Lecture 1: Phase transitions explored in soft-matter systems

S-RSI Physics Lectures:
Soft Condensed Matter Physics

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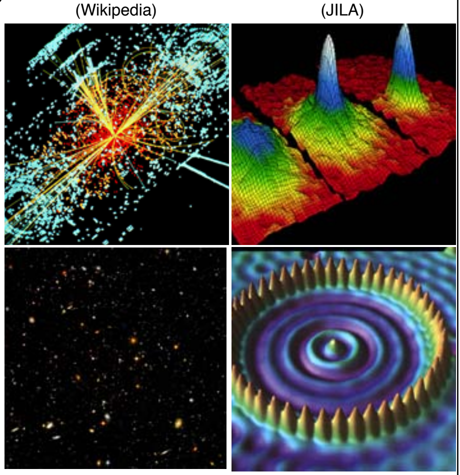
What is **condensed matter**?

- *High energy physics:* study of fundamental particles that make up matter (quarks, neutrinos, photons, electrons, gluons, bosons, etc.)
- *Atomic/molecular/optical*: study of the physical properties of single atoms and molecules (hydrogen, helium) and their interactions with light
- *Astrophysics*: study of the physical properties and interactions of celestial objects (galaxies, stars, etc.)
- *Condensed matter*: study of macroscopic properties of matter (especially with large numbers of strongly interacting particles)

Simulated Higgs boson data (Wikipedia)
Bose-Einstein condensate (JILA)

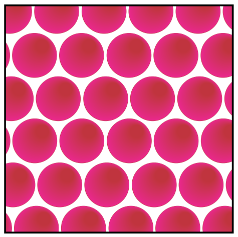


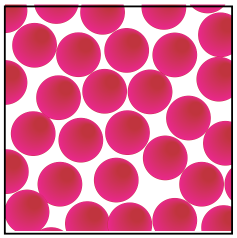
Hubble Ultra Deep Field (Wikipedia)
Electron density distribution (pitb.physics.ubc.ca)

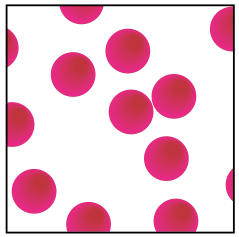
States of condensed matter

SOLID | **LIQUID** | **GAS**

Arrangement of atoms or molecules:







Images taken from Wikipedia

What is **soft** condensed matter?

- *Solid-state physics*
  - Primarily concerned with <u>crystals</u>: atoms in a regular solid-like arrangement
  - Phase transitions: how the <u>phase</u> of a system changes in response to an external parameter (e.g. melting)
- *Soft-matter physics*
  - Concerned with materials whose mechanical properties are intermediate between solids/liquids/gases
- Soft-matter physics is closely related to:
  - *Nanotechnology:* How physical properties change as materials are made very small
  - *Biophysics*: Physical properties of biological systems

Soft condensed matter physics

- Lecture 1: statistical mechanics and phase transitions via colloids
- Lecture 2: fluid mechanics for physicists
- Lecture 3: physics of bacteria
- Lecture 4: biophysics of cell mechanics
- Lecture 5: Dr. Conrad’s work

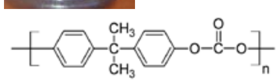
Amorphous solids: glasses

A glass is a solid in which the atoms or molecules are not arranged in a regular lattice — structurally, the solid glass “looks” like the liquid

Materials applications:

