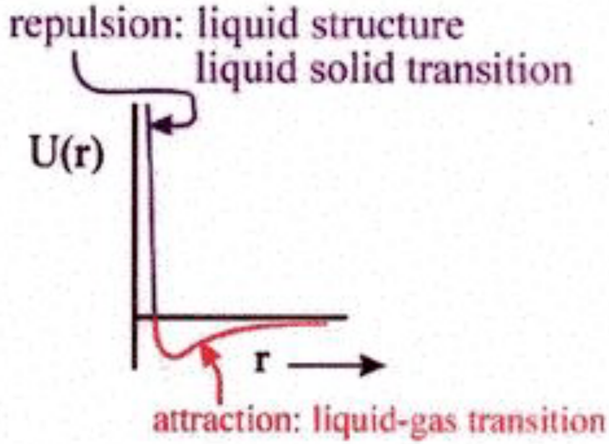
$\Delta F = -T\Delta S$


a) Colloids as Model Systems
Liquids, crystals, glasses
Packings: Random, Crystal,
Spheres, Ellipsoids
←∇E ⊗E
1μ colloidal
hard spheres
Liquid
Crystal

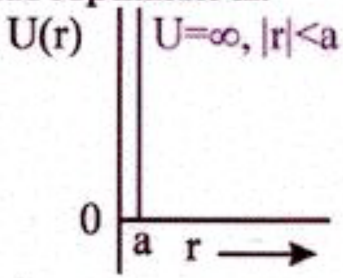
Why Hard Particles?



typical interparticle
potential

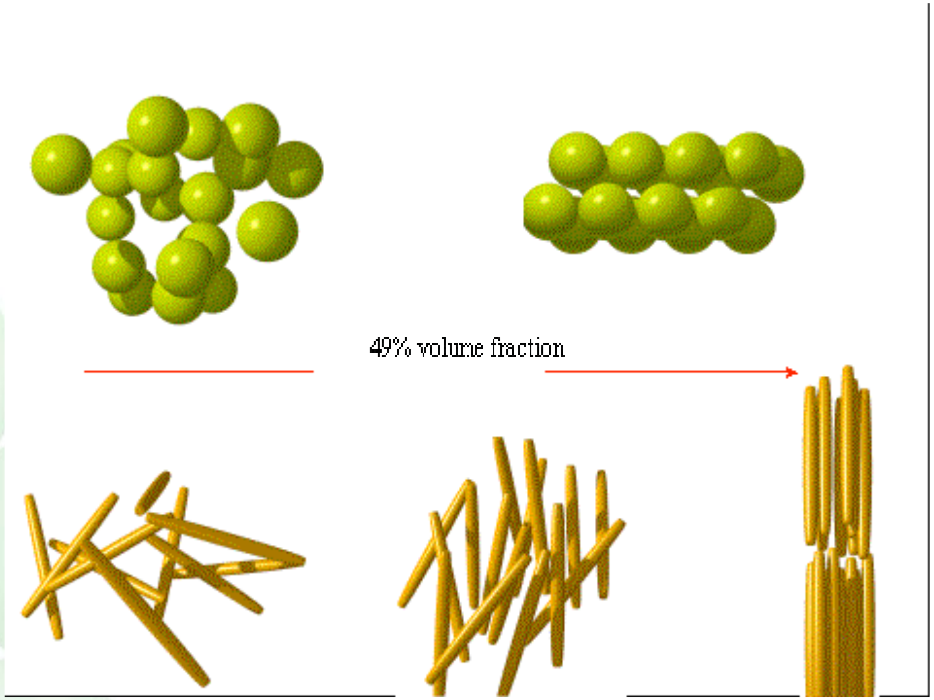


Most interesting things depend on repulsive part
simplest repulsion is:



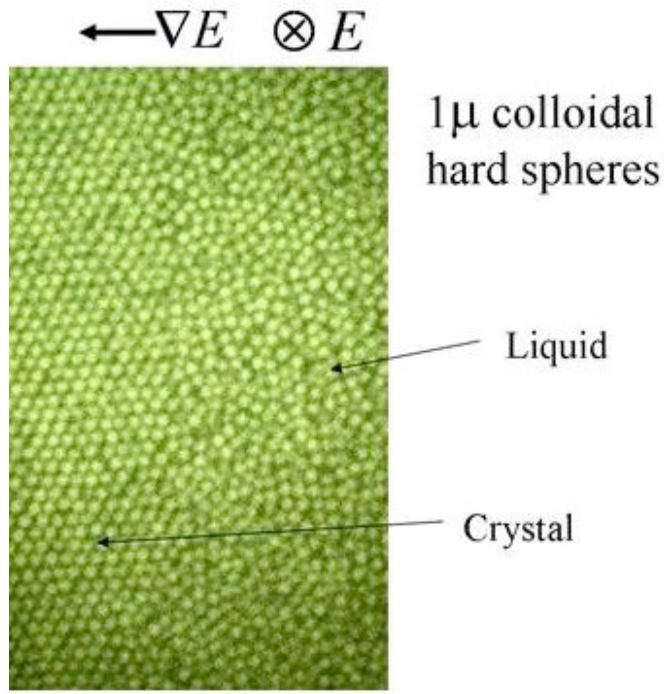
The essence of the problem -- **Hard Spheres**

Entropically-driven order-disorder transitions



$$\Delta F = -T\Delta S$$

Order-disorder transitions in colloids



Packing Densities for Spheres

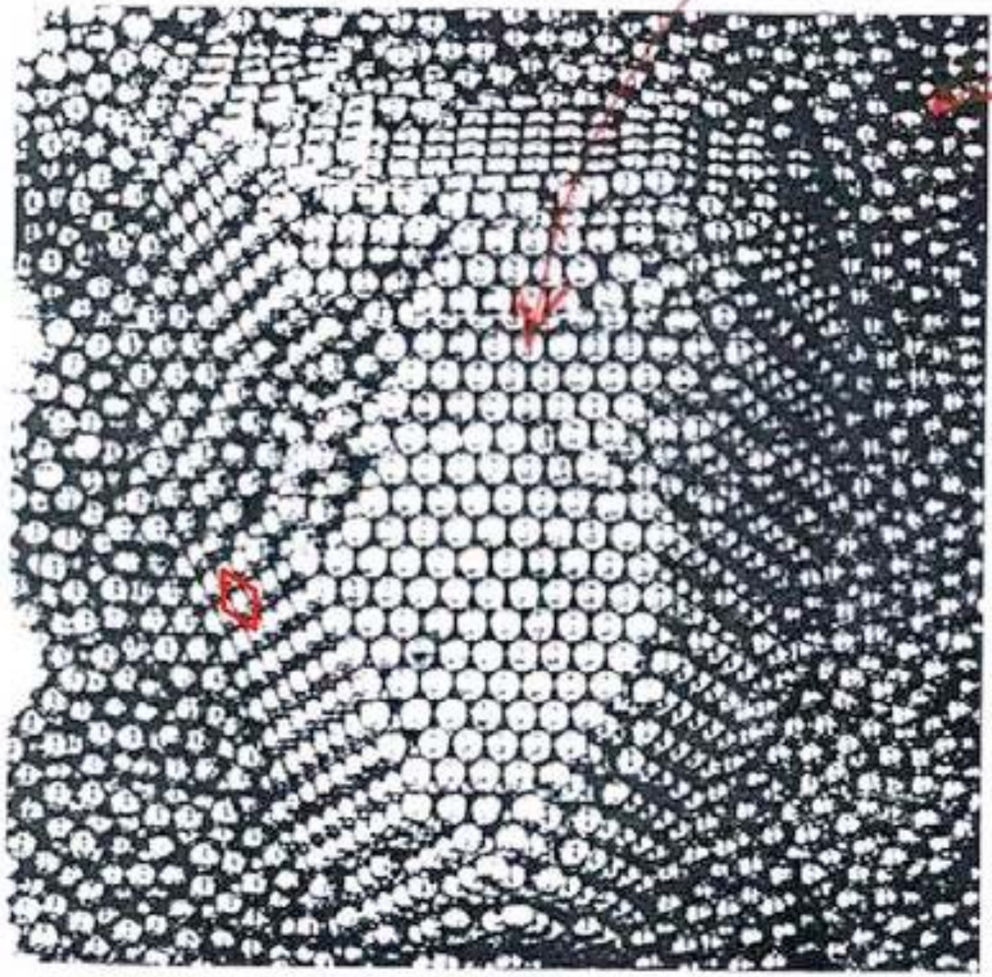


FIGURE 14. Face-centred cubic 'crystal' surrounded by 'liquid' caused by shearing ball-bearing mass. 111 face is shown at the top surface.

Packing of Hard Particles

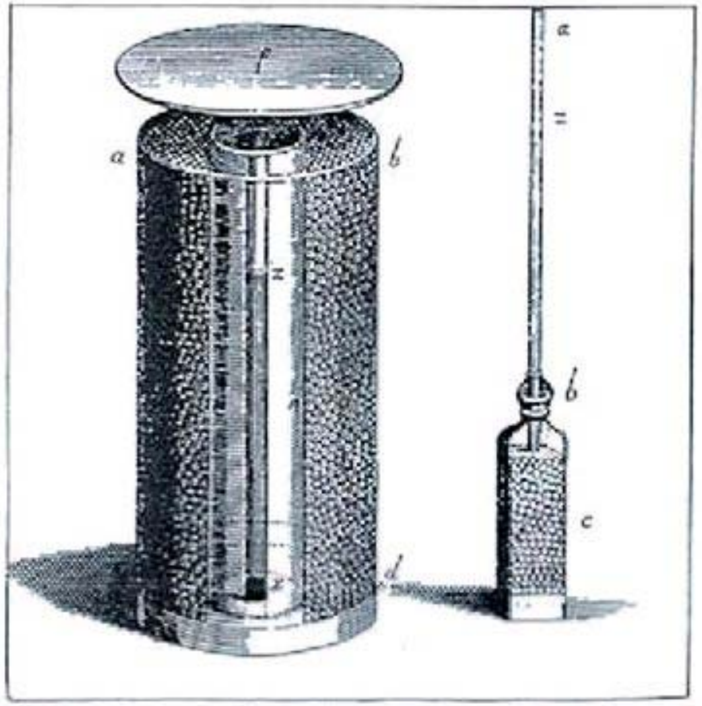
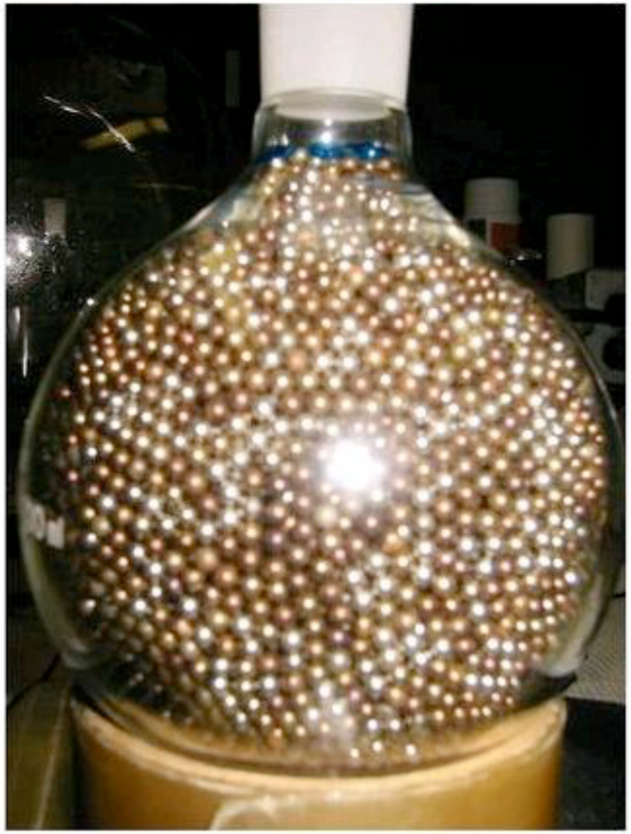
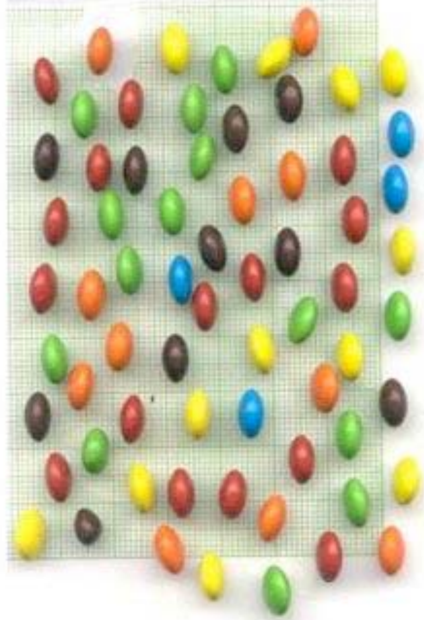
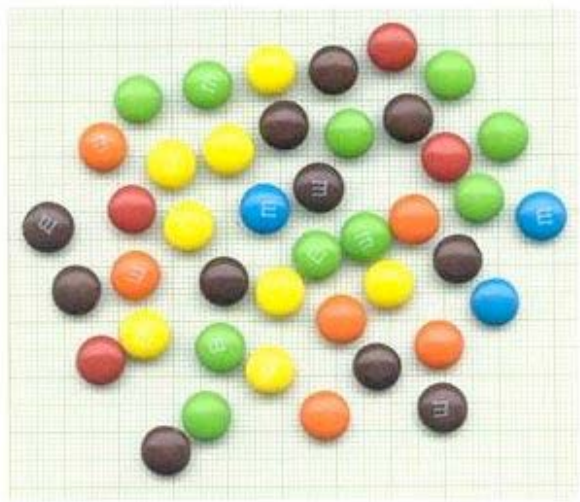


