LECTURE 1:
Disordered solids: Structure properties

• What is an disordered solid
• How do we measure disorder
• How are amorphous solids typically formed
What are amorphous solids?
• inorganic compounds (e.g. SiO$_2$/silicates, B$_2$O$_3$/borates, GeO$_2$/germanates, etc)
• organic compounds (e.g. polymers)
• elements (e.g. sulfur)
• metal alloys (e.g. Fe$_{80}$B$_{20}$)
• Granular matter

Where do we encounter amorphous materials?

- Food products: mayonnaise, chocolate mousse, ketchup
- House products, cosmetics
- Plastic
- Transformers core material,
- Biomedical implants,
- Watches
- Fiber optics
- etc
Crystals

- Long-range order
- Regular atomic arrangement

Amorphous solids

- Short-range order
- Random atomic arrangement
$\text{B}_2\text{O}_3$ (crystal)

Borate glass
How do we measure disorder?

• Statistical measures: Probability distribution functions

• Thermodynamics measures: Excess volume
How do we measure disorder?

- **Statistical measure:** Probability distribution functions
  - Statistical description of atomic positions
  - Describes important features of the atomic arrangements
  - Accessible experimentally through scattering experiments
Single particle distribution function

- N atoms in the volume V of the material
- Average density $n_0 = \frac{N}{V}$
- Single particle distribution function
  
  $$n_1(r) = \langle \sum_i \delta(r - r_i) \rangle$$

- Ensemble average over possible configurations (statistical description)
- $n_1(r)dr$ is the average number of atom centers in a volume element $dr$ around $r$
- $n_1(r)dr$ can be interpreted as the probability to find an atom center between $r$ and $r+dr$
Two-particles distribution function

• N atoms in the volume V of the material

\[ n_2(r_1, r_2) = \langle \sum_i \sum_{j \neq i} \delta(r_i - r_1)\delta(r_j - r_2) \rangle \]

• Probability to find atom centers simultaneously in a shell of thickness \( dr_1 \) around \( r_1 \) and a shell \( dr_2 \) around \( r_2 \) is \( n_2(r_1, r_2) dr_1 dr_2 \)

\[ \int dr_2 n_2(r_1, r_2) = (N - 1)n_1(r_1) \]
Atomic correlations

• Probability of having an atom at \( \mathbf{r}_2 \) is correlated with the probability for an atom at \( \mathbf{r}_1 \), if these positions are not too far apart.

• This is expected due to inter-particle forces and constraints due to chemical bonds.

• Homogeneous material: \( n_1(\mathbf{r}_1) = \rho \)

• If \( |\mathbf{r}_1 - \mathbf{r}_2| \gg 1 \), atoms are uncorrelated and: \( n_2(\mathbf{r}_1, \mathbf{r}_2) \sim \rho^2 \)

• Generally we can write

\[
n_2(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(\mathbf{r}_1, \mathbf{r}_2)
\]
Pair distribution function (PDF)

- General definition: \( g(r_1, r_2) = \frac{n_2(r_1, r_2)}{n_1(r_1)n_1(r_2)} \)

- Put \( r_2 = 0 \), then define \( r = r_1 - r_2 \)

- Homogeneous material

- \( g(r_1, r_2) = g(r) = n_2(r)/\rho^2 \) describes the correlations in the atom positions

- \( \rho g(r) dr \) is interpreted as the probability to find an atom in \( dr \), a vector distance \( r \) from another atom at the origin.

- \( \rho \int g(r) dr = N - 1 \)
Isotropic materials

- $r$ is the distance between $r_1$ and $r_2$, $r ≡ r_2 - r_1$
- $\rho g (r)$ can be integrated to give the average density of atoms in a spherical shell around the origin

$$\int_{r_0}^{r_0+\Delta r} dr \ \rho g (r) = 4\pi^2 r_0^2 g(r_0) \Delta r = \rho R(r_0) \Delta r_0$$

- Radial distribution function $R(r)$

$$R(r) = 4\pi^2 r^2 g(r)$$

- Integrate $R(r)$ around the first peak -> Coordination number of the first shell
Pair Distribution Function (PDF)

• PDF show oscillations due to nearest neighbor next nearest neighbor shells, etc.

• Oscillations damped out as $r$ increases

• $g(r) \sim 1$ for large $r$
PDF for ideal crystal vs glasses
Radial distribution function

The number of neighbors to the origin atom situated between $r_1$ and $r_2$ is given by the area integral under the first peak.

\[
\# \text{neighbors}_{(r_1,r_2)} = \int_{r_1}^{r_2} dr \ R(r)
\]

http://www.globalsino.com/EM/page3097.html
Radial distribution function

http://www.globalsino.com/EM/page3097.html
How do we measure disorder?

• Statistical measures: Probability distribution functions

• Thermodynamics measures: Excess volume
What is glass (amorphous solid)?