Oxide glasses: e.g. SiO_2

Polymer glasses: e.g. polycarbonates



Metallic glasses: usually alloys

Images taken from Wikipedia

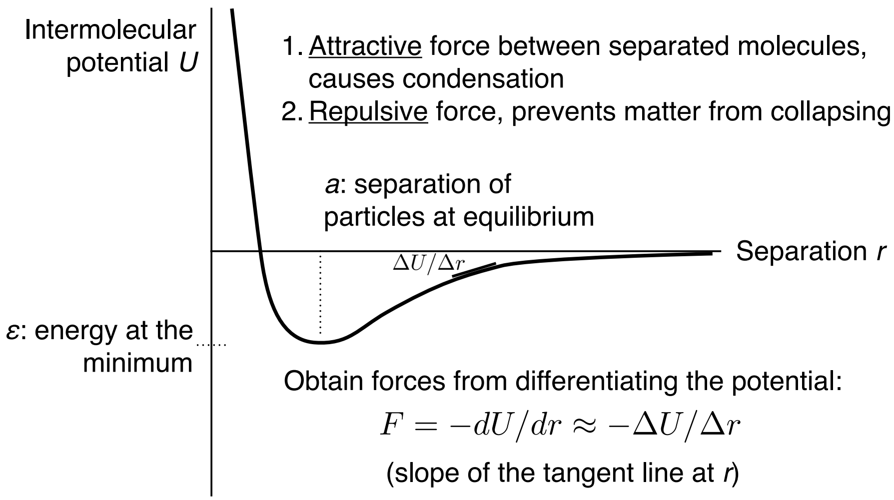
Big question for today's lecture

How does a disordered liquid become a disordered glass? and how can soft matter contribute to the study of phase transitions?

Intermolecular interactions

What forces must act between atoms/molecules in a condensed matter system?

1. Attractive force between separated molecules, causes condensation
2. Repulsive force, prevents matter from collapsing



Obtain forces from differentiating the potential:

$$F = -dU/dr \approx -\Delta U/\Delta r$$

(slope of the tangent line at r)

What drives phase transitions? 1

Total energy of a water molecule: sum of potential energy and kinetic energy

$$E = U + K$$

Apply thermodynamics and the kinetic theory of gases:

Ideal gas law: $PV = Nk_BT$

From kinetic theory of gases (derivation: conservation of momentum): $P = \dfrac{Nm\overline{v^2}}{3V}$

Equate to obtain expression for kinetic energy: $K \equiv \dfrac{1}{2}N\overline{v^2} = \dfrac{3}{2}Nk_BT$

Result: kinetic energy depends on the temperature of the system

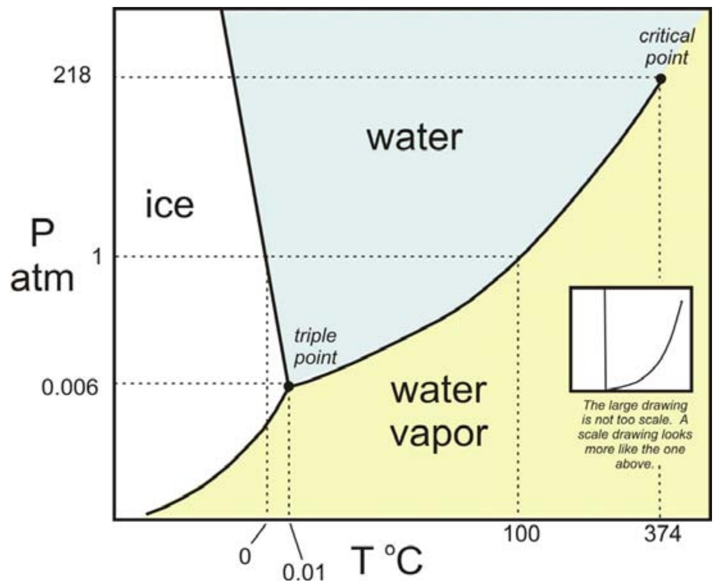
P: pressure
V: volume
N: number of molecules
k_B: Boltzmann constant
T: temperature
v: velocity

What drives phase transitions? 2

Changes in importance of contributions to total energy

- At high temperatures (T > 100C): Gas has mostly kinetic energy
  - Potential energy (interactions) unimportant
- As temperature lowered: Attractive interactions become more important
  - Increase in correlations between molecules (pairs, triplets)
  - Correlations lead to deviations from ideal gas law
- Transition to liquid water occurs when clusters become permanent
  - Contributions to energy: interparticle attraction + kinetic energy + short-range repulsion
  - Competition between attraction (packing of molecules) and repulsion (minimum separation between molecules)
- Transition to solid ice resolves this competition by creating a regular packing of molecules
  - Higher-density ordered state (large attractive contribution) state still satisfying minimum-distance constraint (repulsion)

Phase diagram of water



Phase diagram: serc.carleton.edu

Simplified interactions: hard spheres

We will consider a simplified model for interparticle interactions: <u>hard spheres</u>

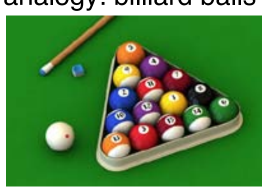
Intermolecular potential U

1. Infinite <u>repulsion</u> at contact ($r = 0$)
2. No interaction for $r > 0$

To study phase behavior, need a <u>model system</u> of small particles that exhibit thermal fluctuations