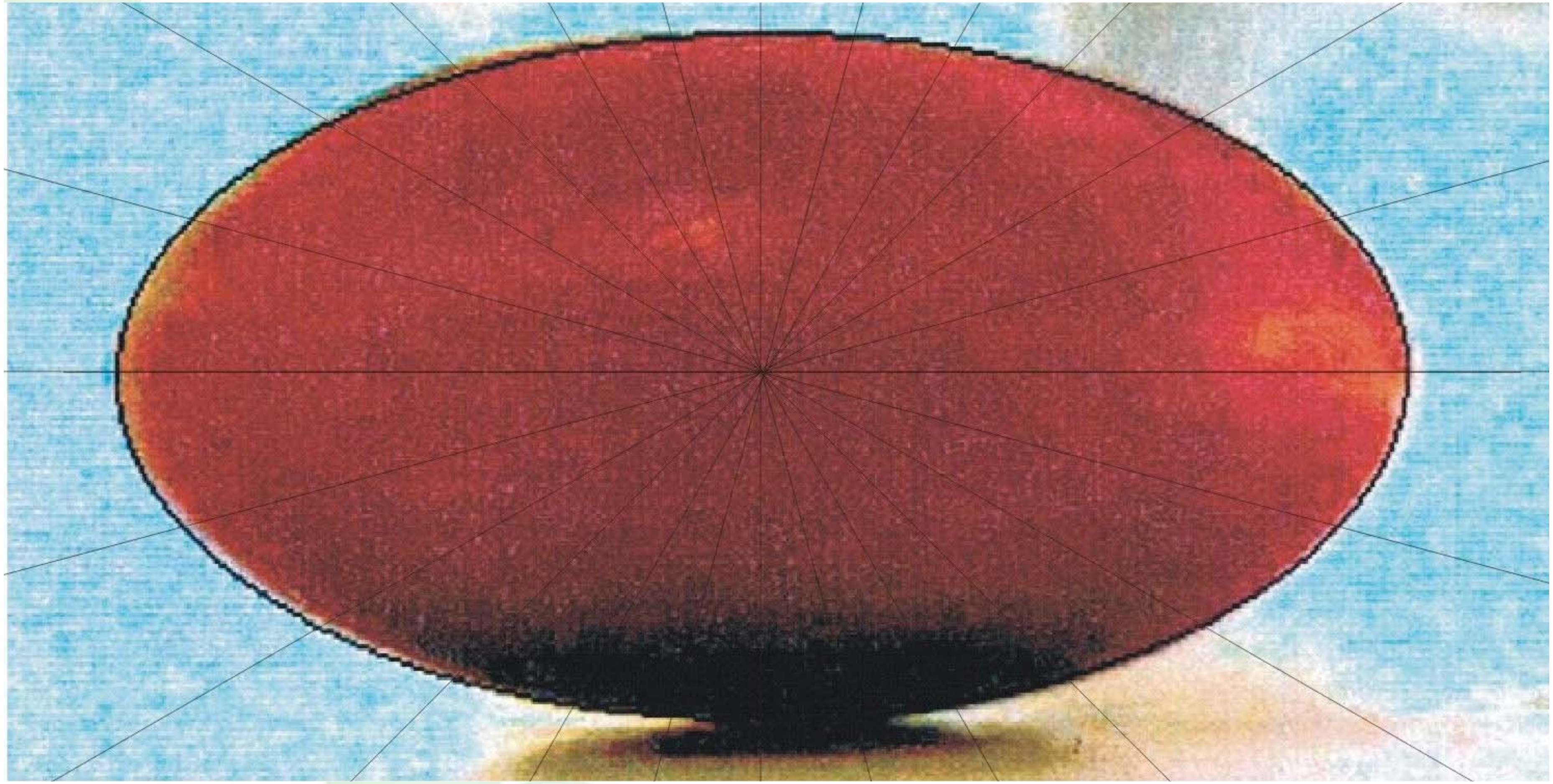
Figure 2.9 Stephen Hales (1727) was a highly gifted biologist whose interests included the uptake of water by plants. The diagram on the left shows the apparatus he used to demonstrate the substantial force exerted by dilating peas. However, when the lid (f) was covered with a weight great enough to prevent its lifting, the dilated peas deformed into the Wigner–Seitz cells of the rcp structure. The peas in the bottle at right, used by Hales in a related experiment, would not have served so well to illustrate random close packing because of the presence of the crystallinity-inducing planar walls.

Packing of Hard Particles

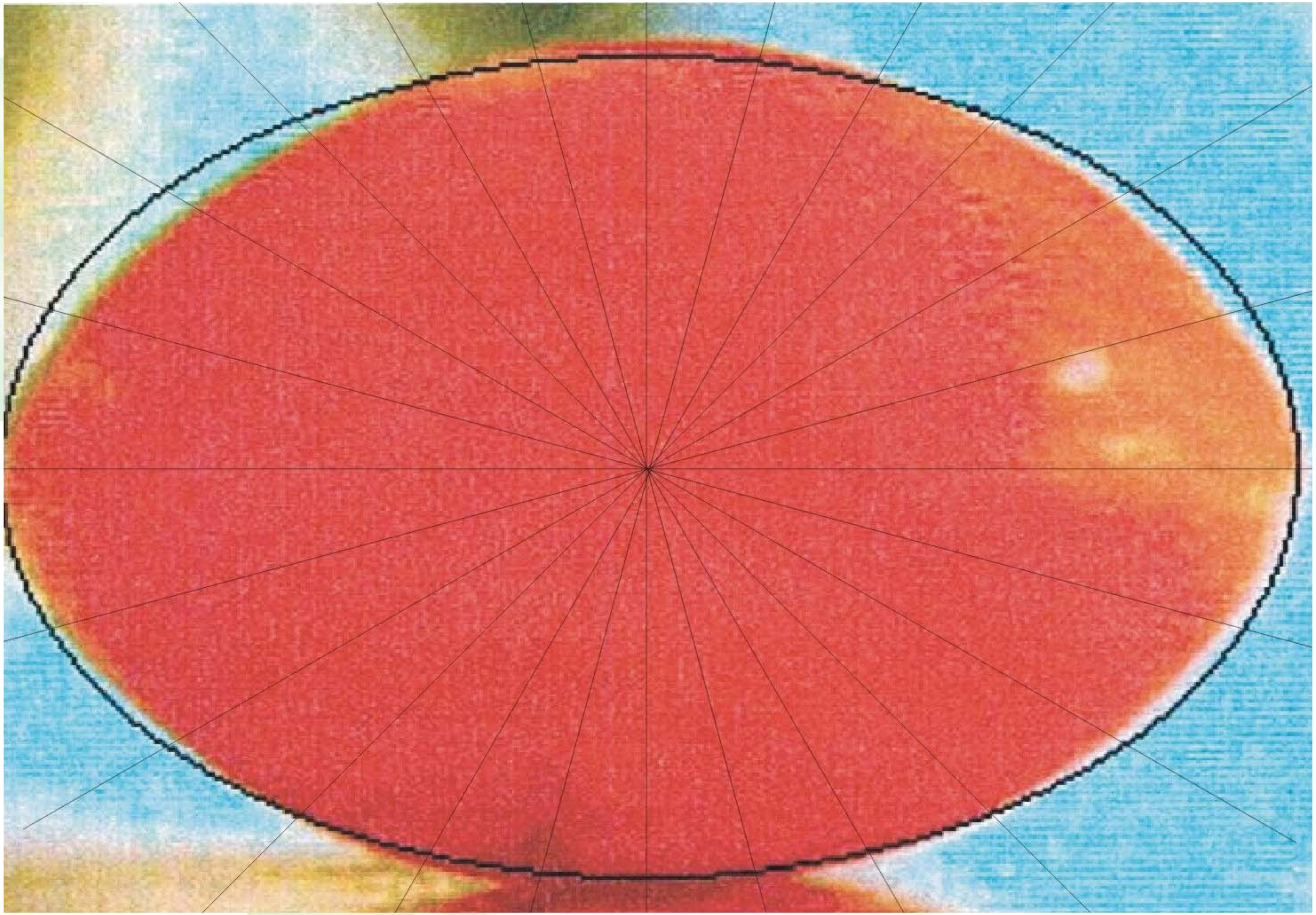








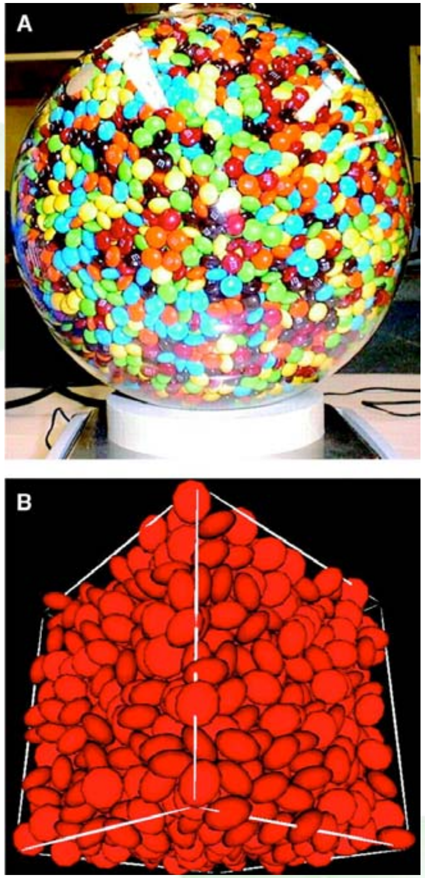
M&M ® $(\delta r^2/\langle r\rangle^2)^{1/2} < .01$



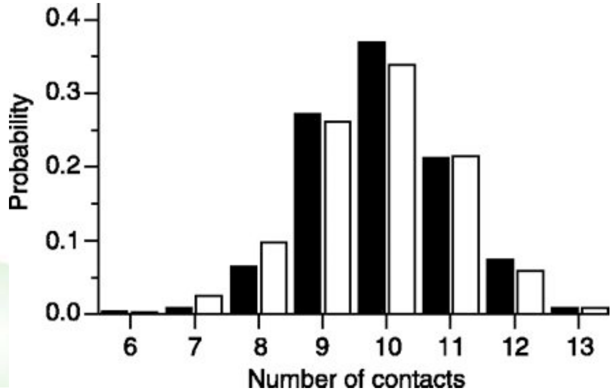
Skittle ® $(\delta r^2/\langle r\rangle^2)^{1/2} \sim .03$

