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)
States of condensed matter

<table>
<thead>
<tr>
<th>SOLID</th>
<th>LIQUID</th>
<th>GAS</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Solid" /></td>
<td><img src="image2" alt="Liquid" /></td>
<td><img src="image3" alt="Gas" /></td>
</tr>
</tbody>
</table>

Arrangement of atoms or molecules:

Images taken from Wikipedia

What is **soft** condensed matter?

- **Solid-state physics**
  - Primarily concerned with **crystals**: atoms in a regular solid-like arrangement
  - Phase transitions: how the **phase** 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. SiO2
- 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

\[ F = -\frac{dU}{dr} \approx -\frac{\Delta U}{\Delta r} \]

(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):
\[ P = \frac{Nmv^2}{3V} \]

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

Result: kinetic energy depends on the temperature of the system

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

- Ice
- Water
- Water vapor

We will consider a simplified model for interparticle interactions: hard spheres

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

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

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

MATERIALS
- Silica
- Clay platelets
- Nanotubes

BIOLOGY
- Viruses
- Blood cells
- Bacteria

Colloids as suspensions of micron-size particles in fluid

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Scattering by colloids

Bragg’s law (classical physics):

\[2d \sin \theta = n\lambda\]

- \(d\) = spacing between planes of atoms
- \(\theta\) = incident angle of light
- \(\lambda\) = wavelength of light

Regular planes of atoms create constructive or destructive interference of light

Materials example:
- “play of color” in precious opal

Opal image: mardonjewelers.com

Opal image: mardonjewelers.com
Phase diagram from bulk


Direct imaging of colloids

Confocal microscopy

Single-particle tracking

Tracking code based on:
Crocker and Grier, J. Colloid Interface Sci. (1996)
Non-equilibrium phase diagram

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Coexistence</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>49%</td>
<td>54%</td>
<td>58%</td>
</tr>
<tr>
<td>63%</td>
<td>63%</td>
<td>74%</td>
</tr>
</tbody>
</table>

φ ≈ 0.48
φ ≈ 0.54
φ ≈ 0.63
φ ≈ 0.74

Glass transition related to arrest of particles

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

\[
\langle \Delta x^2(\Delta t) \rangle = \langle (x(t + \Delta t) - x(t))^2 \rangle_t
\]

The dynamics of particles in liquids and glasses are different:

1. In liquids: \( \langle \Delta x^2(\Delta t) \rangle = 2D\Delta t \)
   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.

Cage escape and relaxations

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

In dense liquids, this happens via cage escape: 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 dynamic arrest: 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:

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

**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

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**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:

\(< 0.5^\circ\)

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
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 shape 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


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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

Towards realistic colloidal molecules

Assemble colloids into structures that better resemble molecules:


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