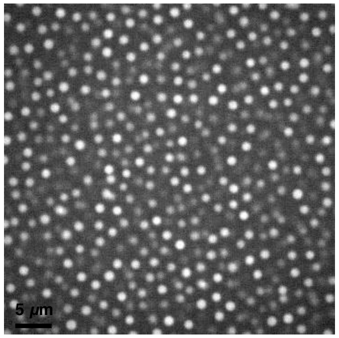
Separation r

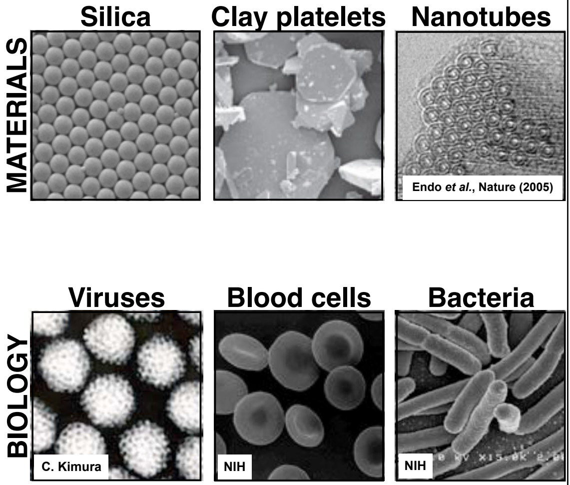
Real-world analogy: billiard balls



Colloids as a soft-matter model system

Colloids are suspensions of micron-size particles in fluid



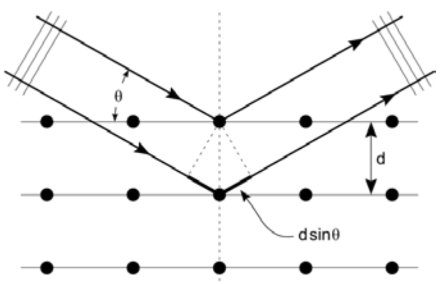


- Particle size ~ 0.05–5 μm
- Thermal fluctuations important
- Energy scale ~ kT

Scattering by colloids

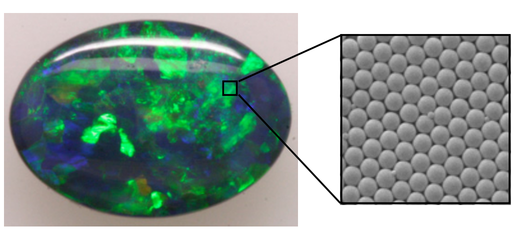
Bragg's law (classical physics): $2d\sin\theta = n\lambda$

d = spacing between planes of atoms
θ = incident angle of light
λ= wavelength of light



Regular planes of atoms create <u>constructive</u> or <u>destructive</u> interference of light

Materials example: "play of color" in precious opal



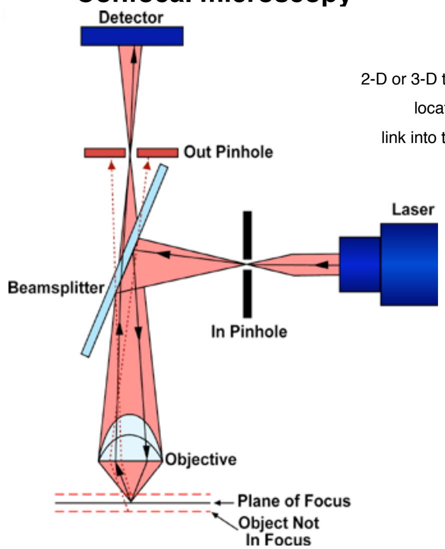
Opal image: mardonjewelers.com

Phase diagram from bulk

Pusey and van Megen, Nature (1986)