Improving the Density of Jammed Disordered Packings with Ellipsoids

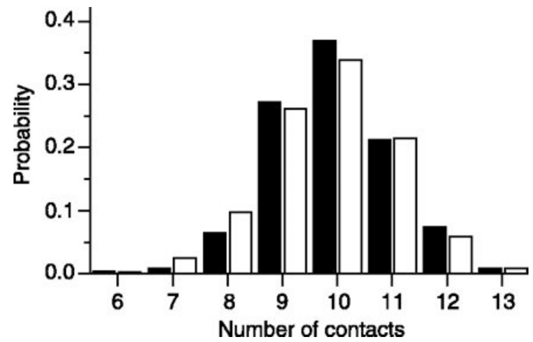
M&M's

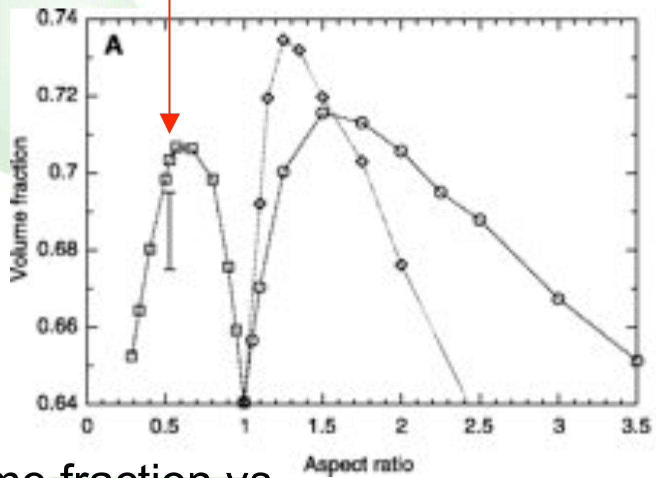


Chaikin, Torquato *et al.*
Science, Feb. 13 2004

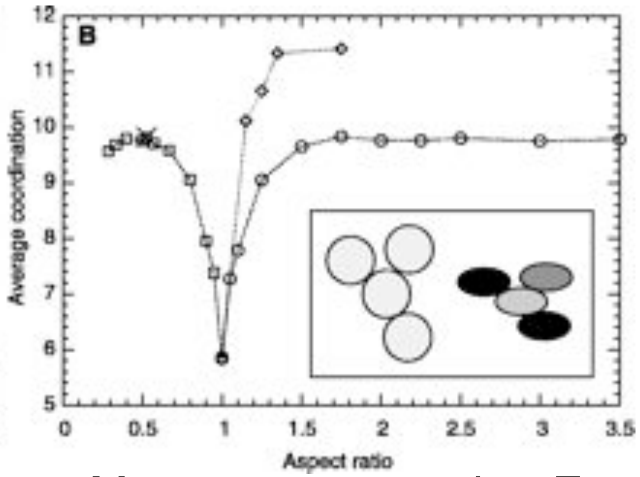


Improving the Density of Jammed Disordered Packings with Ellipsoids

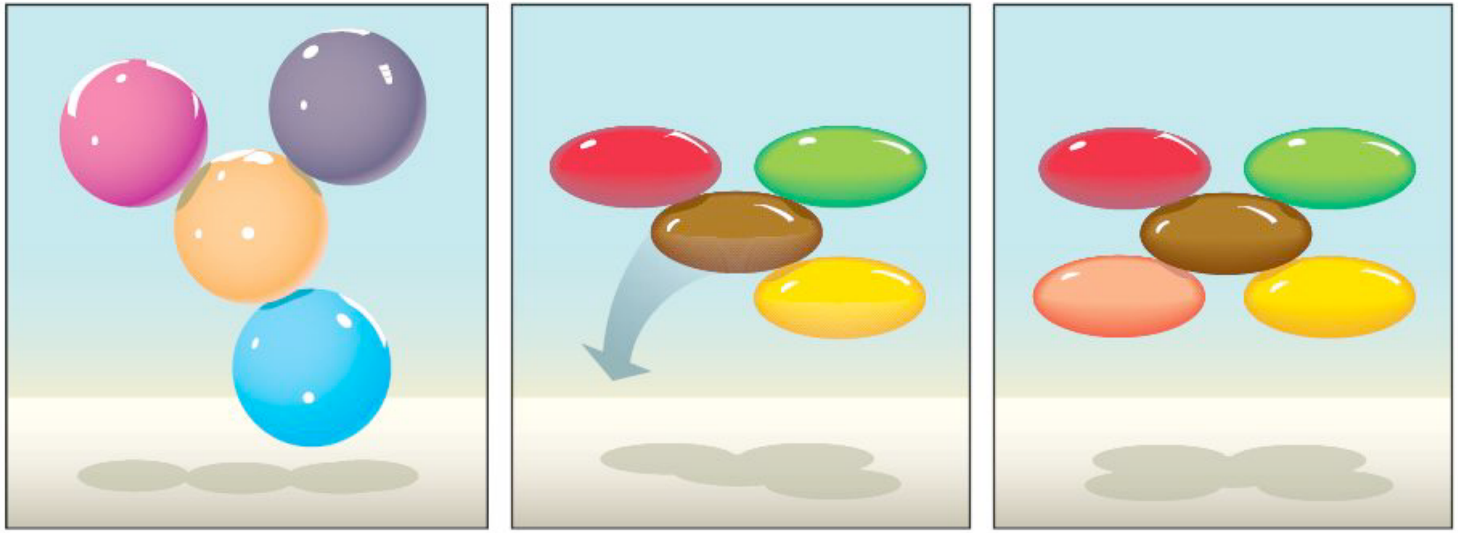




Volume fraction vs aspect ratio from simulations



Mean contact number Z vs aspect ratio



Shape is destiny. The shape of objects has a big effect on how densely they can be packed into a given volume. (**Left**) Spherical objects can only be pushed sideways and not rotated by neighbors, so they cannot experience torque. (**Middle**) Ellipsoidal objects can be rotated away by their neighbors and escape confinement. (**Right**) As a result, more neighbors (and denser packing) are required to balance the forces on an individual ellipsoid than on a sphere.

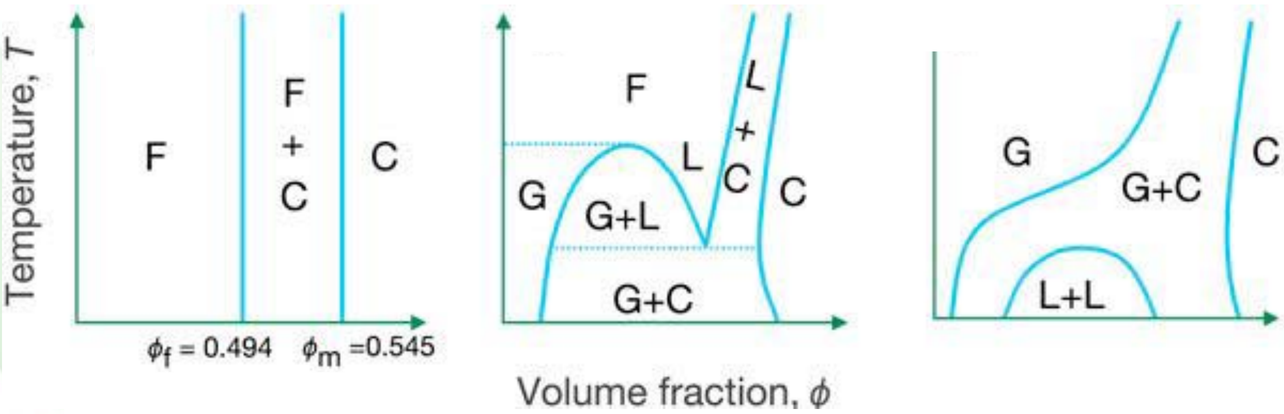
CREDIT: PRESTON HUEY/*SCIENCE*

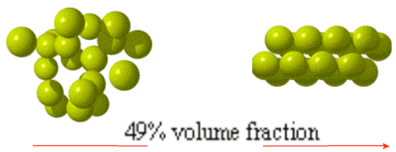
Naturally Occurring Phase Diagrams

Hard spheres

Long-range attractions

Short-range attractions

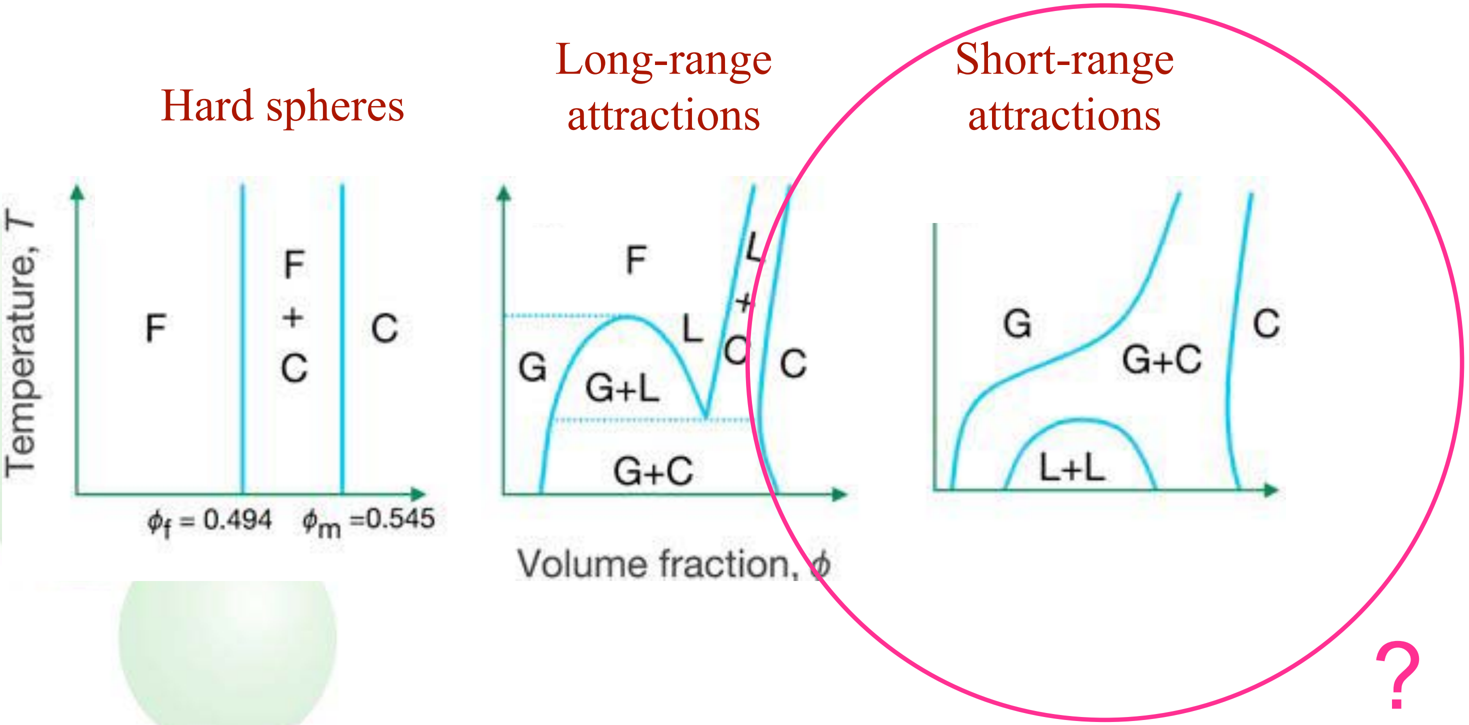




Entropically-driven order-disorder transition

$$F = U - TS$$

Naturally Occurring Phase Diagrams



Soft Solids

Easily deformable → Low Elastic Constant: $\frac{\text{Energy}}{\text{Volume}}$

Atoms: $\frac{eV}{\dot{A}^3}$ ~GPa

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

Colloidal Particles:

- Slow speed
- Large size (microns)

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

Consequences of Being Soft:
Unifying Characteristics

- Easily driven from equilibrium

- Slow relaxations

- Forces which would otherwise be negligible become important: Gravity, thermal fluctuations

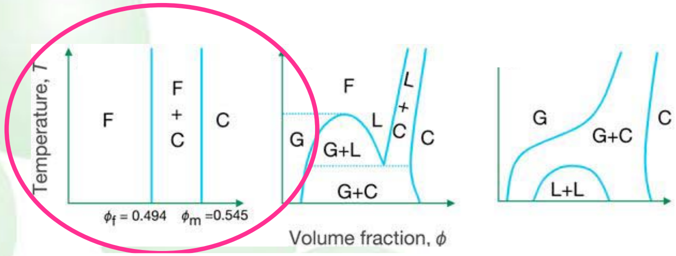
- Interfaces are important: Surface tension-driven structures

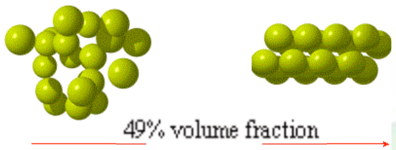
"Big Questions"

- Rigidity
  - -jamming
  - -glass transition, ergodicity breaking
- Self-Assembly and Pattern Formation
- Networks
- Driven Dynamics and Effective Temperature
- Interface with Biology – are there guiding principles?
  - -- membranes, surfactants, emulsions, polymers, l.c.'s

→ Notions from statistical mechanics play a special role

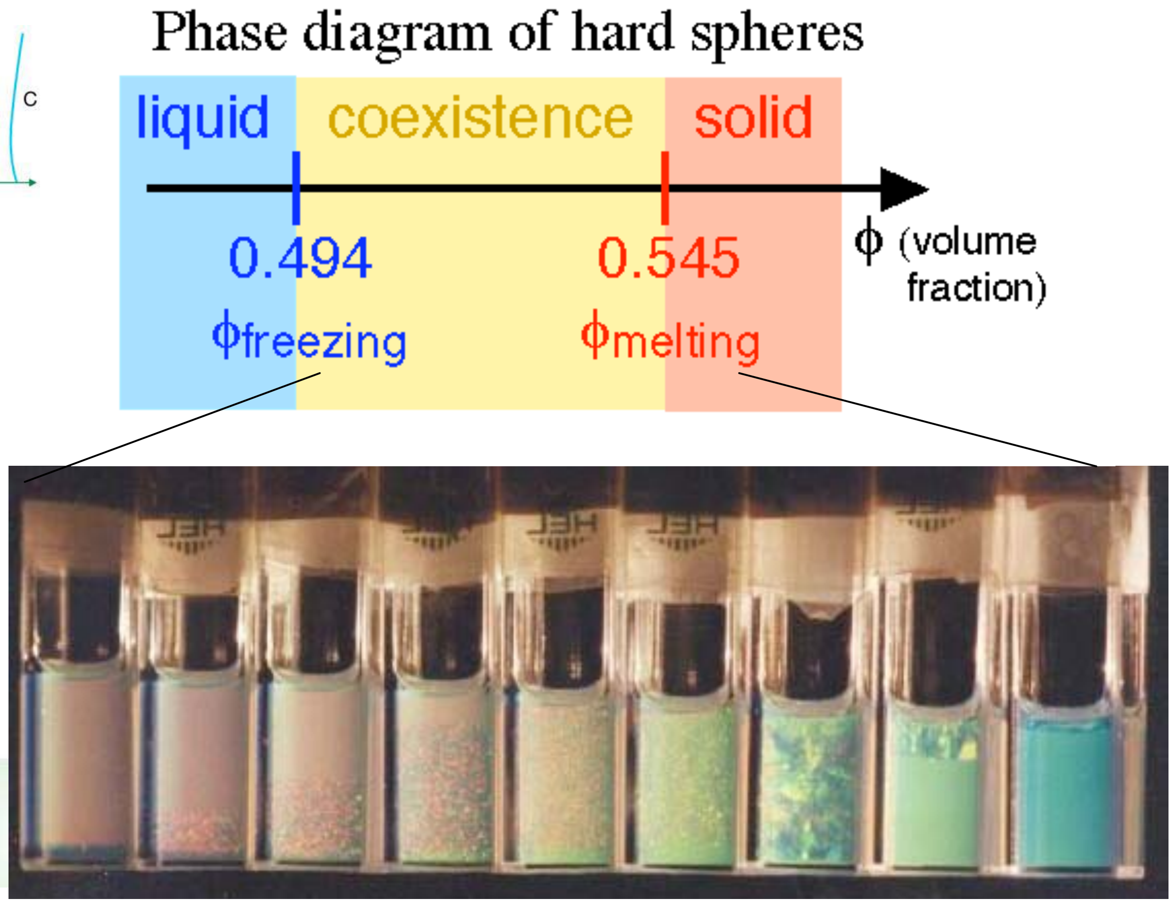
Naturally Occurring Phase Diagrams: Hard spheres



