

Introduction to Materials Modelling:

The role of defects in fast ion conduction in the fluorite lattice

1. Aims and Objectives

The aim of this task is to introduce the methods of molecular mechanics and molecular dynamics for atomistic simulation. We will look at how to build a simple model of a periodic ionic solid (calcium fluoride, CaF_2) using a package called METADISE, and use this to calculate some defect energies. The structural model will then be used to carry out molecular dynamics (MD) simulations using a package called DL_POLY, developed at Daresbury Laboratory. A detailed manual for DL_POLY is contained on the Daresbury Laboratory website http://www.cse.scitech.ac.uk/ccg/software/DL_POLY/ and is essential reading for those intending to use the package seriously. We will mainly be using METADISE to set up simulations and analysing the output obtained from MD simulations using a package called VMD. Once this task is complete we will explore how the introduction of defects affects the properties of the fast ion conductor.

By the end of this task you will be able to:

1. Generate the unit cell of a crystal structure given its cell dimensions, space group and atomic coordinates.
2. Appreciate what is required to define the potential interaction between ions.
3. Use METADISE to generate DL POLY input files for crystalline system.
4. Calculate an activation energy for the fluoride diffusion in CaF_2 .
5. Work with the various DL POLY output files and use VMD to generate animations of the simulation.

2. Molecular mechanics calculations using METADISE

2.1. *Generating structural input files for METADISE*

The structure of a three-dimensional solid requires the input of three main sets of information: the unit cell, the fractional coordinates and types of the atoms, and finally the space group symmetry.

Start by logging into one of the Windows PCs, and open the Network Drive labeled H: (this is the fileserver and saving any files you create here means they will be available in future on any of the University PCs). Create a new folder called 'Computing'. Double-click to enter the folder and create a new text file called `caf2.txt` by choosing *File > New > Text Document* from the menu.

Double click on the new text file you have just created, and add a Ca ion at fractional coordinate (0,0,0) and a F ion at fractional coordinate (0.5,0.5,0.5) by typing the following

```
fractional
Ca 0.0 0.0 0.0
F 0.25 0.25 0.25
ends
```

Next add the information about the unit cell. CaF_2 is cubic and has a cell parameter of 5.464 Å. This information goes above the fractional key word. Finally we need to add information about the space group, Fm-3m in this case (you may already know about space groups, but if not then please accept this for now). Once you have done this, the input file should like:

cell 5.464 5.464 5.464 90.0 90.0 90.0	Values of $a, b, c, \alpha, \beta, \gamma$ for CaF_2 unit cell
Space full fm-3m 225	FM-3M is space group of lattice
	Other commands tell program not to simplify cell using symmetry, and 225 is reference number for FM-3M
Fractional	
Ca 0.0 0.0 0.0	
F 0.25 0.25 0.25	
ends	

Finally, we need to add some keywords to tell the program what type of calculation we want to do and to define the force field we want to use. At this stage we only want to generate the crystal structure, so all you need to add to the bottom of your file is:

Nopotential	No force field (or potential parameters) will be defined
Check	Just read in the input we give it then write it back out again
Stop	Tells program that is not going further (to calc surfaces etc.)
Start	We have finished giving input to the program so it can do any calculation we have asked for
Stop	Gives us control of the computer back when the calculation has finished

Save the file, and rename it `CaF2.met` (hint: remember to disable 'Hide extensions' for know files)

If you set up your working directory as instructed then you can use the following 'batch' file to launch your METADISE job. Make a new text file called `RunMetadise.bat` and add the following lines of text :

```
%~d1
cd %~dp1
copy %1 input.txt
"c:\Program Files\MD_programs\programs\metadise.exe"
```

Having saved this file, you can now drag-and-drop the `CaF2.met` file onto it to launch it. Please ignore any security warnings which may appear and click 'OK'

Note: if having problems, replace 2 top lines by:

```
cd h:\Computing
h:
```

The program will only take a second or so to run and will produce several output files. The `code*.out` file is the main output file from METADISE and `sum*.out` is a summary of this file. Both can be opened in text editors WordPad or Notepad. The remaining files display the crystal structure in formats that can be read by various visualization packages and by METADISE itself (in the case of the `.res` files). The `.xyz` `.car` and `.cif` are all in a format that can be read by ACCELRYSDISCOVERYSTUDIO.

Double click on the `af*.car` file and VIEWER-LITE should open displaying the CaF_2 crystal you have just created. *If you are not sure what the structure should look like, ask a demonstrator to check your results.*

Experiment with using the viewer to manipulate the cell.