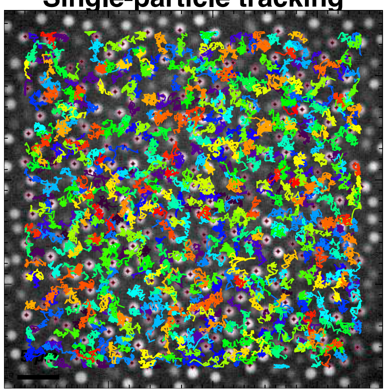
Direct imaging of colloids

Confocal microscopy



Single-particle tracking

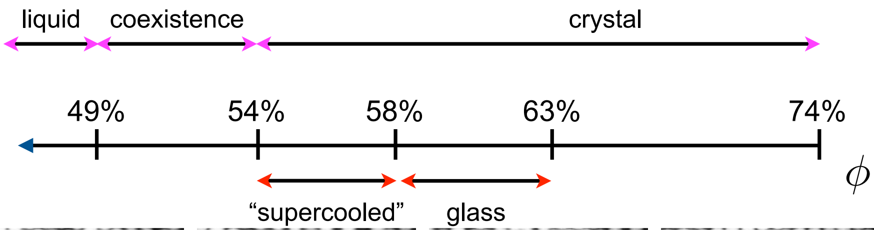
2-D or 3-D time series
locate features
link into trajectories

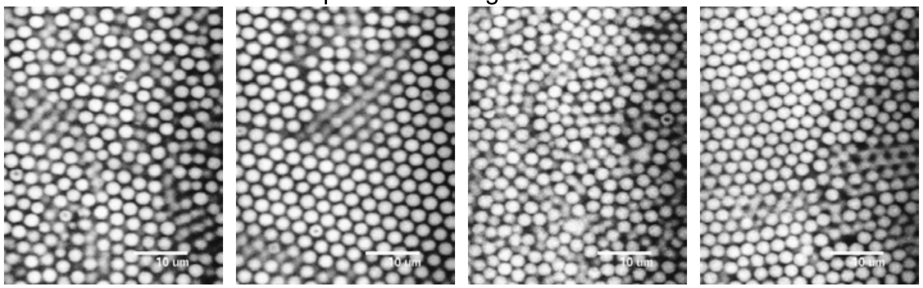


Confocal schematic: olympusmicro.com

Tracking code based on:
Crocker and Grier, *J. Colloid Interface Sci.* (1996)

Non-equilibrium phase diagram





$\phi \approx 0.48$ $\phi \approx 0.54$ $\phi \approx 0.63$ $\phi \approx 0.74$

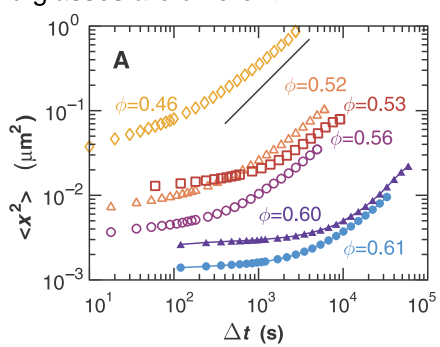
Glass transition related to arrest of particles

Measure the dynamics as a function of time via the <u>mean-square displacement</u> (MSD):

$$\left\langle \Delta x^2(\Delta t) \right\rangle = \left\langle (x(t+\Delta t) - x(t))^2 \right\rangle_t$$

The dynamics of particles in liquids and glasses are different:

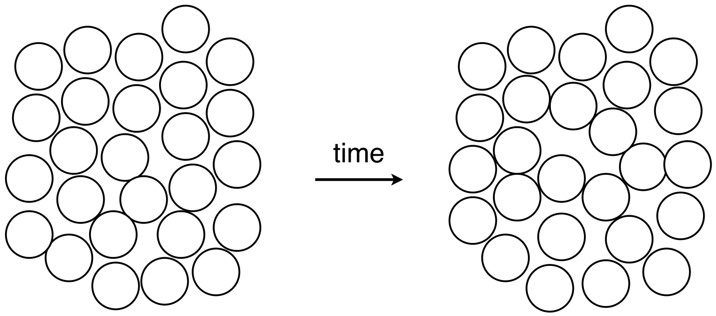
1. In liquids: $\left\langle \Delta x^2(\Delta t) \right\rangle = 2D\Delta t$
   where D is given by the Stokes-Einstein equation:
   $$D = \frac{k_B T}{6\pi\eta a}$$
2. In glasses, the MSD is nearly independent of time.



