Disordered Materials: Lecture I

Concepts of disorder:
How we quantify it and
How we measure it

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Disordered Materials:
Lecture II

Finding and refining a structural model

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A well known example of disorder...
How to avoid traffic congestion...
Molten $\text{Al}_2\text{O}_3$
Molten $\text{Al}_2\text{O}_3$
Disorder affects us in many different ways...

- Avalanches
- Sand, shingle and earth piles
- Congestion in shopping centres, etc.
- Football crowds
- Blood clots
- ...
- Gases, liquids and glasses
What is common to all these examples?
• No two objects can occupy the same space.
• Nonetheless, (usually) there is overall attraction between objects, some force which brings them closer together.
• Only relative positions are correlated.
• No overall arrangement, therefore resort to correlation functions to describe arrangement.
In reality not quite so simple...

- Three- and many-body forces may be important.
What are the fundamental requirements for disordered correlation to occur?

- Some attractive forces…
- Some repulsive forces…
- High packing fractions.
- Random positions.
Disordered materials can be classified as: “Atom jams with marked positional correlations.”

In a gas the atoms are free to move (almost) anywhere.

In a liquid the atoms and molecules are jammed but can still diffuse - “slowly”.

In a glass the atoms are highly jammed and are unable to diffuse.
A “typical” liquid, water...
The water molecule
This results in a material which looks like this:-
and this:-
An interesting fact about water:

- It takes about 41.5 kJ per mole (i.e. 18 gm) to bind a water molecule in the liquid.
- This means for every second that it rains, 41.5 kJ of heat energy is released for every 18gm of water deposited on the ground.
- A heavy rain shower producing 2.5mm of rain over 1km² releases $5.764 \times 10^{12}$ J (=1 cycle of ISIS!).
So how do you characterise structure in a disordered system?

By counting.

This gives the "radial distribution function", $g(r)$:
2.5 - 3.5 Å: 12 atoms
3.5 - 4.5 Å: 8 atoms
4.5-5.5Å: ~20 atoms
Average over every site in the liquid $\sim 10^{23}$ sites...
What is this radial distribution function, $g(r)$, telling us?

- It tells us about the nearest-neighbour numbers and distances;
- It tells us about the hardness of the atomic core repulsion;
- It tells us about the attractiveness each atom has for its neighbours;
- In other words it tells us about the local potential energy environment of an atom in the material.
There is a complication however...

- Typical interatomic potentials are not oscillatory – they have a repulsive core and are attractive beyond the core – van der Waals forces.
Corresponding $g(r)$:

- At zero density, formally exact result:

$$g(r) = \exp\left[ -\frac{U(r)}{kT} \right]$$
• So why does $g(r)$ oscillate?
• Many body effects…
Effect of many body correlations

Many body correlations give rise to the oscillations...

BUT we can’t estimate them without the aid of computer simulation
Now consider a 2-component system:
1.6 - 2.3 Å: 5 atoms
2.3 - 3.0 Å: 1 atom
3.0 - 3.7 Å: 3 atoms
Partial $g(r)$'s for $Al_2O_3$
For “N” components there are \( N(N+1)/2 \) site-site radial distribution functions.

How do we measure these?
You can’t measure $g(r)$

Instead you have to use a diffractometer to do the atom counting.

This produces a structure factor, $D(Q)$.
(Actually a differential scattering cross section)

Very different from the crystalline lattice structure factor as it has only a few peaks!
ISIS SANDALS
(liquids diffractometer)

Sample position

Incident neutron beam
Diffraction from disordered materials - a simple experiment in principle:

\[ Q = \frac{4 \pi \sin \theta}{\lambda} \]
X-ray diffractometer
... gives some data:

![Graph showing data for X-ray and Neutron](image-url)
Now... NIMROD
Wide length-scale data from NIMROD

- Dry MCM-41
- Partially N₂ loaded MCM-41
- Fully N₂ loaded MCM-41

$F(Q)$ (barn sr⁻¹ atom⁻¹) vs. $Q$ (Å⁻¹)
Differential scattering cross section

• The differential scattering cross section is related to:-

\[
\frac{d\sigma}{d\Omega}(Q_E, \theta) = F_s(Q_E, \theta) + F_d(Q_E)
\]

• For neutrons the self term is subject to inelasticity corrections.