For example you might try to change the display type or grow the crystal.

Being able to generate a structural model of our crystal is only the first step of the calculation. We also need to choose a suitable potential model to describe the interactions in our system and calculate key properties such as energies, elastic constants and electrostatic constants. We are now going to select the potential parameters required to model CaF_2 . At this point you might want to refer back to the briefing notes on force fields and potential models if you are unclear about any terms used below.

Open the input file you used to create the fluorite structure above and change the keyword `nopotential` to `potential` and on the next line add the word `ends`. The details of the potential model will go between these two lines. First add the long-range Columbic interactions. This simply requires details of the atomic species in the cell and their charge. The keyword `Buckingham` is used to indicate how the short-range interactions will be defined. In our model we will assume the Ca—Ca interaction is totally Columbic (a common assumption in these models) so we only need to add details of the Ca—F and F—F interactions. Once you have done this, the potential section of your input file should look like this:

<code>potential</code>	keyword to indicate the potential model will follow
<code>species</code>	keyword to indicate a list of ionic species and charges will follow
<code>Ca 2.0</code>	Ca^{2+}
<code>F -1.0</code>	F^-
<code>ends</code>	The end of the list of ionic species
<code>Buckingham</code>	keyword to indicate a list of potential parameters will follow
<code>Ca F 797.42 0.3179 0.0 0.0 20.0</code>	Potential parameters for Ca-F interaction
<code>F F 1127.7 0.2753 15.83 0.0 20.0</code>	Potential parameters for F-F interaction
<code>ends</code>	The end of the list of potential parameters
<code>ends</code>	The end of the potential model definition

Once you have added these parameters to your potential model, the final step is change the `check` keyword so it reads `comp` to request that METADISE performs an energy minimization calculation to constant pressure. Now, save your file as `caf2_pot.met` and run METADISE by same method as in section 2.1.

Once METADISE has completed open the `code*.out` file and scroll to the bottom of the file. If the calculation was successful you will find the phrase *valid minimization to constant pressure* a few screens up from the bottom. Try searching for text string “valid” to find it.

Below this you will find the lattice vectors of the relaxed system, the lattice energy and various bulk properties. These serve as a useful check on how well our chosen model reproduces the true behaviour of the system we are studying. Make a note of the *lattice energy* listed below that phrase: you will need this presently. The `fin*.res` file contains the coordinates of the relaxed system in METADISE input file format, useful as the starting point for additional calculations. Of course, you can also view the relaxed structure in ACCELRYSDISCOVERYSTUDIO. The `af*.car` file contains the structure after minimization and the `bf*.car` the initial structure we defined in the input file. Compare the two to see if there has been an appreciable change in the structure.

3.0 Molecular dynamics of ion conduction

3.1 *Generating input files for DL_POLY*

Open the CaF₂ *non-defective* structure `caf2_pot.met` that you generated in section 2.2 in WordPad and add the following line to the top of the file:

```
print dlpoly 1
```

This indicates that we require DL_POLY input files to be generated when we run METADISE.

We also need to make a few more modifications to the file. One requirement of DL_POLY is that the size of the simulation cell must be at least twice the potential cut-off range (i.e. the point at which the program considers the particles no longer interact). Experience has shown that in order for the electrostatics to converge adequately the cut-off needs to be about 10 Å. Thus we must grow the cell so all the lattice dimensions are approximately 20 Å.

The CaF₂ unit cell is cubic and has a cell dimension of 5.464 Å. So in order to fulfill the cut-off criterion described above we will need to scale the unit cell so it is *four* times larger in each linear dimension (i.e. 64 times in volume) The METADISE keyword for this is `grow 4 4 4`, and this command is added immediately above the `start` command.

Finally, before running METADISE, change the keyword `comp` back to `check`. This will save time as we don't need to minimize the cell's geometry, since we will be using DL_POLY to do this. Save the amended file as `caf2_4x4x4.met` and submit it to METADISE.

Once the program has run you should get the same output files as we generated in section 2, but in addition you should have three files with the suffix `*.dlp`.

Open the file `CONFIG*.dlp` in WordPad. This file contains information about the system's configuration and is equivalent to the LATTICE and BASIS section of a METADISE input file. Close the file and rename it `CONFIG` (all capitals with *no suffix* – ignore any warnings about changing suffix type).

Now open the file `FIELD*.dlp`. This contains information about the force field and is analogous to the potential section of a METADISE file. Hence, the order in which the atoms appear is important, and must be *exactly* the same order as in the `CONFIG` file. Because we are only using a simple pair-wise potential model the `FIELD` file is quite simple, however this is not always the case. Close the file and rename it `FIELD` (again, all capitals with *no suffix* – ignore any warnings about changing suffix type).