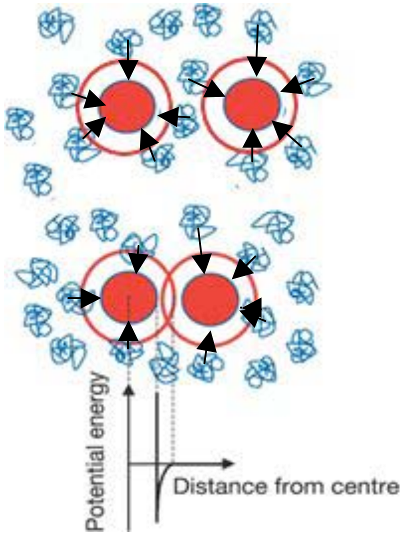


Entropically-driven order-disorder transition

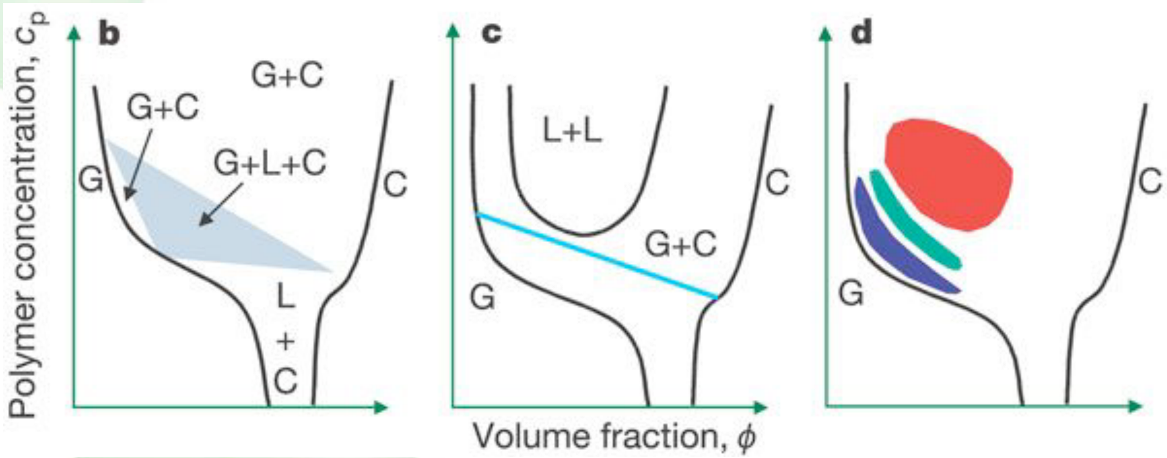
$$F = U - TS$$



Naturally Occurring Phase Diagrams



Depletion:
Asakura & Oosawa, *J. Chem. Phys*. 1958;
Vrij, *Pure Appl. Chem*. 1976



Microscopic Structure

Local Crystallization Order Parameter

defines nearest neighbor particles

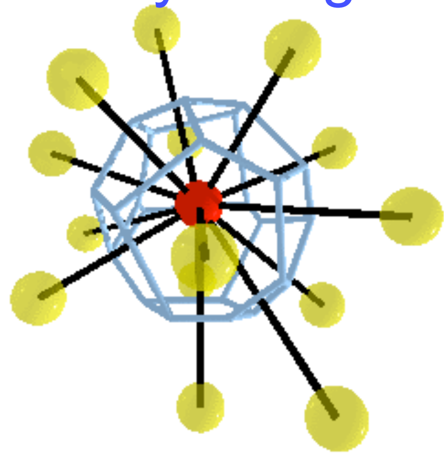
Steinhardt, Nelson, Ronchetti,
Phys. Rev. B **28**, 1983.

- Find nearest neighbor connections r_{ij}
- Resolve connections in spherical harmonics:

$$q_{lm}(i) = \langle Y_{lm}(r_{ij}) \rangle_j$$

- Define Order Parameter
- Several order parameters possible
- Best metric $l=6$

Voronoi polyhedra -- Delaunay triangulation



("Wigner-Seitz cell")

Colloids

- A colloid is a suspension of near-micron size particles
- Excellent realization of hard spheres

Control:

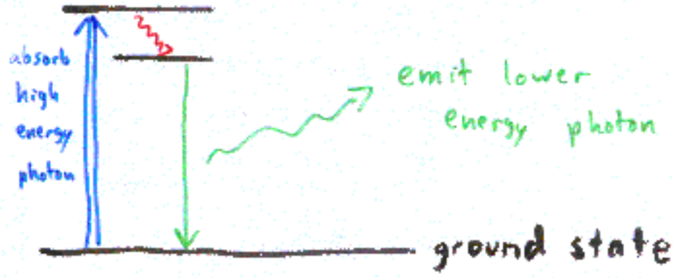
•Concentration or volume fraction ϕ

•Particle interaction energies (attraction, repulsion, hard sphere behavior)

•Viscosity of the liquid suspension

•Density of the particles relative to the liquid suspension → control gravity

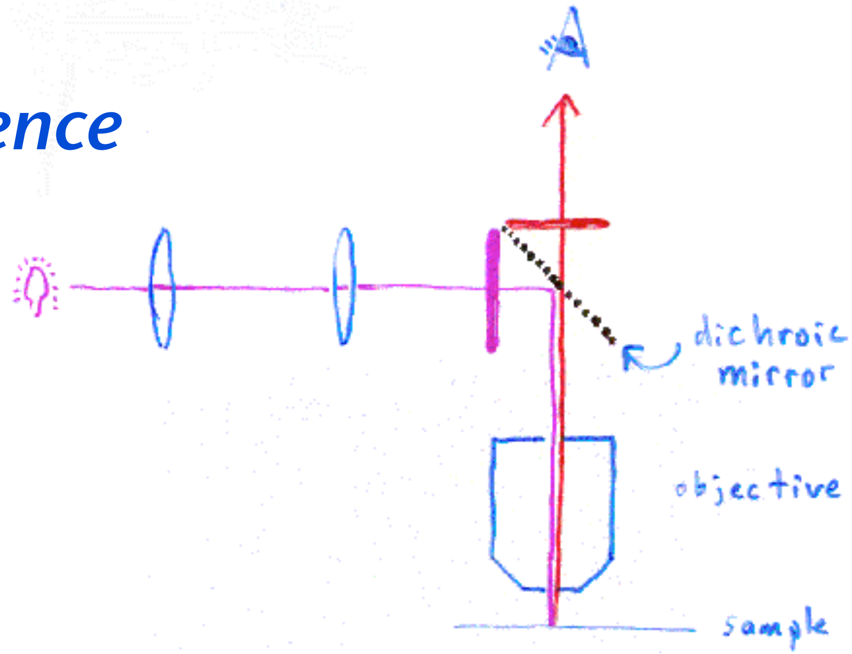
What is fluorescence?



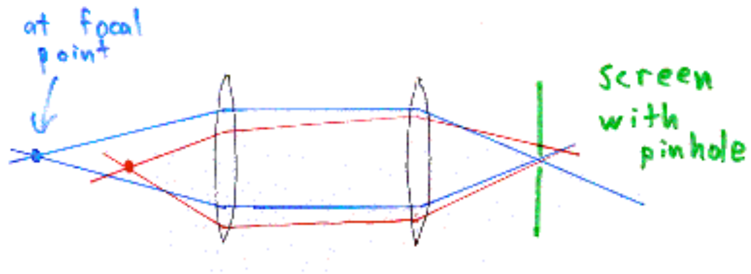
→Can attach fluorescent dye molecules to specific parts of your sample

→Can use more than one type of dye to distinguish two different parts of your sample

How does a fluorescence microscope work?



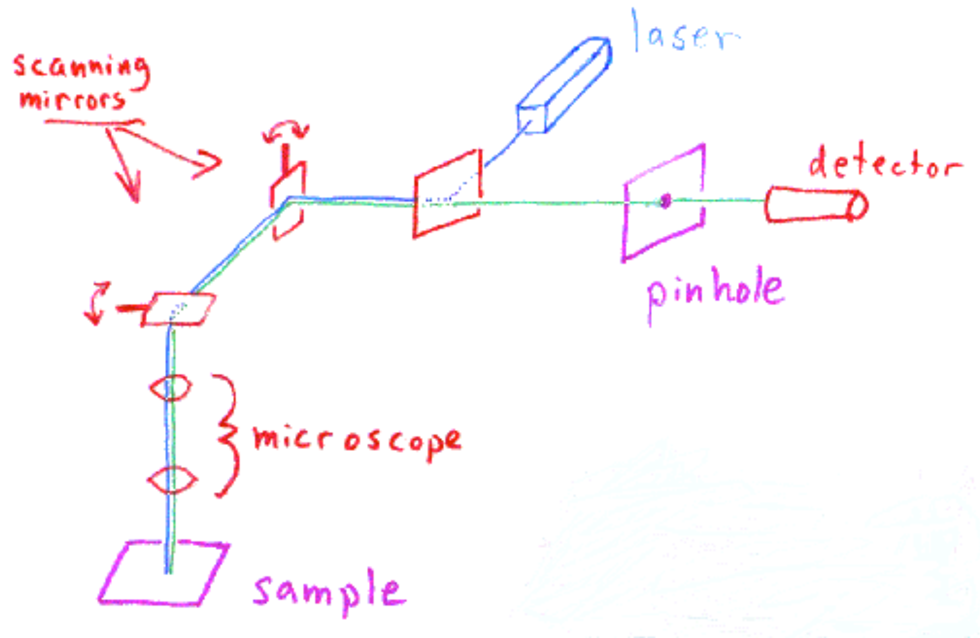
And the leap to confocal microscopy?



- Red and blue are two different sets of rays of light (not different λ's)
- Pinhole to reject out of focus light
- Solves one of the problems with regular microscopy:
  all of sample is fluorescing → hazy images

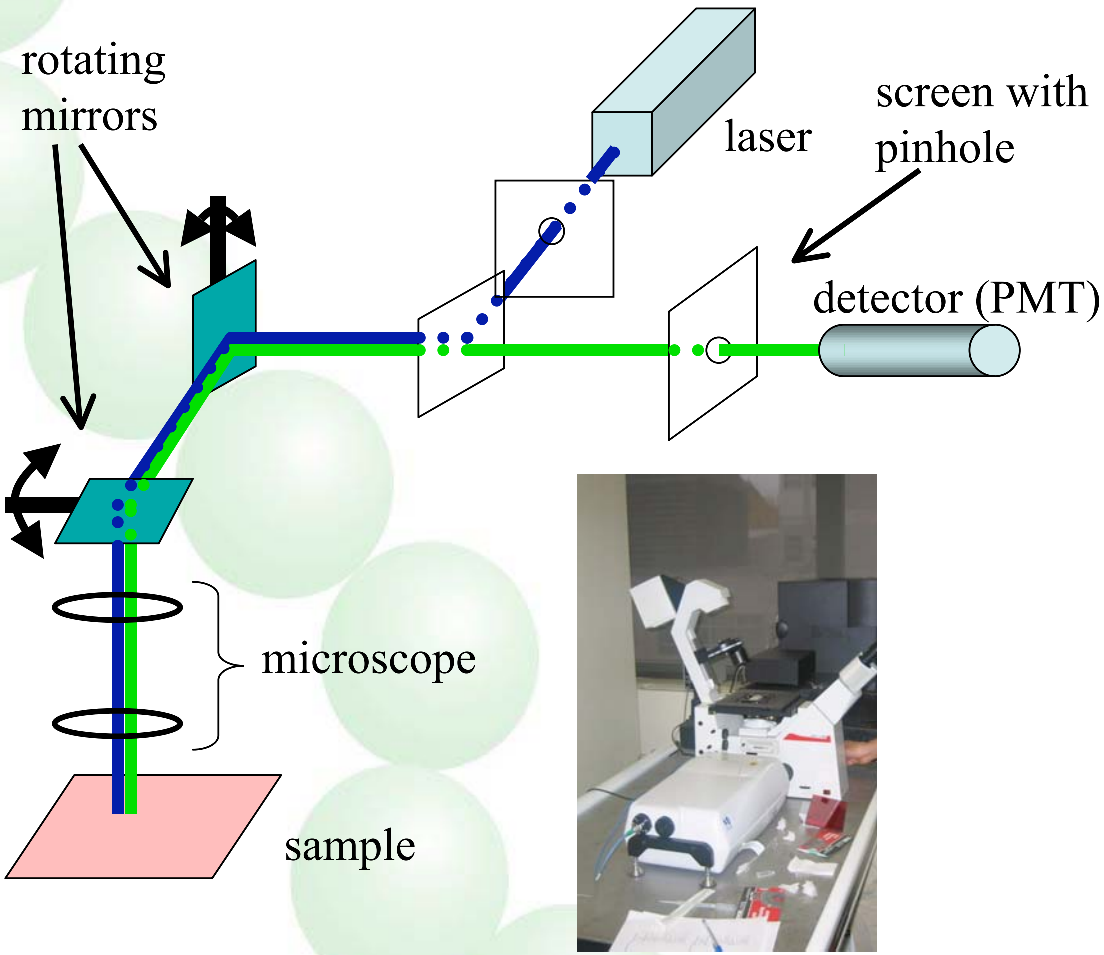
Focal point of objective lens and pinhole are "**con**jugate points"

