# Computing Class Case Study:
# Atomistic Modelling of Ionic Conductors

## Briefing document

with acknowledgement to

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## A1. Overview

This exercise provides an introduction to a class of materials known as fast ion or superionic conductors. Please read through these briefing notes in advance of the class: they will help you understand the scientific background behind it. There will be a separate script to guide you through the details.

The objective is to explore the properties of such materials and characterise their behaviour and in doing so see how Molecular Dynamics can be used to study ionic solids at the atomistic level.

## A2. Background

Many inorganic materials conduct an electric current in the solid sate. This happens because one or more of the ions is capable of diffusing rapidly through the system while it is still in the solid state.

An example of such a material is Fluorite ($CaF_2$).

With increasing temperature however the structure shows increasing disorder. It is the nature of this disorder that we are going to investigate and characterise.

# A3. Fluorite – (CaF$_2$)
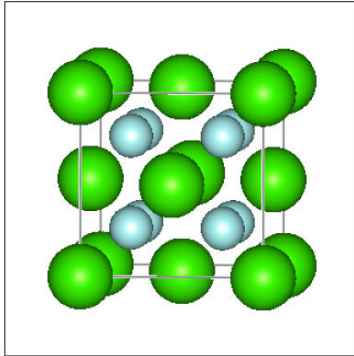


To build an atomistic model we basically need 3 pieces of information
1) The dimensions of the unit cell
2) Position and types of ions
3) A space group
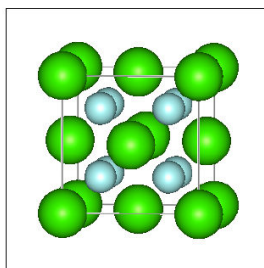(description of the symmetry of the ions in the unit cell)

## For CaF$_2$
a=b=c= 5.46Å
Space Group = FM-3M (225)
Ca$^{2+}$   0.0    0.0    0.0
F$^-$      0.25   0.25   0.25

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# A4. Born Model of Solids



We use parameterised functions to describe the energy of a system as a function of atoms' positions.

$$V(r_{ij}) = \frac{q_i q_j}{r_{ij}} + \phi(r_{ij})$$

Long range interactions
Coulombic energy

Short range interactions
Van der Waals Bond stretch
Angle Bend Torsion
e.g. Buckingham Potential

$$\phi(r) = A\exp(-r/\rho) - C/r^6$$

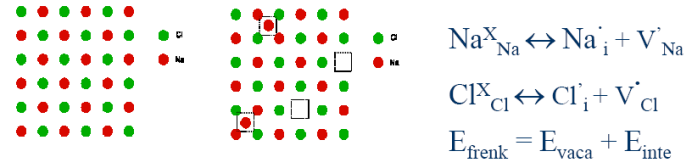Potentials are fitted to experimental properties
or using *ab-initio calculations*
Published well tested models of CaF$_2$ already exist.
We will be using rigid-ion model *J. Phys: Condens. Matt.* **1**:1205-1212 (1989)
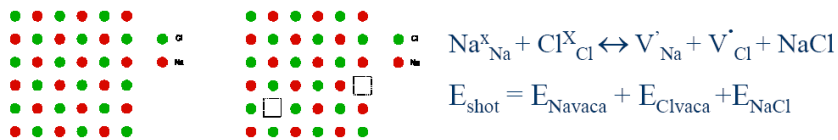
# A5.1 Defect Calculations

A quick way of investigating how ions may move within a structure
*Model validation -- Can Use Static Methods*