Open the remaining file, `CONTROL*.dlp`. This file, as its name suggests, contains all the control variables for the simulation, i.e. it tells the program what to do. METADISE generates a template file with some standard values for a typical simulation; however for the simulation we are going to perform we will need to change a few of these values.

1. Check that the time step is set at 0.001 ps (1 fs)
2. Change the number of 'steps' to 20000
3. Select an npt constant pressure ensemble by placing # in front of the line `ensemble nve` and removing the # from in front of the line below and changing the keyword `nst` to `npt`. The # is the comment character and means that the program will not read the remainder of the line. Running the NPT ensemble enables the size of the simulation cell to change during the MD run.
4. Change the values `nstraj= 1 istranj= 250` to `nstraj= 0 istranj= 100`. This changes how often the program writes out to the `HISTORY` file (more on this later)
5. Select a *temperature* to run: since we investigating ion mobility as a function of temperature, each student should select a different temperature between 1200 and 2400 K. Replace the '300 K' in `CONTROL` file by your chosen value

Once you have made these changes save the file as `CONTROL`. (again, all capitals with *no suffix* – ignore any warnings about changing suffix type).

NOTE: The reliability of the result will depend on the number of steps as this improves the statistics. Thus, if the computer is fast enough, or you are leaving it running etc, try increasing the number of steps, but be careful or you may spend too much time waiting.

All DL_POLY simulations should be run in separate folders.

To run DL POLY, create a 'batch' file called `RunDL_POLY.bat` with following text:

```
%~d1
cd %~dp1
"c:\Program Files\MD_programs\programs\dlpoly220.exe"
```

Then, save this file to the same directory as your `FIELD`, `CONFIG` and `CONTROL` files, and double-click the batch file to launch (no need to drag-and-drop files).

The DL_POLY jobs will take just under 10 minutes to run – if you find that yours is terminating immediately, or lasting for significantly longer than 15 minutes, *please inform a demonstrator*. Once the job has finished, you should find a number of new output files in the working directory: `HISTORY`, `OUTPUT`, `RDFDAT`, `REVCON`, `REVIVE` and `STATIS`.

Open the `OUTPUT` file in WordPad or Note Pad and search for the word "Diffusion". Under this line, you should find your diffusion coefficients calculated for Ca and F ions. What do you notice about their magnitude?

3.2 Arrhenius plot for ionic diffusion in CaF_2

By simulating the CaF_2 structure at a range of different temperatures, the change in rate of ionic diffusion (as measured by the diffusion coefficient) as a function of temperature can be used to determine the thermal activation barrier for the ionic transport. This value may be compared directly with the defect formation energies, to shed some light on the mechanisms of diffusion at finite temperature.

Using either class data, or sample data provided by demonstrator, produce an Arrhenius plot of $\ln(D)$ versus $1/T$. The formula for the Arrhenius relationship is

$$D = A \exp(-E_a/RT) \text{ or } \ln D = \ln A - E_a/RT$$

where $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and A is some constant. Use this to determine a value for the activation energy E_a for F diffusion in CaF_2 . How does this value compare with the Schottky and Frenkel defect formation energy? What does this suggest about the structural mechanism of F diffusion in CaF_2 ?

3.3 Structural analysis and visualization using VMD

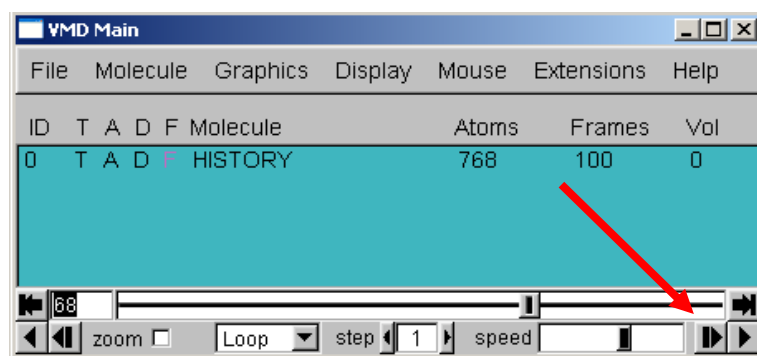
In order to look in more detail at structural mechanisms of ionic diffusion in CaF_2 , it is necessary to visualize the trajectories directly using a package called VMD (Visual Molecular Dynamics). As well as visualization, VMD can also calculate radial distribution functions to enable a more quantitative structural analysis. A 'shortcut' to launch this program can be found on your Desktop.