- A metastable solid with no long-range atomic order

**Graph:****

- **$E$**
- **Structure**
- Metastable glassy state
- Thermodynamically stable crystalline state

- Glasses are metastable with respect to their stable crystalline phase
- Atoms can rearrange to form a more stable state given enough time and thermal energy

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Measure of disorder: Excess molar volume

• Energetics of bond density

• Ordered crystal has higher packing -> more bonds per unit volume

• Binding energy $E_{xtal} < E_{glass}$

• Binding energy <-> molar volume $V$

• $V_{glass} > V_{xtal}$

• Excess molar volume $\Delta V = V_{glass} - V_{xtal}$ is a measure of disorder
Glass formation from liquid

Cooling curve
Heating curve

Volume

Glass transformation range
Super-cooled liquid
Stable liquid
Process of melting and crystallization

Glass on fast cooling
Glass on slow cooling
Crystal

T_g
Glass transition temp.

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Glass formation from liquid

Cooling curve
Heating curve

$T_m$ function of composition

$T_m$ glass transition temp.

$T_m$ glass transformation range

glass on fast cooling

glass on slow cooling

process of melting and crystallization

super-cooled liquid

stable liquid

volume
Glass formation from liquid

![Diagram showing cooling and heating curves for glass formation.](image)
Glass formation from liquid

Cooling curve
Heating curve

- glass on fast cooling
- glass on slow cooling
- glass transformation range
- super-cooled liquid
- stable liquid
- process of melting and crystallization
- crystal

T_g
glass transition temp.

volume

temperature
Glass formation from liquid

$T_g$ depends on

(1) \((\text{atom mobility})^{-1}\)
(2) \((\text{complexity of crystal structure})\)
(3) \((\text{cooling rate})\)
(4) \((\text{composition})\)
Glass formation from liquid

Excess Volume (disorder)

- Cooling curve
- Heating curve

- Glass transformation range
- Super-cooled liquid
- Stable liquid
- Process of melting and crystallization

- Glass on fast cooling
- Glass on slow cooling
- Crystal
- \( T_g \) (glass transition temp.)
Summary LECTURE 1:
Disordered solids: Structure properties

• What is an disordered solid
• How do we measure disorder
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Summary LECTURE 1:
• What is an disordered solid
  • Solids with short-range disorder

• How do we measure disorder
  • Pair-correlation function
  • Excess volume

• How are amorphous solids typically formed
  • Glass transition
LECTURE 2
Atomic diffusion: equilibrium and non-equilibrium structures

• Diffusion of atoms

• Diffusion limited aggregation, crystal growth

• Fractals and fractal measure
Diffusion

• At any $T > 0K$, all atoms irrespective of their aggregation (gas, liquid, solid, etc) are in constant motion -> thermal motion

• Movement of atoms is associated with collisions -> single particle trajectory is a zigzag – diffusive particle

• A collection of diffusive particles has an observable drift from high to lower concentrations
Flow and dispersion

Molecular dispersion (Diffusion)

Dispersion by laminar channel flow
Molecular mixing - diffusion

Diffusion coefficient

\[ D_0 = \frac{1}{2d} \lim_{t \to \infty} \frac{\langle x^2 \rangle}{t} \]

Related to microscopic constants (length of random steps, time between steps)

\[ D_0 = \frac{a^2}{2\tau} \]

Macroscopic Law

\[ \partial_t C = D_0 \nabla^2 C \]

\[ C(r, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{(r-r_0)^2}{4Dt}} \]
Mean-square displacement

- **Superdiffusion**
  \[ \langle r^2 \rangle \propto \tau^\alpha, \quad \alpha > 1 \]

- **Normal diffusion**
  \[ \langle r^2 \rangle \propto D \tau \]

- **Subdiffusion**
  \[ \langle r^2 \rangle \propto \tau^\alpha, \quad \alpha < 1 \]
Fick’s law

- Flux = (conductivity) x (driving force)
- For atomic or molecular diffusion: “conductivity” = diffusivity constant $D$
  - $D$ reflects the mobility of the diffusing particles and depends on the environment: e.g. $D$ is larger for particles in gases, than in liquids.
- “Driving force” = - concentration gradient

\[
J = -D \nabla C
\]

\[
J \left( \frac{\text{moles}}{\text{cm}^2 \text{s}} \right) = -D \frac{dC}{dx} \left( \frac{\text{moles} \cdot \text{cm}^{-3}}{\text{cm}} \right)
\]

$[D] = \text{cm}^2 / \text{s}$
Fick’s second law (dynamics)

- \( J_x - J_{x+dx} = \frac{\partial c}{\partial t} \, dx \)

- Taylor series for \( dx \to 0 \):
  \[ J_{x+dx} = J_x + \frac{\partial J_x}{\partial x} \, dx + \ldots \]

- \( \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \, dx = \frac{\partial c}{\partial t} \, dx \)

- \( \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \)
Steady-state concentration

• Equilibrium concentration satisfies

\[ \nabla \cdot (D \nabla C) = 0 \]