• For X-rays the self term is subject to Compton scattering corrections.
Properties of the neutron differential cross section – effect of inelastic scattering

• According to van Hove (1954) the dynamic structure factor, $S(Q,\varepsilon)$, splits into two terms:
  – The self term, $S_s(Q,\varepsilon)$, corresponds to atoms correlating with themselves.
  – The distinct term, $S_d(Q,\varepsilon)$, corresponds to atoms correlating with other atoms.

• The total scattering cross section is related to:

\[
\frac{d^2 \sigma}{d\Omega \, d\varepsilon} \sim \frac{k_f}{k_i} \left\{ \langle b^2 \rangle S_s(Q,\varepsilon) + \langle b \rangle^2 S_d(Q,\varepsilon) \right\}
\]
Sum rules: the “static” structure factor

• For distinct scattering :

\[ \int_Q S_d(Q, \epsilon) d \epsilon = S(Q, \Delta t = 0) - 1 = \frac{4\pi \rho}{Q} \int r \left( g(r, \Delta t = 0) - 1 \right) \sin Qr dr \]

  - “Instantaneous structure” averaged over positions

• This must be carefully distinguished from the **elastic** structure factor from Bragg scattering

\[ S_d(Q, \epsilon = 0) \equiv \int S_d(Q, \Delta t) d \Delta t \]

  - “Time averaged structure”
Time averaged structure
Sum rules: the “static” structure factor

- For self scattering:

\[ \int Q S_s(Q, \varepsilon) \, d\varepsilon = 1 \]
Effect of energy transfer

- Kinematics of neutron scattering:
  \[ Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos \theta \]
  \[ \varepsilon = \frac{\hbar^2}{2m} \left( k_i^2 - k_f^2 \right) \]

- In a diffraction experiment the neutron detector integrates \( S(Q,\varepsilon) \) at constant \( \theta \), NOT constant \( Q \).
Fixed incident energy plot

\[ E_i = 1\text{eV} \]

Increasing \(2\theta\)
**Effect of energy transfer**

- For distinct scattering (Placzek, 1952):
  \[ \int Q \epsilon S_d(Q, \epsilon) d \epsilon = 0 \]

- For self scattering:
  \[ \int Q \epsilon S_s(Q, \epsilon) d \epsilon = \frac{\hbar^2 Q^2}{2M} \]

- \( M_p \approx M_n \) means significant energy loss on scattering by protons.
Fixed incident energy plot

$E_i = 1eV$

Recoil energy

Increasing $2\theta$
Reactor data

- \( I(Q) \) / barn steradian\(^{-1}\) atom\(^{-1}\)
- \( Q(\text{Å}^{-1}) \)

- \( \text{H}_2\text{O} \)
- \( 0.65 \text{H}_2\text{O}: 0.35 \text{D}_2\text{O} \)
- \( \text{D}_2\text{O} \)
Time of Flight diffraction

- Energy dispersive.
- Detector at fixed scattering angle.
- Detector still integrates at constant angle, but each time of flight channel corresponds to a range of incident energies:

\[
\frac{1 + R}{k_e} = \frac{1}{k_i} + \frac{R}{k_f}, \quad k_e = \frac{Q_e}{2 \sin \theta}
\]
Constant time-of-flight plots:
$2\theta = 30^\circ$
Pulsed Source Data

(a) and (b) show plots of DCS [barn/atom/sr] vs. $Q_e$ [Å$^{-1}$].
Our raw diffraction data need to be corrected:

- Normalise to incident beam monitor readings.
- Correct for background.
- Put on absolute scale by comparison with vanadium scattering.
- Correct for multiple scattering.
- Correct for attenuation and container scattering.
- Produce differential scattering cross-section per atom or molecule of sample.
- Remove the single atom scattering.
- Merge detectors into a single pattern.
The structure factor:

The partial structure factors, \( H_{\alpha \beta}(Q) \)

\[
F_d(Q) = \sum_{\alpha, \beta \geq \alpha} \left( 2 - \delta_{\alpha \beta} \right) c_\alpha c_\beta b_\alpha b_\beta 
\]

The site-site radial distribution functions, \( g_{\alpha \beta}(r) \)

\[
4 \pi \rho \int r^2 2 \left( g_{\alpha \beta}(r) - 1 \right) \frac{\sin Qr}{Qr} dr
\]

Atomic fraction of component “\( \alpha \)”

The atom scattering factor or “form factor”
A much more tricky question: how do we interpret the data?