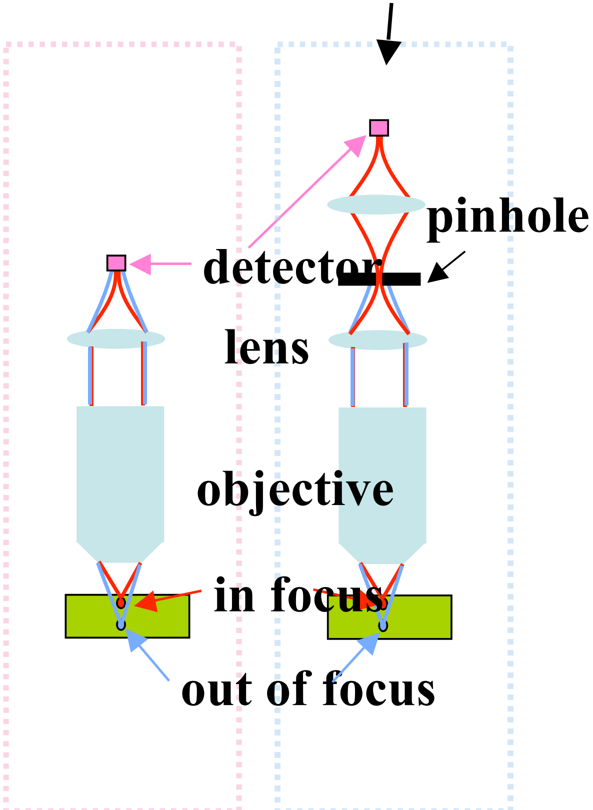
How a confocal microscope works:



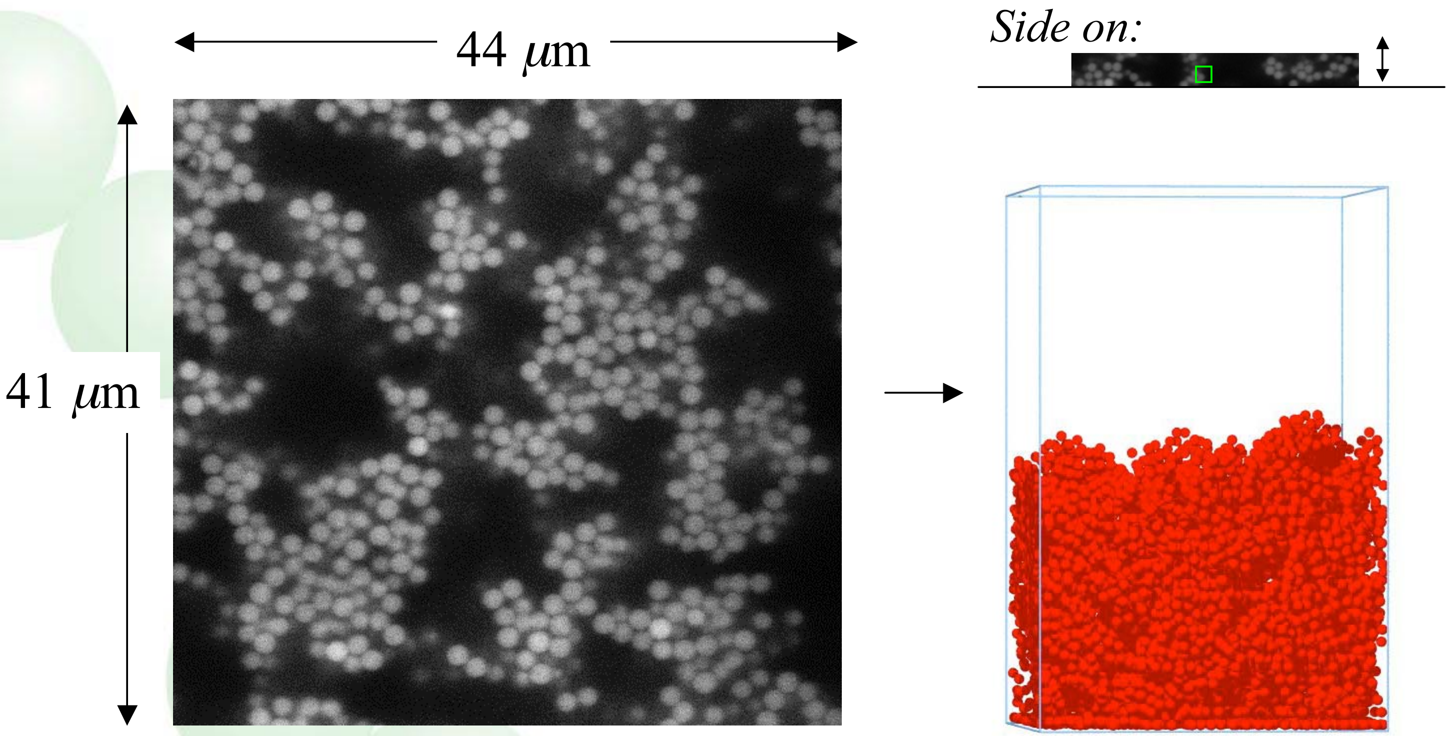
Invented by:
Marvin Minski, 1962

Confocal microscopy



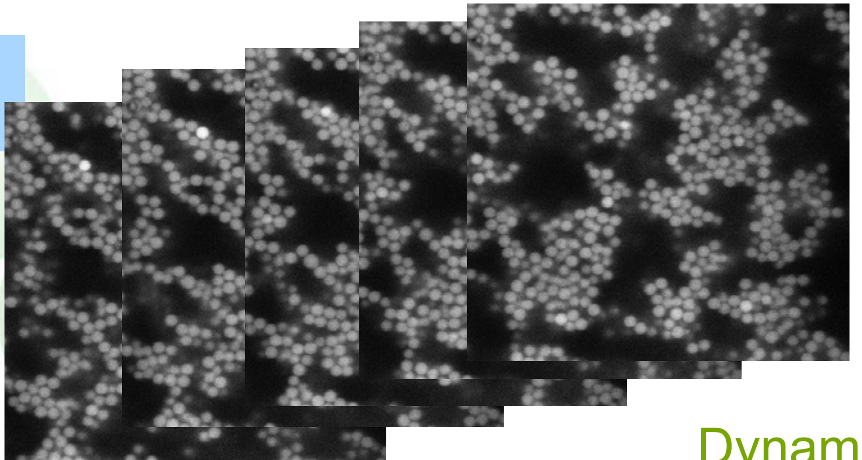


3D - Tracking in Depth:
Find the particles for all of your data



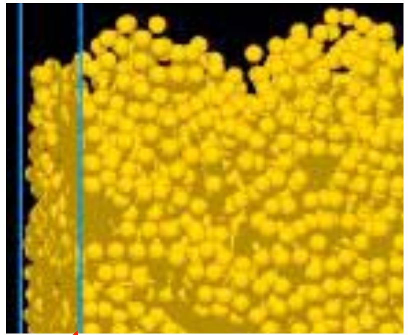
Full 3D Structure In PMMA-PS Depletion Gels

$\Delta z = 0.25 \mu m$
$d = 1.26 \mu m$



$\rightarrow \begin{bmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ \vdots & \vdots & \vdots \end{bmatrix}(t)$

reconstruct



Dynamics
$\left\langle \left(r(t) - r(0)\right)^2 \right\rangle$

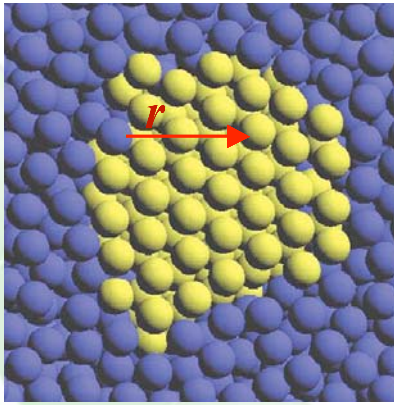
Spatial Correlations and Order
g(*r*), *T*, *Q*

Structure

Analyze the 3D data to do your science

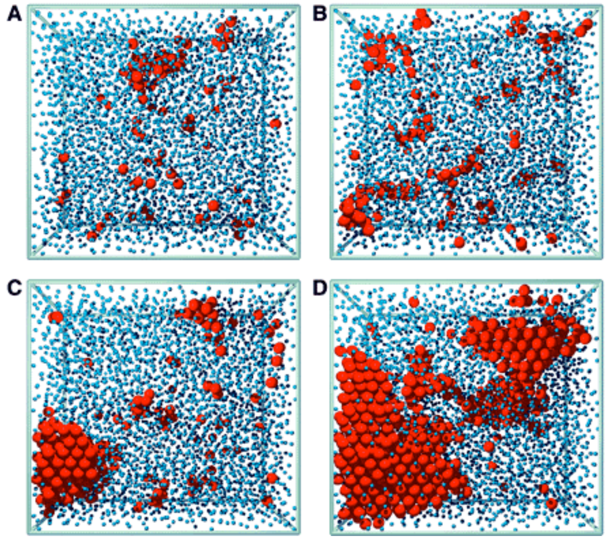
Crystallization: nucleation and growth

$$\Delta G = 4\pi r^2 \gamma - \frac{4\pi}{3} r^3 \Delta\mu n$$



Auer & Frenkel *Nature* 2001

Simulation

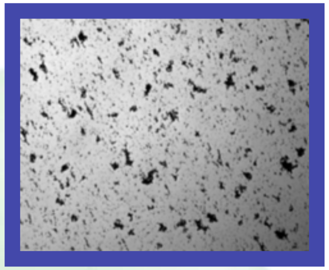


Gasser et al. *Science* 2001

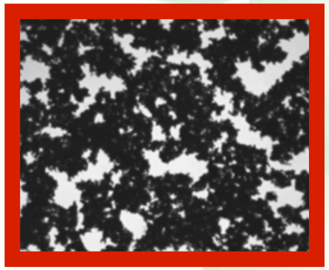
Experiment

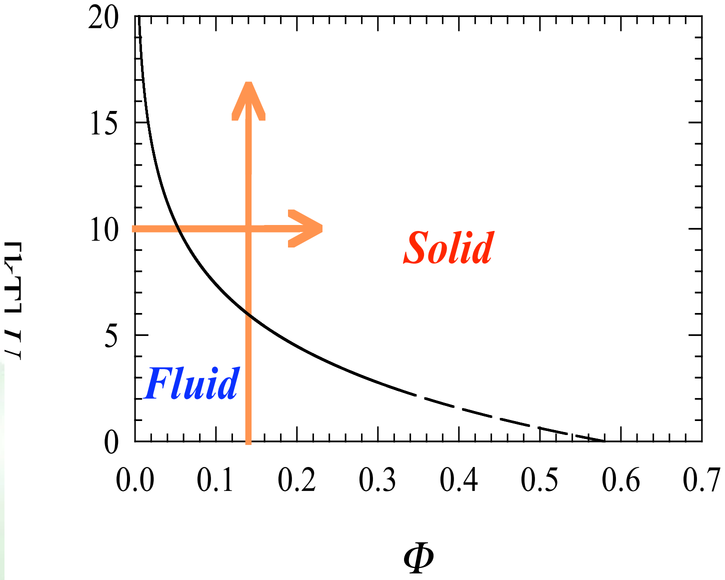
Fluid-Solid Transition

Weakly Attractive Systems

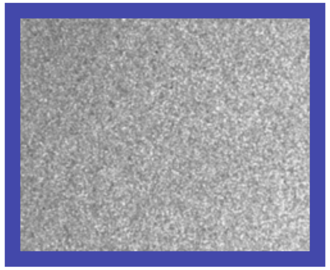


ϕ ↓

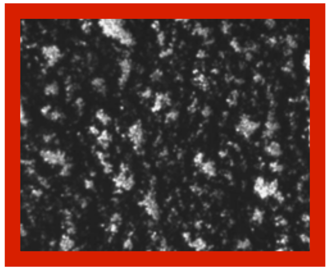




Phase diagram



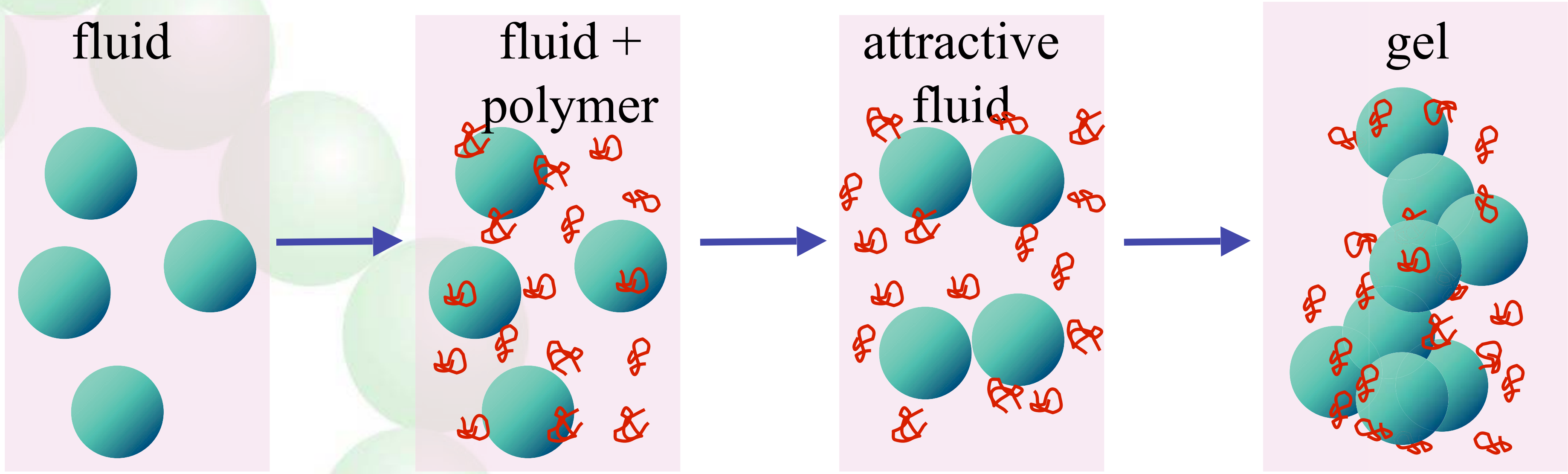
↓ U



Realization of weakly attractive systems:

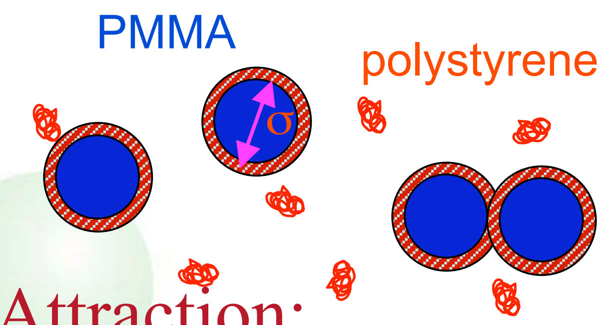
Colloid-polymer mixtures

Depletion attraction



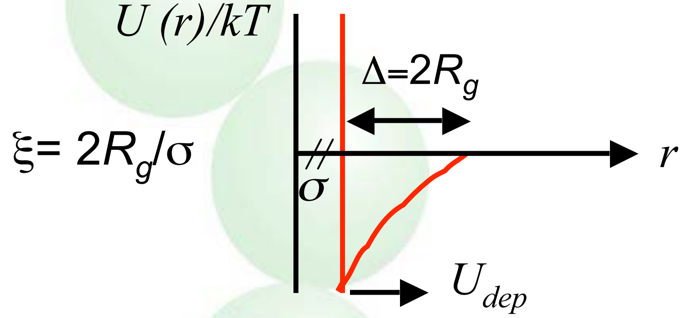
Polystyrene polymer, R_g=46 nm + PMMA spheres, r_c=650 nm

Model systems of colloid-polymer mixture



Attraction:

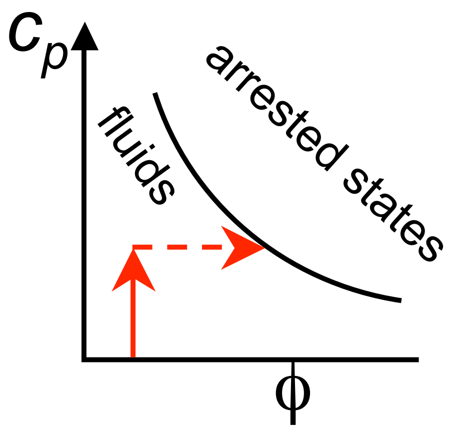
Depletion Interaction



PMMA as colloids

PS nonadsorbing polymer as depletant

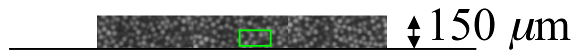
Asakura and Oosawa, *J. Polym. Sci* (1958)



System: PMMA (σ=1.326 μm) and Δ~0.14 σ in refractive index-matching and buoyancy-tunable suspending fluids Decalin/Tetralin/CXB

Δn = 0 and $\Delta\rho$ = 0.011g/cm^3

Side view:



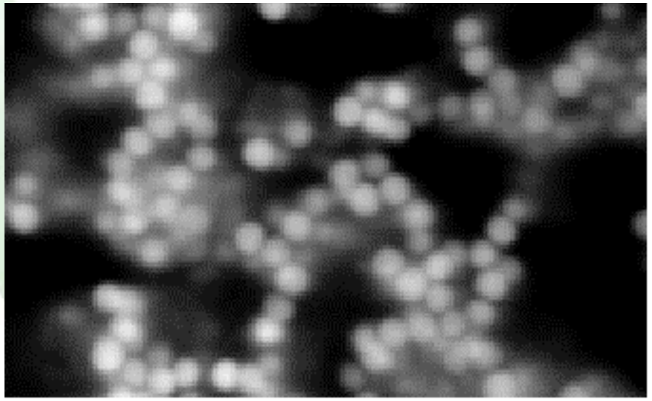
Confocal microscopy 3D real-space imaging

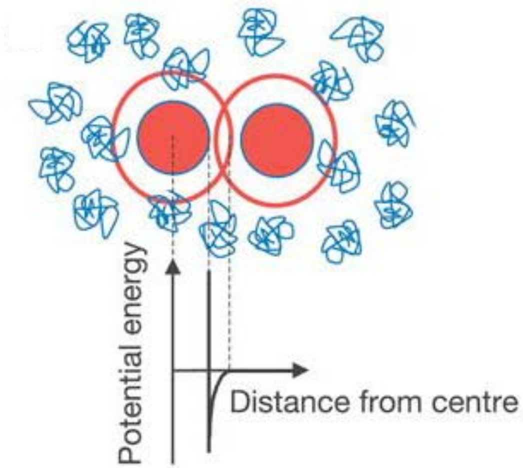
typical volume:

(22.6 X 22.6 X 10)μm^3

What Are Gels?

Colloidal gel: Network formation of colloidal particles





Gels are network of strongly attractive particles

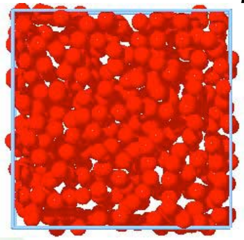
The attractive force is induced by adding polymer which introduces a depletion force

Microscopic Dynamics

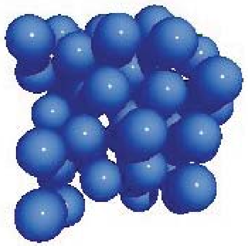
spatial correlations, mean square displacement using confocal microscopy

Dynamical heterogeneity and intermittence

- *Conventional liquids*: dynamical relaxation is achieved through continuous Brownian motion

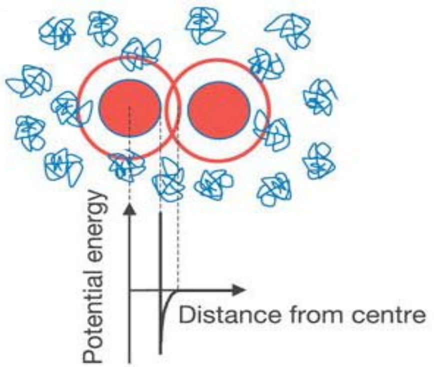


- *Supercooled liquids*: dynamics becomes localized and shows heterogeneity and discontinuity due to cage break-up



Heuer *et al*. *PRL* (1998)
Glotzer *et al*. *PRE* (1999);
Weeks *et al*. *PRL* (2002);

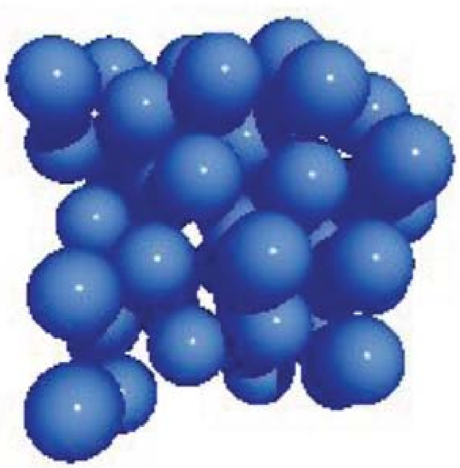
- *Attractive systems*: dynamics shows heterogeneity and intermittence due to bond breaking and forming



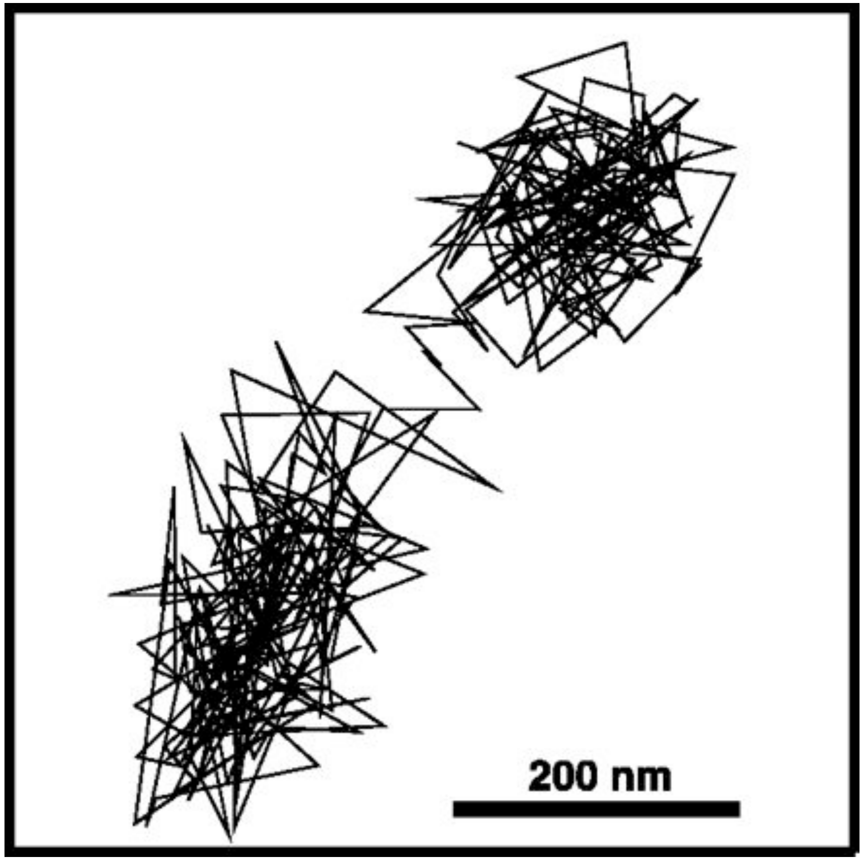
Light scattering+MCT: Manley *et al.* (2005)
MD Simulation: Cates *et al.* (2004)

Caged particles in hard sphere glass

Motion of caged particles
in a colloidial glass



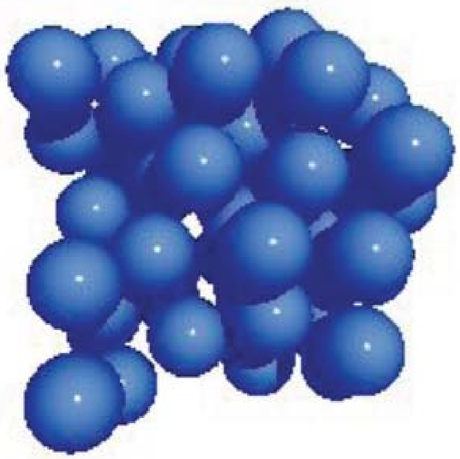
Trajectory of particles caged by neighbours



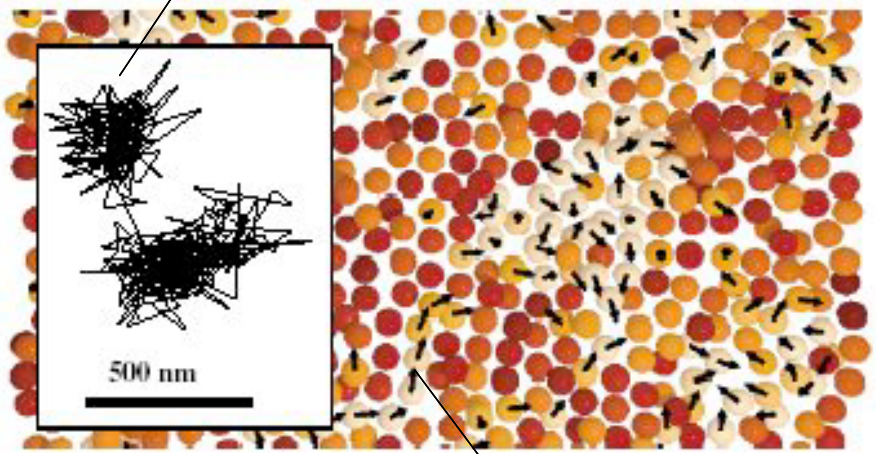
Weeks *et al*., *Science* 287, 627 (2000)

