Outline

- Introduction
- Classical methods: the Born Model
- Static lattice methods
  - energy minimisation
- Molecular dynamics
- Monte Carlo methods
Atomistic Simulations

- Classical or quantum?
- Static or dynamic?
- Availability of computer resources
Atomistic Simulations

- Classical or quantum?
- Static or dynamic?
- Availability of computer resources
Classical v. Quantum

- **Classical**
  - Based on Born Model
    - Electrostatic (point charges) & short-range potentials
    - Representation of inter-atomic forces
  - Can handle tens of thousands of atoms

- **Quantum mechanical**
  - Solutions to Schrödinger wave equation
    - Electronic property calculations
  - Limited to $10^2$ atoms
    - Computationally expensive
Static v. dynamic

- **Static**
  - Structure and physical properties
  - Point defect modelling
  - No explicit temperature handling
  - Not well suited to non-crystalline materials

- **Dynamic**
  - Based on solutions to laws of motion
  - Includes temperature (nominally)
  - Useful for non-crystalline materials
The Born Model

- Ions treated as point charges
  - Coulomb potential is long range
  - Magnitude as model parameter
- Short range potentials
  - Pauli repulsion
  - Dispersion forces
- Polarisability
Structure + Potential = Thermodynamics

- Energy minimisation
  - Perfect lattice properties
  - Point defect energies and structure
- Glasses pose a problem because of non-crystalline structure
  - Hence appeal to computational methods - molecular dynamics (or Monte Carlo)
The Born Model

- Lattice energy:
  \[ E_{lattice} = \frac{1}{2} \sum_{i,j} \frac{q_i q_j}{r_{ij}} + V(r_{ij}) + U(r_{ij}, r_{ik}) \]

- Forces obtained from derivatives of \( E_{lattice} \)

- Equilibrium from zero net forces
  - Second derivatives of \( E_{lattice} \)

- Elastic, dielectric constants are second derivative properties
Polarisability: The Shell Model

- Simple mechanical model
- Ion charge partitioned between core and (mass-less) shell
- Electronic polarisability, $\alpha = \frac{Y^2}{k_{c,s}} + R$
- Other models:
  - Breathing shell
  - Point polarisable ion
- Transferability issues
Short range potentials

Effective potentials:

\[ V(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - C_{ij} \frac{1}{r_{ij}^6} \]

\[ U(r_{ij}, r_{ik}) = \frac{1}{2} k_{ijk} (\theta - \theta_0)^2 \]

- Usually parametrised
- Fit to known physical properties or to quantum mechanically calculated energy surface
Assumptions

- Transferability of potentials
  - Between polymorphs
  - Between compounds, e.g. oxygen...oxygen interaction
- Oxygen ion polarisability
- Restriction to pair potentials, and/or three body terms
Energy minimisation

- Structure refinement/prediction
- Calculation of physical properties
- Thermochemistry
- Zero Kelvin technique
  - Can include temperature behaviour through use of phonon calculations (e.g. Helmholtz energy)
- Supercell approach to defects
Structure Refinement/Prediction

- **Refinement**
  - Equilibration of an ideal model

- **Prediction**
  - *Ab initio* generation of crystal structure parameters
  - Exercise in global optimisation
## Potential Model for MgF$_2$

### Crystal Properties

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<thead>
<tr>
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<th>Experimental</th>
<th>Calculated</th>
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<tbody>
<tr>
<td>$C_{11}$</td>
<td>13.99</td>
<td>13.59</td>
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<td>$C_{12}$</td>
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<td>9.59</td>
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<tr>
<td>$C_{22}$</td>
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<td>6.19</td>
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<tr>
<td>$C_{33}$</td>
<td>20.42</td>
<td>23.19</td>
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<td>$C_{44}$</td>
<td>5.70</td>
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<tr>
<td>$C_{66}$</td>
<td>9.54</td>
<td>9.63</td>
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<tr>
<td>$\varepsilon_0 \perp$</td>
<td>5.5</td>
<td>5.6</td>
</tr>
<tr>
<td>$\varepsilon_0 \parallel$</td>
<td>4.8</td>
<td>4.6</td>
</tr>
<tr>
<td>$\varepsilon_\infty \perp$</td>
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<td>1.9</td>
</tr>
<tr>
<td>$\varepsilon_\infty \parallel$</td>
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<td>1.9</td>
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</table>