Launch VMD from the shortcut. After a few seconds, you should see three windows appear, the top-most being the 'VMD Main' window. From the 'File' menu of the main window, select 'New Molecule' and 'Browse' to the directory in which you carried out your DL_POLY simulation in 3.2 above. Then, select HISTORY file and change the setting of 'Determine file type' drop-down menu to 'DLPOLY V2 History'. Now, select 'Load' and VMD will load in the frames of your simulation. If you don't see anything appear in the VMD Display window, please ask a demonstrator for help.

VMD can build various visual representations of your model, which are accessed from the 'Graphics' menu of the main window. You can rotate and zoom in/out on these using mouse.

Select 'Representations' from the 'Graphics' menu to bring up the 'Graphical Representations' control panel. Change the 'Drawing Method' to 'VDW' and you should be able to see the Ca (blue) and F (green) ions clearly. Increase 'Sphere Resolution' to around 20 to get better definition of the spheres. Now, change text in 'Selected Atoms' box from `all` to `name CA`. You should now just see the Ca ions. What do you notice about their arrangement? Now, change 'Material' to 'Transparent', and then click on 'Create Rep' button near top left-hand corner of 'Graphical Representations' box. This will create a new representation, which is initially identical to the first. Change text in 'Selected Atoms' box in new representation from `name CA` to `name F`, and change 'Material' back to 'Opaque'. You should now just see both the Ca and F ions, but Ca will be transparent. What differences can you see between the arrangements of Ca and F ions?

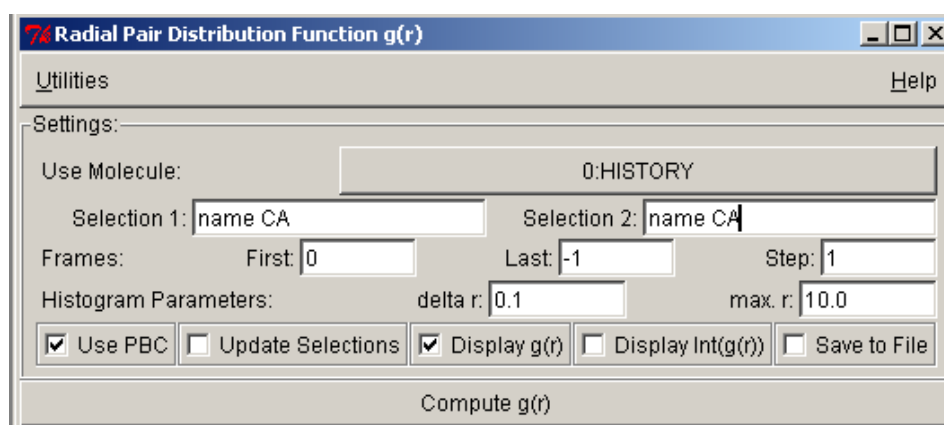
You can step through the frames in your simulation by returning to the ‘VMD Main’ window and clicking on the advance single frame button.



You can also animate the frames by pressing play button, and adjust the speed from the slider. Although your simulations will only have a small number of frames, some evidence of F motion should be seen at the higher temperatures. However, simulations at 300 K should show very different behaviour.

3.3.1 Calculating RDFs with VMD

To show quantitatively the different degrees of structural order in Ca and F sub-lattices, the radial distribution function can be used. To access this from VMD, go to the ‘Extensions’ menu from the main window, and from the ‘Analysis’ sub-menu, select ‘Radial Pair Distribution Function $g(r)$ ’. This should bring up the following window:



Change the text in ‘Selection 1’ and ‘Selection 2’ boxes to `name CA`, as above, and then click on ‘Compute $g(r)$ ’ button. Then, repeat this with ‘Selection 1’ and ‘Selection 2’ boxes containing `name F`. This will generate the Ca and F pair radial distribution functions. What do you notice about their form? Can you use these to make a qualitative statement about the relative degree of ordering in the Ca and F sub-lattices?

If you have time, you can plot the Ca—F RDFs as well, by entering ‘Selection 1’ as `name CA` and ‘Selection 2’ as `name F`, respectively. You can make a series of plots of $g(r)$ at different temperatures to see the effect of temperature on the ionic ordering.

4 *Investigation of role of defects in fast ion conduction in the fluorite lattice*

A number of different tasks are given below, do not consider that you must cover them all.

4.1 *Effect of Intrinsic defects*

There are two types of intrinsic defects to consider (a) Schottky and (b) Frenkel.