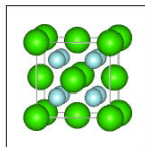Frenkel Defect – Energy required to create an isolated vacancy and interticial

$$Na^X_{Na} \leftrightarrow Na^{\cdot}_i + V^{'}_{Na}$$

$$Cl^X_{Cl} \leftrightarrow Cl^{'}_i + V^{\cdot}_{Cl}$$

$$E_{frenk} = E_{vaca} + E_{inte}$$

Shottky Defect – Energy Required to remove one formula unit

$$Na^x_{Na} + Cl^X_{Cl} \leftrightarrow V^{'}_{Na} + V^{\cdot}_{Cl} + NaCl$$

$$E_{shot} = E_{Navaca} + E_{Clvaca} + E_{NaCl}$$

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# A5.2 Defect Calculations
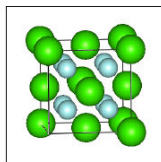
Need to perform 5 energy minimisation calculations

Pure $CaF_2$ (cell contains 4 $CaF_2$)

$E_{latt}$ = -107.36eV

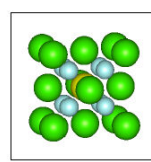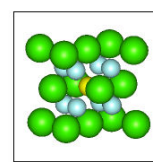And four defective $CaF_2$ cells
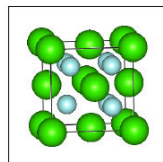
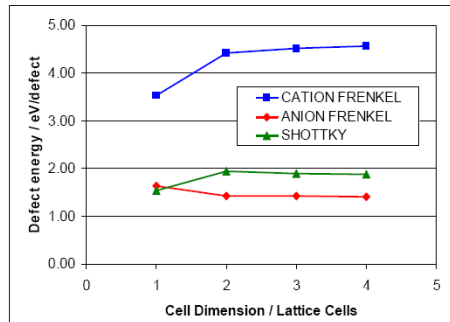| Ca Vaca | F Vaca | Ca Inte | F Inte |
|---------|--------|---------|--------|
| -85.92 eV | -102.36eV | -121.76eV | -109.10eV |

# A6. Finite Size Effect

The Shottky and Frenkel energies and defined relative to *isolated* defects
In the 1x1x1 calculations the concentration of defects is far from this
High charge relative to size of cell also causes problems
Results suggest Shottky is slightly favoured over Anion Frenkel



Anion Frenkel is now the most stable intrinsic defect
Suggest anions will move through system via interstitial sites

For anion Frenkel and Shottky a 2x2x2 supercell is sufficient to achieve convergence

# A7. Molecular Dynamics

Whilst static Energy Minimisation can tell us a lot about our system  and the behaviour of defects within them the fact that there is NO temperature included in them and the fact that we have no way of considering the atomic motions directly severely limits what can be done.

Many Properties cannot be explained by a static model
Thermal Properties (Heat Capacity), Thermal Expansion,
Phase Transitions (melting), Transport Properties (Diffusion)

MD provide a simple way of studying such phenomena directly.
This will be the topic of the remainder of the lecture.

## A8. Size Effects and Convergence Testing

To ensure periodic images do not interact MD codes require a the short-range cut-off is set to at least half the dimensions of the unit cell

We therefore need a cut-off which ensures our results are accurate but small enough that our system size isn't too large

|   | Energy / KJ/mol | a / A | volume / A3 | time / s |
|---|---|---|---|---|
| 1 | -10410 | 5.44 | 160.89 | 22 |
| 2 | -10313 | 5.52 | 168.43 | 306 |
| 3 | -10312 | 5.52 | 168.41 | 2423 |
| 4 | -10311 | 5.52 | 168.55 | 11225 |
| 5 | -10312 | 5.52 | 168.37 | 41144 |

This system converges rapidly experience has shown that in general as cut-off of 8Å - 10Å is required which therefore requires a cell 16Å - 20Å
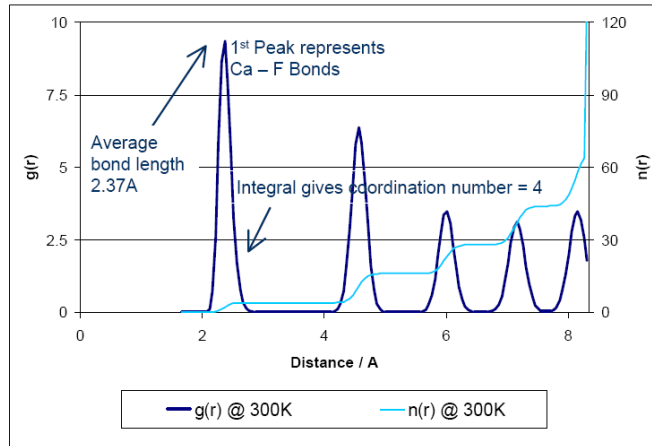
This is only a rule of thumb and convergence test should always be performed when working with a new system