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

Cage escape and relaxations

Microscopically: particles in a liquid can relax in a finite amount of time



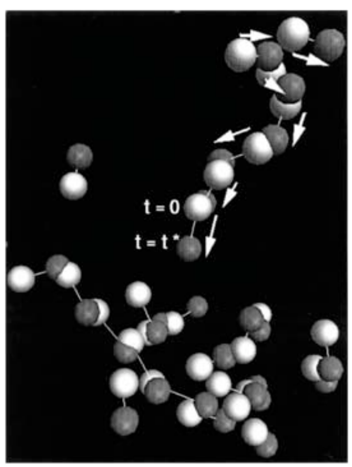
In dense liquids, this happens via <u>cage escape</u>: a particle can only relax if it can escape from the cage that is formed by its neighbors

Prediction: dynamical heterogeneities

Hypothesis: the glass transition is driven by <u>dynamic arrest</u>: the size of cage rearrangements needed to allow the system to flow increases as the system becomes more concentrated

First shown using computer simulation models: only particles that move large distances over a time t* are shown:

$$|r(t^*) - r(0)|$$

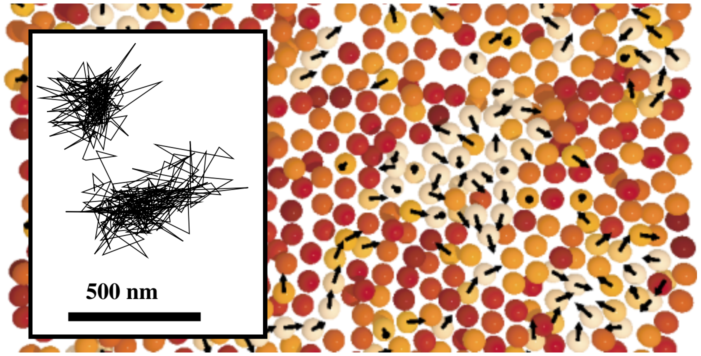


Donati *et al.*, Phys. Rev. Lett. (1998)

Experiments: colloidal glasses

Experimentally: identify 5% fastest particles by their total displacement:

$$|r(t^*) - r(0)|$$



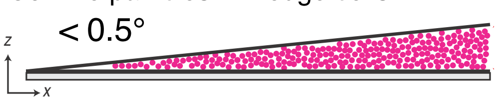
Fast-moving relaxing particles move in a chain of rearrangements

Weeks and Weitz, *Phys. Rev. Lett.* (2002)

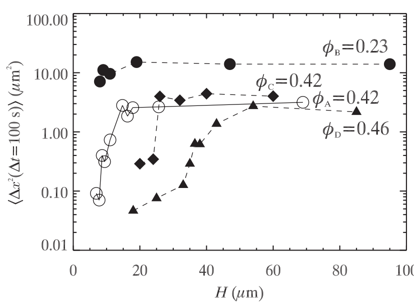
Colloidal glasses in confinement

Hypothesis: If the size of the rearranging region is important, then confining the sample between parallel walls should change the volume fraction at which a liquid becomes a solid glass

Confine particles in wedge cells:



and measure the mean-square displacement at a fixed time as a function of the thickness of the chamber (H).



The dynamics of supercooled fluids arrest and become glassy when confined below 20 particle diameters

Nugent *et al.*, *Phys. Rev. Lett.* (2007)

Brief summary for spheres

- Colloidal model systems can be used to study the liquid-to-solid glass transition.
- Supercooled fluids relax cooperatively, with relaxing particles forming stringlike chains.
- As the glass transition is approached (by increasing concentration), the size of cooperatively relaxing regions increases.
- Confining a glass leads to an earlier onset of solid behavior, because the size of the relaxing regions reaches that of the container at lower volume fractions.

Improved model: non-spherical particles

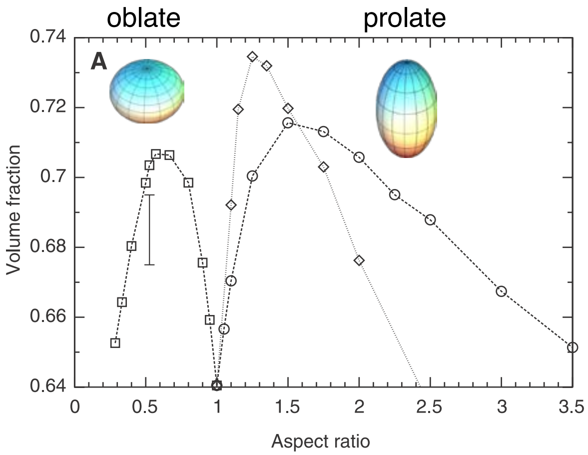
Molecules containing more than one particle are not typically spherical; other shapes provide a better approximation of the effects of <u>shape</u> on the glass transition.