Caged Particles in Glasses

Cage effect of neighboring particles in a colloidal glass



Trajectory of particles caged by their neighbors

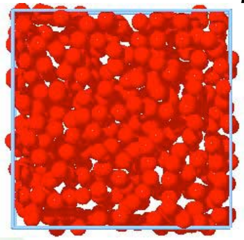


Cooperative motion

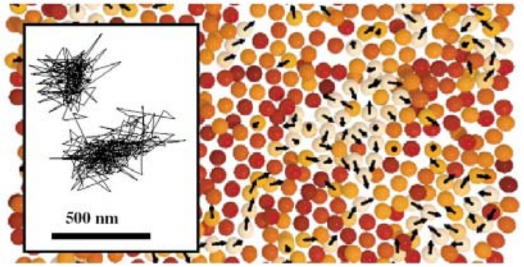
Eric R. Weeks *et al.*, *PRL* vol 89, 095704 (2002)

Dynamical heterogeneity and intermittence

- *Conventional liquids*: dynamical relaxation is achieved through continuous Brownian motion

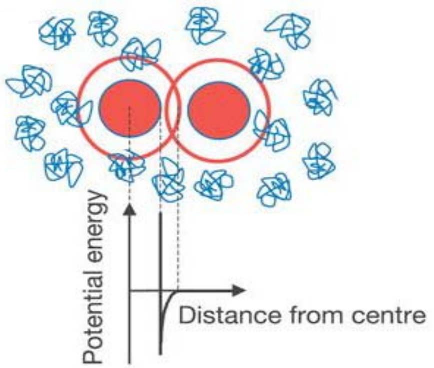


- *Supercooled liquids*: dynamics becomes localized and shows heterogeneity and discontinuity due to cage break-up



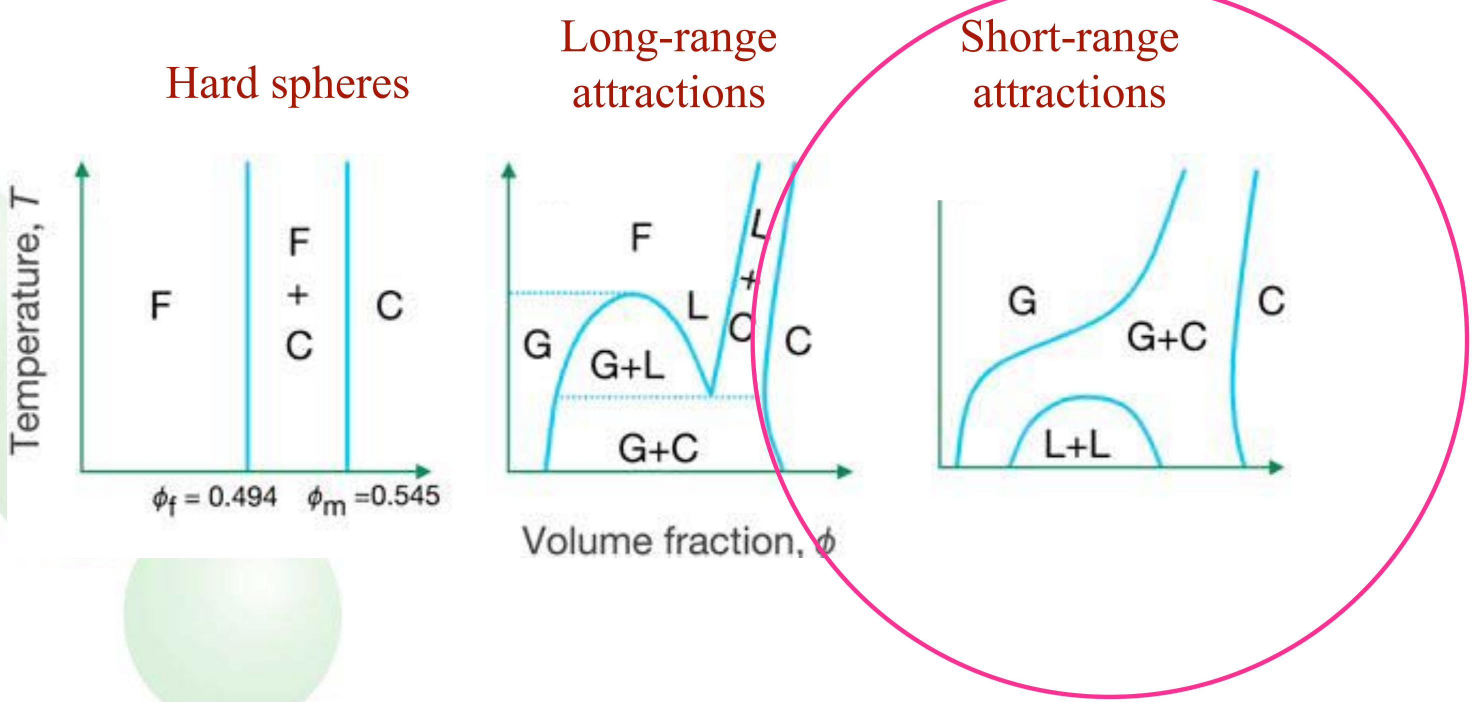
Heuer *et al*. *PRL* (1998)
Glotzer *et al*. *PRE* (1999);
Weeks *et al*. *PRL* (2002);

- *Attractive systems*: dynamics shows heterogeneity and intermittence due to bond breaking and forming

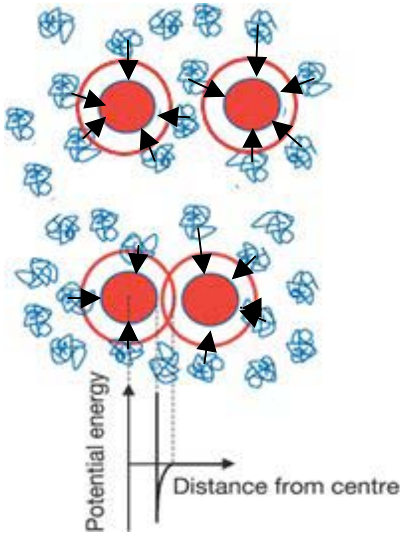


Light scattering+MCT: Manley *et al.* (2005)
MD Simulation: Cates *et al.* (2004)

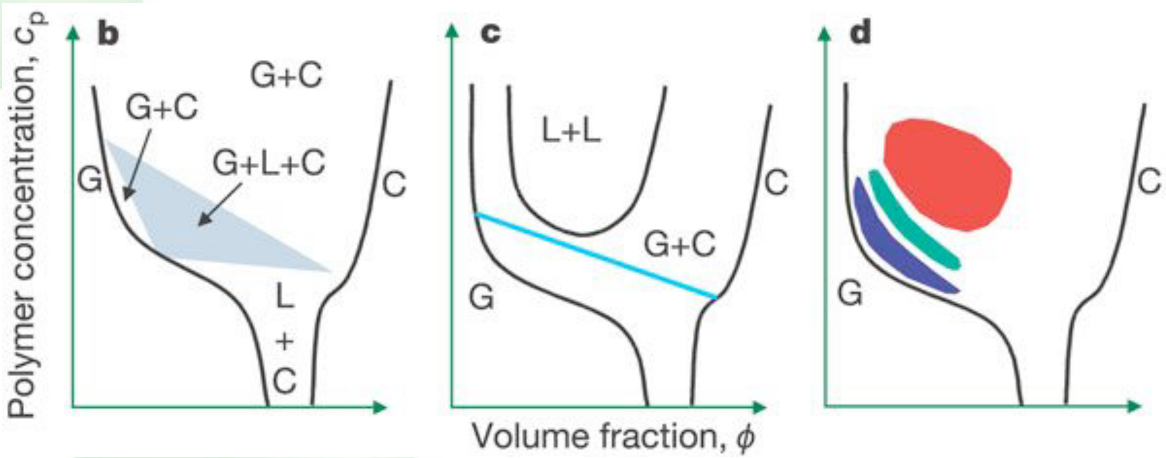
Naturally Occurring Phase Diagrams



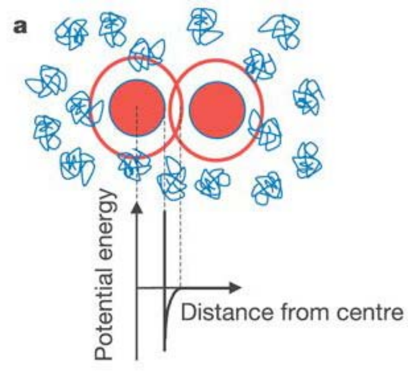
Naturally Occurring Phase Diagrams

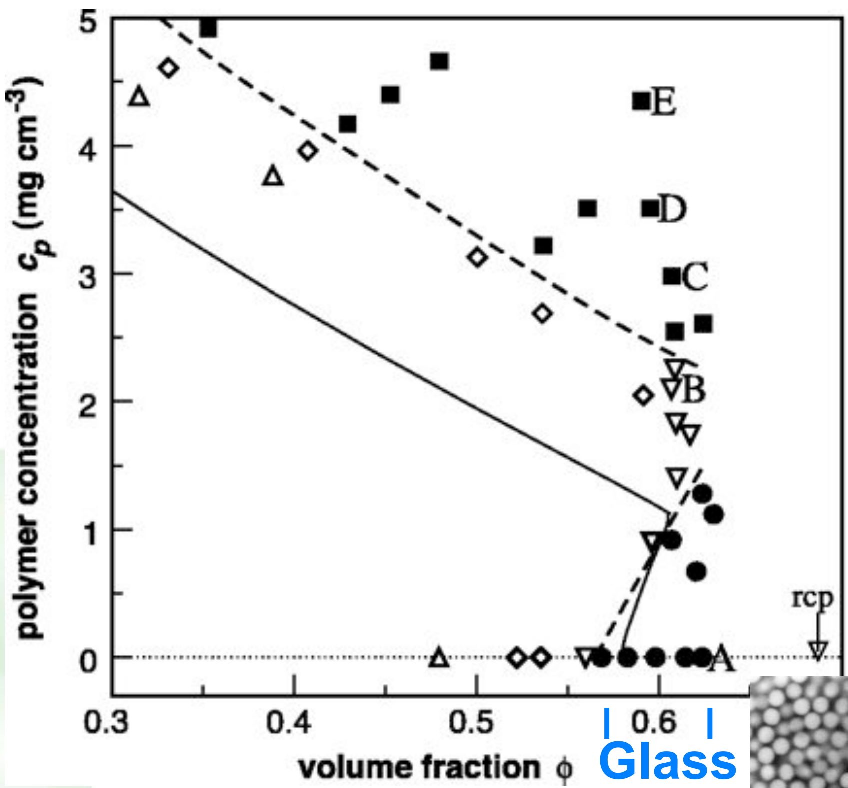


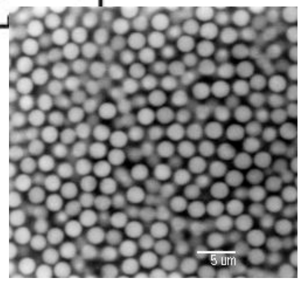
Depletion attraction:
Asakura & Oosawa, *J. Chem. Phys*. 1958;
Vrij, *Pure Appl. Chem*. 1976



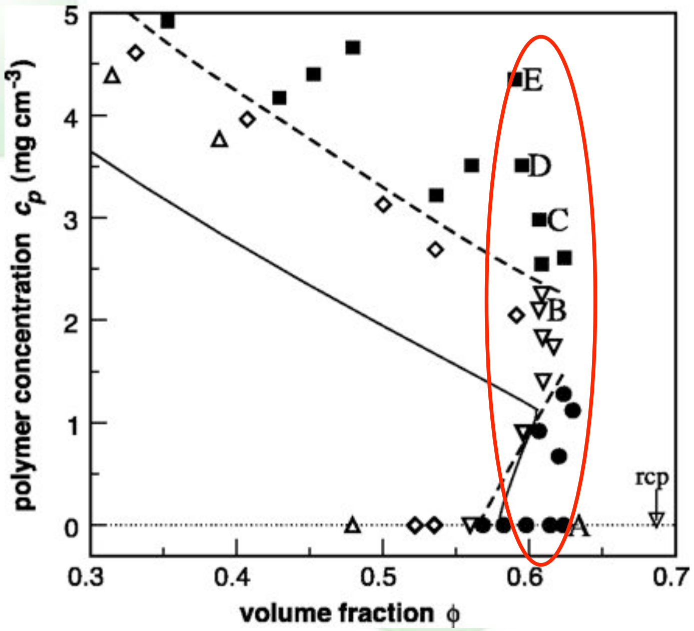
Deviations from hard spheres: added attractive interaction