### Potential Parameters

<p>| | |</p>
<table>
<thead>
<tr>
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<tr>
<td>$A_{\text{Mg-F}}$</td>
<td>682.59</td>
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<tr>
<td>$R_{\text{Mg-F}}$</td>
<td>0.29797</td>
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<td>$C_{\text{Mg-F}}$</td>
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<td>$A_{\text{F-F}}$</td>
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<tr>
<td>$Y_{\text{Mg}}$</td>
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<tr>
<td>$K_{\text{Mg}}$</td>
<td></td>
</tr>
<tr>
<td>$Y_{\text{F}}$</td>
<td>1.23357</td>
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<tr>
<td>$k_F$</td>
<td>17.496</td>
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</tbody>
</table>

E$_{\text{lattice}}$ -60.74 -59.08
Ideal structure of $\text{VO}_2(\text{B})$

Energy minimised structure of $\text{VO}_2(\text{B})$
Crystal structure of BAM: Eu phosphor

Spinel block

Barium site

Al(2) - Possible Mg sites

Al(1)

Al(4)

Al(3)
Comparison between calculated and experimental structures

<table>
<thead>
<tr>
<th>Atom type</th>
<th>$X_{\text{obs.}}$</th>
<th>$X_{\text{calc.}}$</th>
<th>$\Delta X$</th>
<th>$Z_{\text{obs.}}$</th>
<th>$Z_{\text{calc.}}$</th>
<th>$\Delta Z$</th>
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<tbody>
<tr>
<td>Ba</td>
<td>0.6678</td>
<td>0.6667</td>
<td>0.0011</td>
<td>0.2500</td>
<td>0.24662</td>
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<td>Al(1)</td>
<td>0.8343</td>
<td>0.8338</td>
<td>0.0005</td>
<td>0.10544</td>
<td>0.10268</td>
<td>0.00276</td>
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<td>Al(2)</td>
<td>0.3333</td>
<td>0.3333</td>
<td>0</td>
<td>0.02400</td>
<td>0.01848</td>
<td>0.00552</td>
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<td>Al(3)</td>
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<td>0.3333</td>
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<td>0.17416</td>
<td>0.17052</td>
<td>0.00364</td>
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<tr>
<td>Al(4)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.1534</td>
<td>0.1488</td>
<td>0.0046</td>
<td>0.05152</td>
<td>0.05130</td>
<td>0.00022</td>
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<tr>
<td>O(2)</td>
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<td>0.5040</td>
<td>0.0002</td>
<td>0.14799</td>
<td>0.14333</td>
<td>0.00466</td>
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<tr>
<td>O(3)</td>
<td>0.6667</td>
<td>0.6667</td>
<td>0</td>
<td>0.05901</td>
<td>0.05409</td>
<td>0.00492</td>
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<tr>
<td>O(4)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0</td>
<td>0.14437</td>
<td>0.139590</td>
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<tr>
<td>O(5)</td>
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<td>0.3333</td>
<td>0</td>
<td>0.25000</td>
<td>0.24789</td>
<td>0.00211</td>
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</table>
The oxygen layers in olivine rumple from ideal close packing to a lower energy configuration.
Molecular Dynamics

- **What is it?**
  - Approach to the computer simulation of materials

- **What does it do?**
  - Calculates dynamic properties by solving, iteratively, (classical) equations of motion

- **How does it work?**
  - Computational approach to statistical mechanics
Statistical Mechanics

- Conversion of atomic scale information into macroscopic quantities
- Thermodynamic state defined by variables such as P, T, N.
- Other thermodynamic properties, such as ρ, μ, C_v etc., derived from equations of state. Their values are dictated by variables characterizing thermodynamic state
- Atomic positions and momenta define instantaneous mechanical state (phase space)
Statistical Mechanical Ensembles

- Microcanonical: constant $N, V, E$
- Canonical: constant $N, V, T$
- Grand Canonical: constant $\mu, V, T$

- Standard MD simulations model the microcanonical ensemble
  - Newton’s laws conserve energy
Integrating the equations of motion

- Verlet algorithm
  - Direct solution of
    \[ m_i \frac{d^2 r_i}{dt^2} = F_i \]
  - Velocities eliminated by adding Taylor expansions
    \[ r_i(t + \Delta t) = 2r_i(t) - r_i(t - \Delta t) + \Delta t^2 a_i(t) \]
    \[ r_i(t - \Delta t) = r_i(t) - \Delta t v_i(t) + \frac{1}{2} \Delta t^2 a_i(t) \]
NVE \textit{v.} NVT: Thermostats