# A9. Thermal Expansion

A good test of a model is how the cell dimensions respond to Temperature
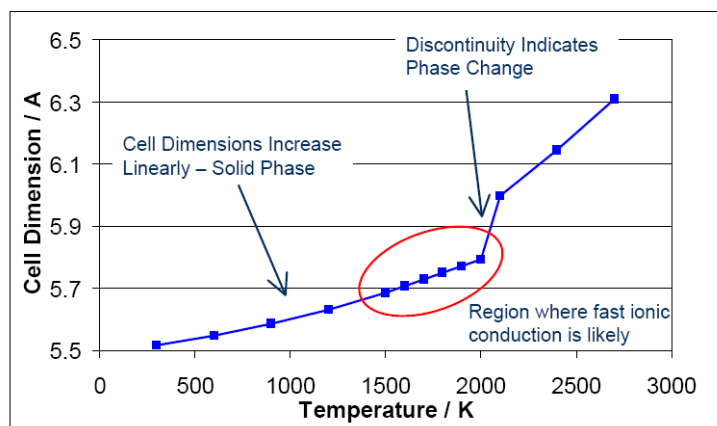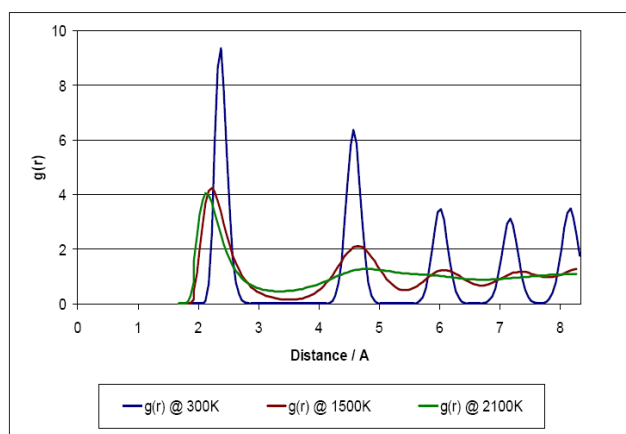
# A10.1 Ca---F RDF

Series of sharp peaks characteristic of a crystalline solid

# A10.2 Ca---F RDF

At 1500K we still see multiple peaks but they are broader Indicating ions are more mobile

Above the melting point we only see the nearest neighbour peak Characteristic of a liquid

# A11. Characterising Ionic Movement

**Mean Square Displacement (MSD)**
A means of determining the average motion of molecules in a liquid, gas or solid. It is directly related to diffusion, which can be measured experimentally, and is easily calculated in an MD simulation. It is, for this reason, a very important link between modelling and the real world.

**Velocity Autocorrelation Function (VACF)**
Provides a means of investigating collision processes in molecular systems. Like the mean square displacement, it can also provide information about diffusion. It is capable of distinguishing between solids, liquids and gases from their molecular motion and it reveals the timescales on which molecular collisions occur.