Work of Chaikin (NYU) and Torquato (Princeton); Donev *et al.*, Science (2004)

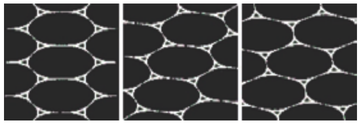
Optimal crystal packings of ellipsoids

Two types of deformed spheres, defined mathematically by the aspect ratio of the polar axis to the equatorial axis:

Oblate: squashed (a.r. < 1)
Prolate: stretched (a.r. > 1)



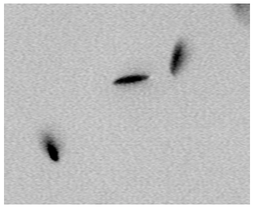
Ellipsoids form denser crystal packings than spheres



Donev *et al.*, Science (2004)

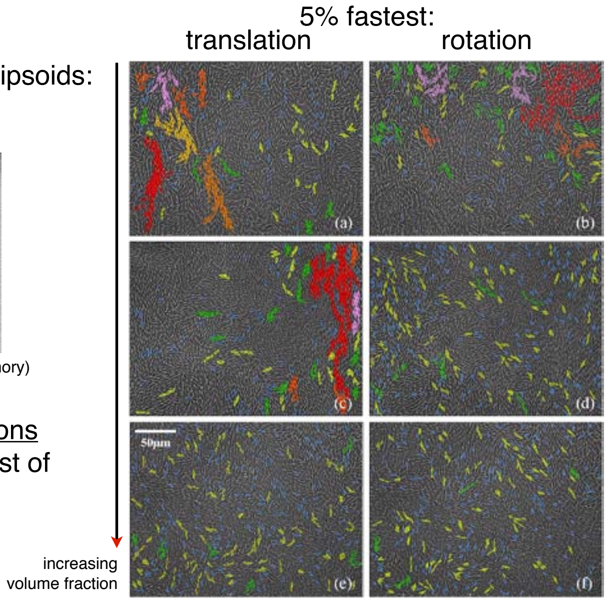
Glasses of ellipsoids

Two types of motion in ellipsoids: rotation and translation



Kenneth Desmond (Weeks group, Emory)

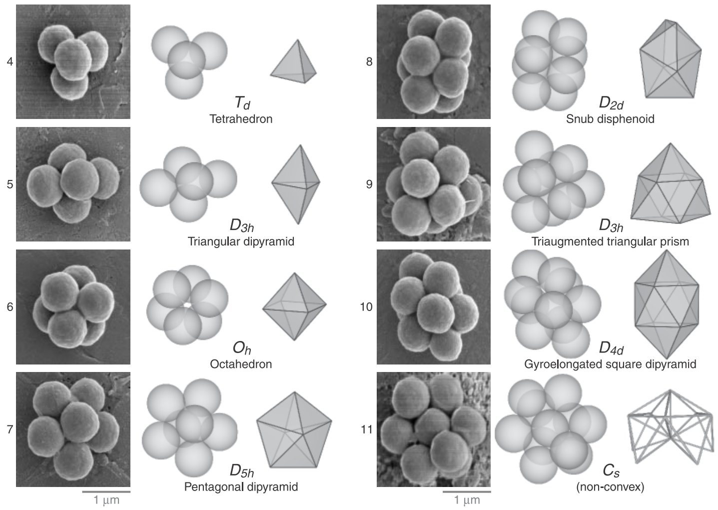
See distinct glass transitions corresponding to the arrest of (first) rotation and (then) translational motion



Zheng *et al.*, *Phys. Rev. Lett.* (2011)

Towards realistic colloidal molecules

Assemble colloids into structures that better resemble molecules:



Manoharan *et al.*, *Science* (2003)

What needs to be incorporated?

- Interparticle interactions
  - Uniform interactions
  - Non-uniform (polar and dipolar)
- Extended macromolecules
  - Models for polymers
  - Analogies between polymer glasses (entanglement) and colloidal glasses (crowding)
- Theoretical treatments
  - Descriptions of structural order in glasses
  - Relationship between structure and dynamics
  - Thermodynamics of phase transitions