• Boundary conditions

constant flux \( \rightarrow D \nabla C = \text{const.} \)

zero flux at the boundaries \( \rightarrow D \nabla C = 0 \)
Example of diffusion on a crystal lattice

Discretized model:
if 1 step = move by 1 bond length, we expect:

$$RMS = \sqrt{\langle R_N^2 \rangle} = \sqrt{N} \ d_{NN}$$

fcc:  \(d_{NN} = a_0 \frac{\sqrt{2}}{2} = 0.71a_0\)

bcc:  \(d_{NN} = a_0 \frac{\sqrt{3}}{2} = 0.87a_0\)

sc:  \(d_{NN} = a_0\)

lattice parameter = 1A

RMS displacement (Angstrom)

(number of steps)

(\(\Rightarrow D \text{ depends on the structure of the lattice}\))
Diffusion mechanisms in solids

Interdiffusion: e.g. alloys
Atoms migrate from high concentration to low concentration regions

https://www.slideshare.net/IbrahimAbuawwad1/ch05-48057054
Diffusion mechanisms in solids

Vacancy diffusion

- Atoms exchange positions with vacancies
- Applies to substitutional impurities atoms

https://www.slideshare.net/IbrahimAbuawwad1/ch05-48057054
Diffusion mechanisms in solids

Self-diffusion: single element solids, eg monoatomic metals

- Atoms hop in the crystal lattice and diffuse when their thermal motion exceeds an activation energy for self-diffusion

https://www.slideshare.net/IbrahimAbuawwad1/ch05-48057054
Diffusion mechanisms in solids

Interstitial diffusion

- Interstitial atoms diffuse between atoms

![Diagram showing interstitial diffusion](https://www.slideshare.net/IbrahimAbuawwad1/ch05-48057054)
Diffusion-limited aggregation: crystal vs amorphous structures

- Limited – a seed particle is placed at the center and cannot move
- Diffusion – another particle is added at an arbitrary position and is diffusing towards the seed particle
- Aggregation – the diffusing particle can stick with the seed particle or any particle within the aggregate cluster (probability of aggregation)
- The process of diffusion-aggregation is repeated several times.

Meakin, Jamtveit, PNAS 2009
Diffusion-limited aggregation: crystal vs amorphous structures

Meakin, Jamtveit, PNAS 2009
Diffusion-limited aggregation: crystal vs amorphous structures

Random cluster growth

Preferred lattice growth

Meakin, Jamtveit, PNAS 2009
Diffusion-limited aggregation: amorphous structures

The amorphous clusters tend to be fractals and have a fractal dimension.

What is a fractal?

What is a fractal dimension?
What is a fractal?

- Self-similarity across many scales (scale-invariant)
  - Lack of an intrinsic lengthscale
- Don’t fill the Euclidean space which embeds them
- Their intrinsic (fractal) dimension is smaller than the Euclidean dimension of the space in which they are embedded
Dimensions and rescaling objects

Double the size, double the mass
\[ M = kL^1 \]
\[ 2M = k(2L)^1 \]

Double the size, quadruple the mass
\[ M = kL^2 \]
\[ 4M = k(2L)^2 \]

Double the size, mass increases by a factor of \( 2^3 = 8 \)
\[ M = kL^3 \]
\[ 8M = k(2L)^1 \]
Dimensions and rescaling objects

\[ M = kL^d \]

\[ aM = k(sL)^d \]

\[ a = s^d, s > 1 \]

\[ d = \frac{\log (\text{# of pieces})}{\log (\text{scale factor})} \]
Fractal dimension: Sierpinski Gasket

• $a = s^D$

• At each iteration, two sides of the triangle are doubled
• $s = 2$
• The number of new triangles increases by a factor of 3
• $a = 3$

$$D = \frac{\log 3}{\log 2}$$
Fractal dimension: the Koch curve

• What’s the fractal dimension?
Fractal dimension: the Koch curve

- $a = \left(\frac{1}{s}\right)^D$
- $s = 1/3$
- The number of segments increases by a factor of 4
- $a = 4$

$$D = \frac{\log 4}{\log 3} > 1$$
Koch snowflake

- Equilateral triangle
- Apply Koch curve to each edge
- Perimeter increases by 4/3 at each iteration → ∞
- Area is bounded

https://en.wikipedia.org/wiki/Koch_snowflake
Fractal dimension

- Amount of mass (or other measure that scales with the size) of an object inside a circle of radius $r$ has a power-law relation.

- DLA cluster in 2D, $D \approx 1.7$
Are real snowflakes fractal?
Are real snowflakes fractal?

Figure 3. Typical log-log plot of the cluster mass \( M \) within a box of edge \( L \) as a function of \( L \). Compared are the model and experimental pattern of figure 1(b). The same slope, \( d_t = 1.85 \pm 0.06 \), is found for both. The experimental data extend to larger values of \( L \), since the digitiser used to analyse the experimental photograph has 20,000 pixels while the cluster has only 4000 sites.
Are real snowflakes fractal?