- Equations of motion conserve energy
- For Temperature control, system is kept in contact with a heat bath
- Thermostats work by scaling the velocities so that the kinetic energy is appropriate to the target temperature
• **Nosé:** \( \mathbf{v}_i = s \mathbf{dr}_i / dt \)

• **Hoover:** \( \mathbf{v}_i = \mathbf{dr}_i / dt = \mathbf{p}_i / m \)
  
  with \( \frac{d\mathbf{p}_i}{dt} = -\nabla \Phi - \zeta \mathbf{p}_i \)

  - with kinetic energy controlled by

\[
\frac{Q}{2} \frac{d\zeta}{dt} = \sum_i \frac{\mathbf{p}_i^2}{2m_i} - g/2k_B T
\]

• **Berendsen:**

  - scale velocities by \( \chi = \left( 1 + \frac{\Delta t}{\tau_T} \left( \frac{T}{T_i} - 1 \right) \right)^{1/2} \)
Calculation of Forces

• MD technique hinges on accurate forces
• Forces are obtained from an inter-atomic potential model
• Classical models based on Born model of solid
  - Point ions with short-range (Pauli) repulsive forces
  - Can include polarisability via the Shell Model
• Models need validation: check on parameters
Computational considerations

- Size of simulation box
  - Periodic boundary conditions used to generate infinite solid
  - Ewald summation of Coulombic interactions

- Length of simulation
  - CPU time per time-step
  - Number of time-steps

- Accumulation of data
  - Post-run analysis
Post-run analysis

- **Structure**
  - Radial distribution functions
  - Co-ordination numbers
  - Spatial distribution of different atomic species

- **Transport**
  - Diffusion co-efficients
  - Migration mechanisms
Snap-shot structure of a lithium sodium silicate glass

Li
Na
Si
O
\( \text{SiO}_2 \text{ glass} \)

\[ Q_{\max} = 45.2 \text{ Å}^{-1} \]

\[ R_x = 5.2\% \]

- SM1
- exp
- SM1-exp
Na-O pdf for 30Na$_2$O•70SiO$_2$ glass deconvoluted into bridging and non-bridging oxygen components. Note the shorter Na-NBO distances. The lines represent crystalline Na-O distances.
Segregation of Li and NBO in a silicate glass containing 5mol% lithia.
Local Cation Environments

- Network formers: tetrahedra
- Network modifiers
  - Nature of polyhedron depends on cation size
- How are modifier polyhedra linked together?
  - Share corners and edges, sometimes faces
  - Underlying feature of the Modified Random Network Model
- Connectivity of modifier polyhedra play key role in diffusion processes
25Na₂O·0.75SiO₂: Si - O pair distribution function
Na - O pair distribution function

25Na₂O-75SiO₂

Radius (Angstrom)

Accumulated Coord. Number

T(r)

NaO
NaBO
NaNBO
Connectivity of Na-O polyhedra from a $25\text{Na}_2\text{O}.75\text{SiO}_2$ glass
Connectivity of Na-O polyhedra from a 25Na\textsubscript{2}O.75SiO\textsubscript{2} glass

In this group, one polyhedron shares edges with two other polyhedra.
Na - O pdf in 1mol% sodium silicate

Majority of co-ordinating oxygen ions are BO
Superposition of trajectories from stoichiometric (Na: green) and non-stoichiometric (Na: blue) Na β-aluminas. The red atoms are oxygens. The Na associated with the O6 do not take part in diffusion.
Monte Carlo methods

- Statistical mechanical approach
- An atom is moved: the move is accepted, if
  - new configuration has lower energy, or
  - increase in energy is less than a randomly generated $\Delta E$.

- Reverse Monte Carlo
  - Moves are intended to improve fit to experimental data
Defect Calculations

- Point defects
  - Vacancies, interstitials, substitutional ions
  - Dopants or impurities; trace elements

- Structure and energetics
  - Formation energy
  - Migration activation energy
  - Association energy
Defect calculations

- Defects remove translational symmetry
- Use embedded regions or supercell methods
  - Atomistic region enclosed by dielectric continuum
- Mott-Littleton approximation
  - Polarisation due to defect (relaxation)
- Computer codes: HADES, CASCADE, GULP
Summary

- Atomistic simulations provide an important complement to experimental structural studies
- Quantum mechanical methods becoming more widely used
  - Restricted to small systems
- Classical methods can be used for “ab initio” determination of complex structures, including non-crystalline materials
Schematic of glass formation: melting a polycrystalline mixture