**For more information look at DEMOCRITUS on your PC**

# A12. Mean Square Displacement
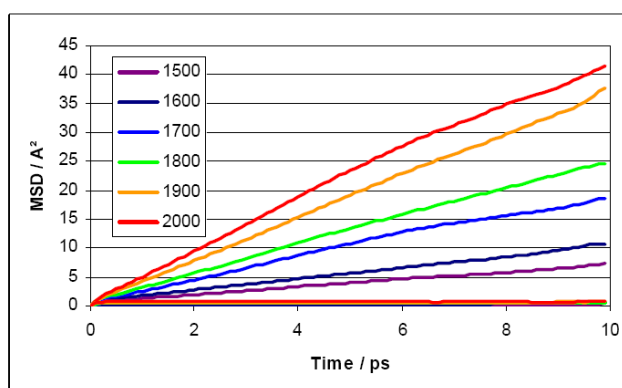


Linear plots show $F^-$ ions are diffusing
Rate of Diffusion increases with Temperature

Zero Gradient indicates $Ca^{2+}$ cations remain static

# A13. Diffusion Coefficient from MSDs

As they travel, the particles are jostled by collisions with other particles which prevent them from following a straight line. If the path is examined in close detail, it will be seen to be a good approximation to a random walk.. It can be shown that the mean square of the distance travelled by particles following a random walk is proportional to the time elapsed.

This relationship can be written as
$<r^2> = 6 D t + C$

where $<r^2>$ is the mean square distance and t is time. D and C are constants. The constant D is the most important of these and defines the diffusion rate. It is called the diffusion coefficient.

Diffusion in solids usually proceeds by hopping; the atoms jump from place to place rather than simply drift. The energy required for a hop can be calculated from the slope of the Arrhenius plot, the steeper the slope the more energy is required. In liquids, diffusion is relatively easy and so the Arrhenius slope is much less steep.
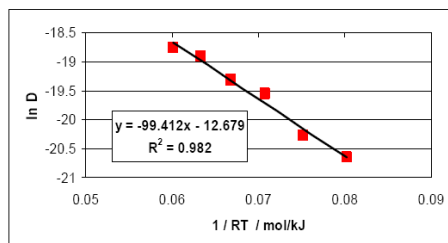
# A14. Calculating the Activation Energy: Arrhenius Plot

From the gradient of the MSD plots we can therefore calculate the diffusion coefficient of the F⁻ ions

| T / K | 1500 | 1600 | 1700 | 1800 | 1900 | 2000 |
|---|---|---|---|---|---|---|
| D / m² /s | 1.07E-09 | 1.57E-09 | 3.19E-09 | 4.12E-09 | 6.13E-09 | 7.12E-09 |

How *D* varies with temperature is related the the activation energy:

$$D = A\exp(-E_a/\mathrm{R}T) \quad \text{or} \quad \ln D = \ln A - E_a/\mathrm{R}T$$



y = -99.412x - 12.679
R² = 0.982

$E_a$ = 99 kJ mol⁻¹ ≈ 1eV
Large energy barrier hence diffusion only occurs at high temperatures

# A15. Summary

We have seen how static and dynamic simulation techniques can be used to study solid state systems

We have considered:
What is required to build a model (Crystal structure, potential, etc)
How static calculations can be used to study bulk defects
Finite size effects on static and dynamic systems
The effect of heating on a crystals structure and how this relates to RDF
Ways of studying the Motion of Particles in a system (MSD)
How to calculate diffusion coefficients from MSD and used them to calculate the activation Energy

# A16. Tasks

- Devise a plan for remaining days
- Some of the issues to explore
  - Intrinsic defects (noting effect of number and type)
  - Different concentrations of impurities (noting if there is any relationship between properties and their ionic radii and charge)
  - Accuracy of potential model (try different models for Ca-F etc.)
  - External effects (pressure or electric field)
- When considering the effect of defects
  - If negligible effect try increasing the defect concentration dramatically
  - If still no effect could even start from a new structure/composition

# A17. Websites

- http://people.bath.ac.uk/chsscp/teach/
  - adv_prac.bho
  - metadise.bho
- http://www.ks.uiuc.edu/Research/vmd/
- http://accelrys.com/products/discovery-studio/
- http://www.cse.scitech.ac.uk/ccg/software/DL_POLY/MANUALS/USRMAN2.17.pdf