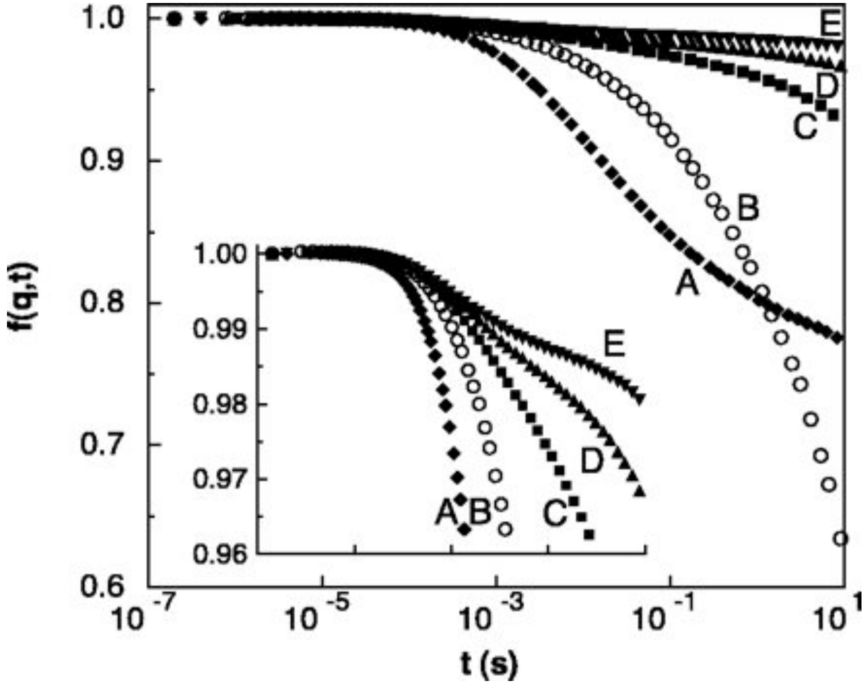






New type of colloidal glass: "Attractive Glass"

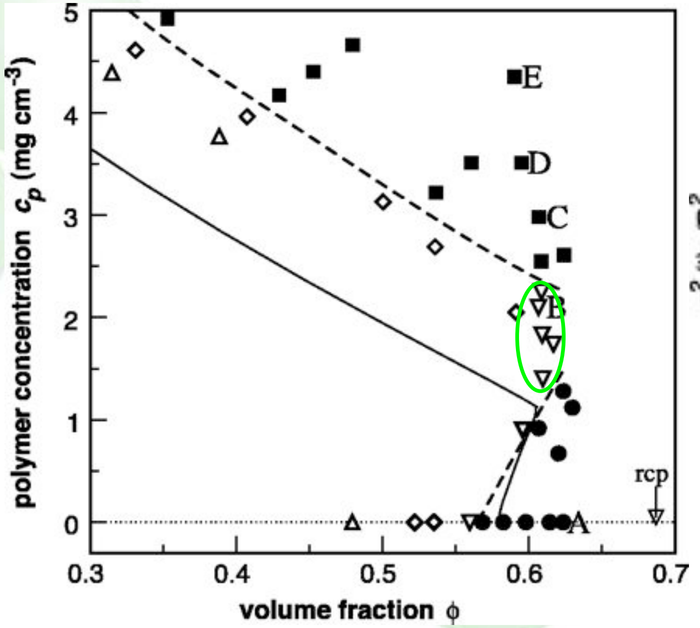


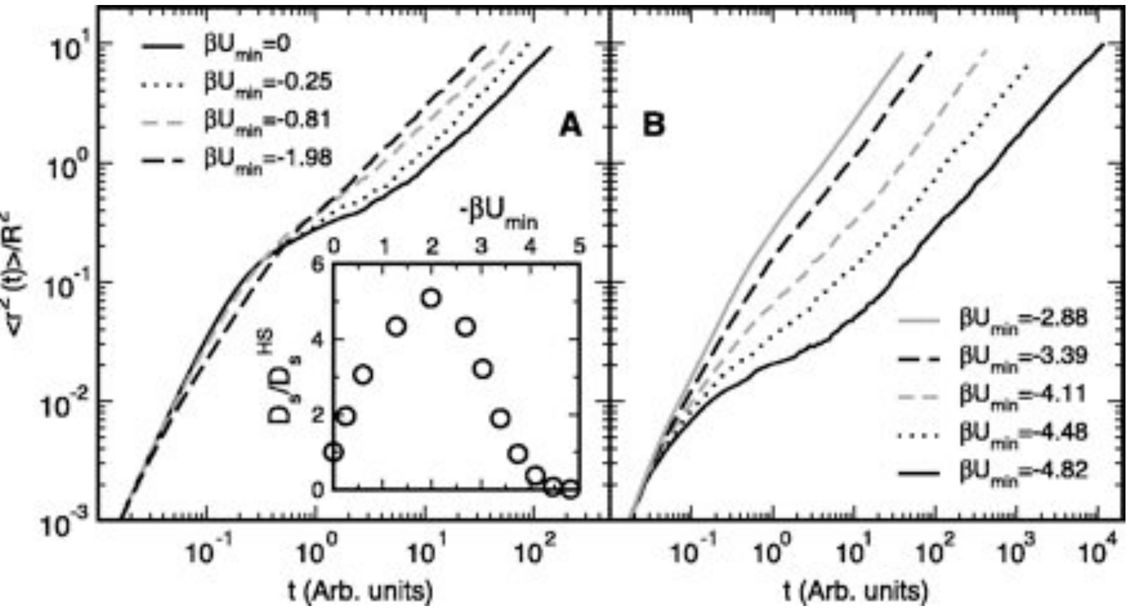


Light scattering: normalized dynamic structure factor

K.N.Pham *et al.*, *Science* 296,104 (2002)

New type of colloidal glass: "Attractive Glass"



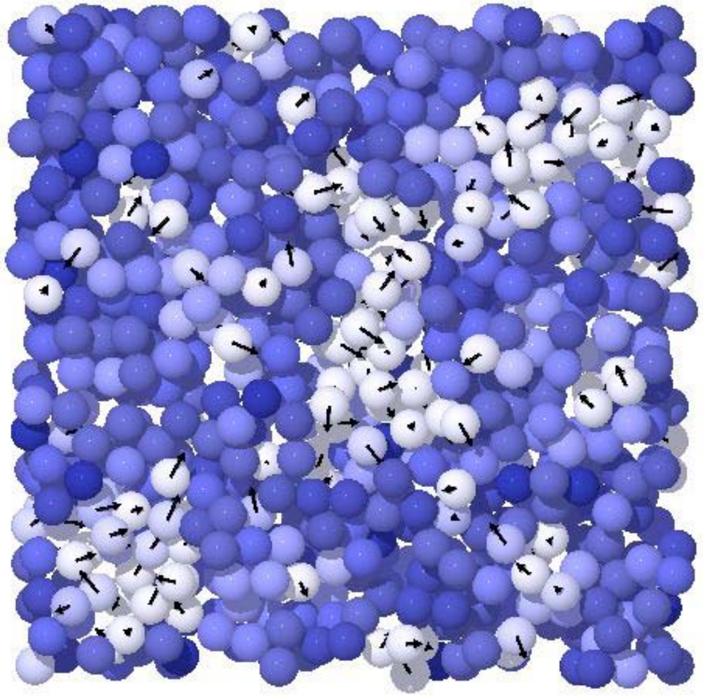


Computer simulation of glass reentrant from repulsive to attractive

K.N.Pham *et al.*, *Science* 296,104 (2002)

Experimental observation of dynamical heterogeneity in an attractive system

ϕ=0.429, U_{dep}=2.86 $k_B T$



$$\Delta r = |\vec{r}_i(t^*) - \vec{r}_i(0)|$$

$\Delta r > 0.5\mu m$

$0.5\mu m > \Delta r > 0.4\mu m$

$0.4\mu m > \Delta r > 0.3\mu m$

$0.3\mu m > \Delta r > 0.25\mu m$

$0.25\mu m > \Delta r > 0.2\mu m$

$0.2\mu m > \Delta r > 0.15\mu m$

$0.15\mu m > \Delta r > 0.1\mu m$

$0.1\mu m > \Delta r > 0.07\mu m$

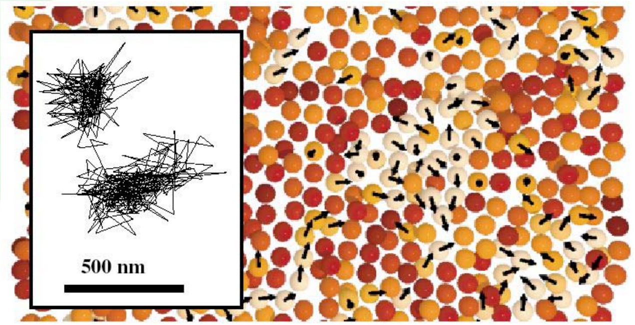
$0.07\mu m > \Delta r > 0.04\mu m$

$0.04\mu m > \Delta r$

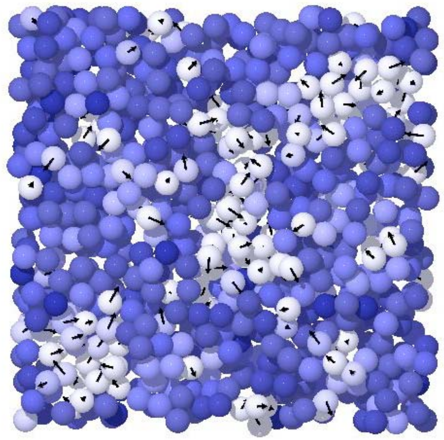
Arrows: unit vectors placed on particles with $\Delta r > 0.35\mu m$

Experimental observation of dynamical heterogeneity in an attractive system

ϕ=0.52, U=0



ϕ=0.429, U_{dep}=2.86 $k_B T$



Arrows: unit vectors placed on particles with $\Delta r > 0.35\mu m$

$\Delta r = |\vec{r}_i(t^*) - \vec{r}_i(0)|$

$\Delta r > 0.5\mu m$

$0.5\mu m > \Delta r > 0.4\mu m$

$0.4\mu m > \Delta r > 0.3\mu m$

$0.3\mu m > \Delta r > 0.25\mu m$

$0.25\mu m > \Delta r > 0.2\mu m$

$0.2\mu m > \Delta r > 0.15\mu m$

$0.15\mu m > \Delta r > 0.1\mu m$

$0.1\mu m > \Delta r > 0.07\mu m$

$0.07\mu m > \Delta r > 0.04\mu m$

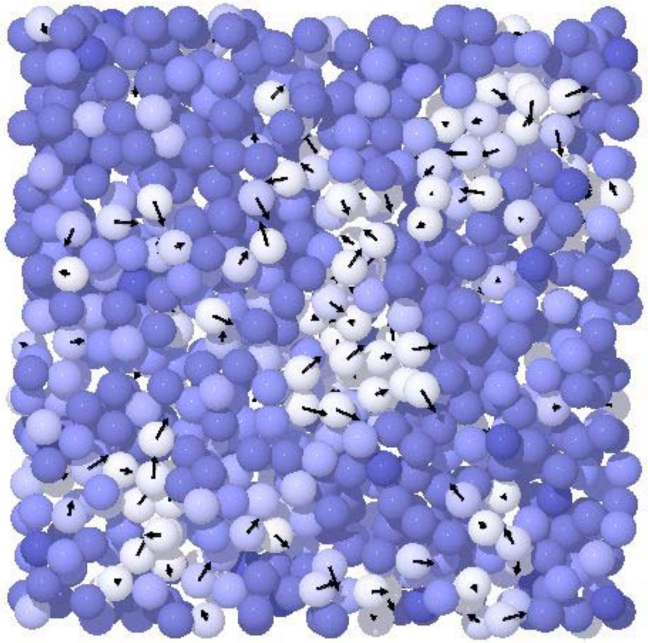
$0.04\mu m > \Delta r$

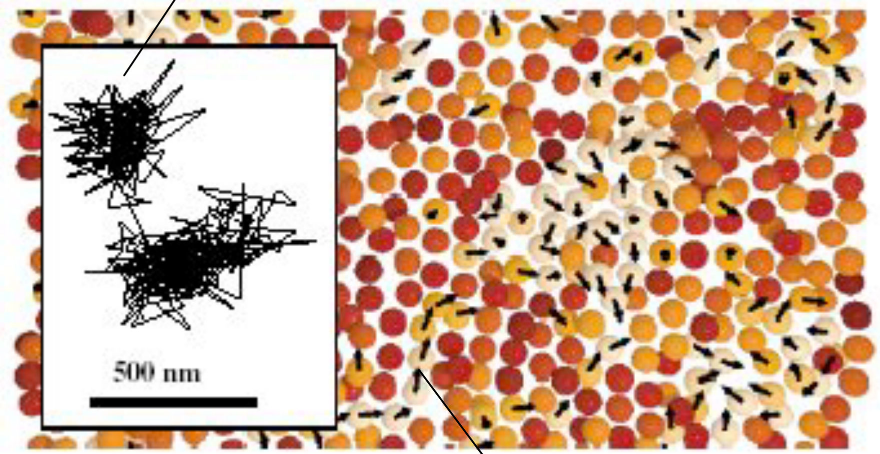
- Mobility nucleates near free volume, qualitatively different from repulsive supercooled liquids
- Appears to confirm the conjecture proposed by Manley *et al.* and Cates *et al.*

Highly Localized Motion in Gels

Confining effect of neighboring particles in a colloidal gel

Trajectory of particles caged by their neighbors





Cooperative motion

Eric R. Weeks *et al.*, *PRL* vol 89, 095704 (2002)

Not really cooperative motion

Conclusions

•Model hard sphere and deviations-from-hard-sphere soft matter systems used to answer some basic questions central to understanding the simplicity and complexity of nature:

- Self assembly
- Rigidity
- Dynamics of systems driven far from equilibrium
- Evolving networks

•Progress can be made in learning from simple systems