- For many years the next step was to simply invert our scattering equation:

\[
d(r) = \frac{1}{2\pi^2 \rho} \int_0^\infty Q^2 D(Q) \frac{\sin Qr}{Qr} dQ
\]

\[
= \sum_{\alpha \geq \beta} \left( 2 - \delta_{\alpha \beta} \right) c_\alpha c_\beta b_\alpha b_\beta \left( g_{\alpha \beta}(r) - 1 \right)
\]
This leads to many problems

- Truncation errors.
- Systematic errors.
- Finite measuring statistics.
- Some site-site terms are more strongly weighted than others.
- These all make interpretation of the data unreliable.
- Radial distribution functions \((g(r))\) do not yield the Orientational Pair Correlation Function (OPCF).
Introduct: computer simulation

• Requires an atom-atom potential energy function.
• Place computer atoms in a (parallelepiped) box at same density as experiment.
• Apply periodic boundary conditions
  – the box repeats itself indefinitely throughout space.
• Apply minimum image convention.
Minimum image convention

Count atoms out to $D/2$
Monte Carlo computer simulation

1. Using the specified atom-atom potential function, calculate energy of atomic ensemble.
2. Displace one atom or molecule by a random amount in the interval $\pm \delta$.
3. Calculate change in energy of ensemble, $\Delta U$.
4. Always accept move if $\Delta U < 0$
5. If $\Delta U > 0$, accept move with probability $\exp[-\Delta U/kT]$.
6. Go back to 2 and repeat sequence.
But there is a problem:

We don’t know the potential energy function!
Introduce Reverse Monte Carlo, \textit{RMC}

1. Build a box of atoms as before. Calculate $\chi^2 = \frac{[D(Q)-F(Q)]^2}{\sigma^2}$

2. Displace one atom or molecule by a random amount in the interval $\pm \delta$.

3. Calculate change in $\chi^2$ of ensemble, $\Delta \chi^2$.

4. Always accept move if $\Delta \chi^2 < 0$

5. If $\Delta \chi^2 > 0$, accept move with probability $\exp\left[\Delta \chi^2\right]$.

6. Go back to 2 and repeat sequence.
Introduce Empirical Potential Structure Refinement, EPSR

• Use harmonic constraints to define molecules.
• Use an existing “reference” potential for the material in question taken from the literature (or generate your own if one does not exist).
• Use the diffraction data to perturb this reference potential, so that the simulated structure factor looks like the measured data.
Introducing the data

\[ F(Q) = \sum_{\alpha, \beta \geq \alpha} \left( 2 - \delta_{\alpha \beta} \right) c_\alpha c_\beta b_\alpha b_\beta H_{\alpha \beta}(Q) \]

- \( M \) measured datasets, \( N \) partial structure factors: (Usually \( M < N \))
- Assign a “feedback” factor \( f \) for the data:
  \[ w'_{ij} = fw_{ij}, \ 1 \leq i \leq M \]
- and \( (1 - f) \) for the simulation:
  \[ w'_{ij} = (1 - f) \delta_{i-M,j}, \ M < i \leq M+N \]
- Form inversion of \( w'_{ij} \), \( 1 \leq i \leq M+N, \ 1 \leq j \leq N \)
Refining the potential: \( M \) datasets, \( N \) partial structure factors

\[
F_{i(=1,M+N)}(Q) = \begin{bmatrix}
\begin{array}{cccc}
fw_{11} & fw_{12} & \cdots & \cdots \\
fw_{21} & fw_{22} & \cdots & \cdots \\
\vdots & \vdots & \ddots & \cdots \\
fw_{M1} & fw_{M2} & \cdots & fw_{MN}
\end{array}
\end{bmatrix}
\times
\begin{bmatrix}
S_1 \\
S_2 \\
\vdots \\
S_N
\end{bmatrix}
\]

\[\Delta U_j(r) = \text{Fourier Transform of } \left\{ \sum_{i=1,M} w_{ij}^{-1} \left( D_i(Q) - F_i(Q) \right) \right\}, \ j = 1, N\]
Summary of Lecture I

- Widespread occurrence of disordered systems (macroscopic as well as microscopic).
- Concept of correlation in disordered systems.
- Use radial distribution function (PDF) to characterise the correlations in a disordered system.
- Use diffraction to count atoms as a function of distance.
- Given some diffraction data, what is the atomic arrangement?
  - Introduce computer simulation.
Summary of lecture II

• Computer simulation as a tool to model disordered materials
• Molecular systems
• Use of computer simulation to go from measurements ($D(Q)$, $g(r)$) to SDF, bond angle distribution, OPCF, etc.
• Some case studies: molten alumina, water, amorphous phosphorus, silica, silicon...