A Schottky defect, see briefing notes, is where you remove a stoichiometric unit i.e. 1 Ca and 2 F i.e. one calcium and two fluorine vacancies. Perhaps most easily done by removing such units in the fin#####.res file generated in 3.1 and renaming this defect.met and running it with METADISE. You can consider the starting location and the number of such defects.

A Frenkel defect, see briefing notes, is where a Ca or a F ion is removed and put somewhere else in the lattice (nb the fluorite unit cell can be thought of as linked cubes, where F occupies the corner and every other cube is filled with Ca, thus the empty cube is an ideal interstitial site), i.e one vacancy and one interstitial, and can be either an anion or cation Frenkel. Again you can consider the starting location and the number of such defects.

Note: You do not need to do an exhaustive search, plan to do sufficient to generate a view of the effect, if any. It is probably worth adding quite a few so as it see whether there is any effect first. You should always keep the simulation cell charge neutral – but if you do decide to play with this, do record the total charge.

4.2 *Effect of Extrinsic defects*

This is when an impurity replaces a lattice ion, and this may also in turn modify the energy of formation of vacancies and interstitials. We will consider cation impurities. The potential, described towards the ends of Section 2.1 in the fin#####.res file generated in 3.1, needs to be modified to account for the impurity. The potential models for a number of cation ion impurities are listed below in the appendices. Again please do not feel that you need to consider all possible defects. Indeed, there are too many possible variations of impurities, vacancies and interstitials. Discuss as group what you have time for, based on previous calculations and select a subset of different types of defects, sufficient to tell a story. Note, consider also the effect of ionic radius and charge (of the impurity), as well as number of impurities, vacancies and interstitials.

Also note, that many of these potentials have never before been tested in CaF₂, so if the calculations fail, it may be a limitation of the potential you have selected, not you, but do find a demonstrator.

4.3 *External Effects*

DL_POLY can incorporate a number of effects in addition to temperature, such as pressure and external fields. Pressure is a keyword (in kbars) in the CONTROL file

while the field information is given in the FIELD file. Do look in the DL_POLY manual for details.

http://www.cse.scitech.ac.uk/ccg/software/DL_POLY/MANUALS/USRMAN2.17.pdf

4.4 *Reliability*

The main factors that will affect the reliability of the calculation are (i) the number of steps, which can of course be adjusted and (ii) the accuracy of the potential model in reproducing the interatomic forces. One alternative model is listed in the appendix, and could be examined to see if it improves the reliability, but there are others in the literature.

Acknowledgement:

Thanks to Dr David J Cooke (Huddersfield) and Dr James Elliott (Cambridge)

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Appendix 1: Potential Model for CaF₂.

potential

```
species
  Ca 2.0
  F -1.0
ends

Buckingham
  Ca F 797.42 0.3179 0.0 0.0 20.0
  F F 1127.7 0.2753 15.83 0.0 20.0
ends
```

ends

Appendix 2a: Additional Cations

```
#
# collection of potentials
#
# Catlow CRA, Norgett MJ and Ross A J Phys C 10, 1630 (1977)
#
#
# Watson G.W., etal for perovskites
# Physics Earth Planetary Interiors 89, 137-144 (1995)
#
poten
```

```
species
Sr core 2.00
Ba core 2.00
Mn core 2.00
Zn core 2.00
K core 1.00
ends
```

```
Buckingham
Sr core F core 2298.500 0.29170 0.0 0.0 20.0
Ba core F core 5193.300 0.27980 0.0 0.0 20.0
K core F core 2674.306 0.28352 0.0 0.0 20.0
Mn core F core 1654.780 0.27591 0.0 0.0 20.0
Zn core F core 1655.530 0.26516 0.0 0.0 20.0
ends
```

ends

Appendix 2b: Alternative CaF₂ potential

```
poten
species
Ca core 2.00
F core -1.00
ends

buckingham
Ca core F core 1272.80 0.29970 0.0 0.0 20.0
F core F core 99731833.99 0.12013 17.02423 0.0 20.0
ends
```

ends

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Appendix 3: Potentials for Rare Earth Elements

```
#
# JACKSON library - collection of potentials
#
# MEG Valerio , RA Jackson and JF de Lima, J Phys Condens Matter
# 12 (2000) 7727 and references therein.
#
# Potentials used in modelling rare earth fluorides.
#
#
#
poten

species
La core 3.00
Ce core 3.00
Pr core 3.00
Nd core 3.00
Sm core 3.00
Eu core 3.00
Gd core 3.00
Tb core 3.00
Dy core 3.00
Ho core 3.00
Er core 3.00
Tm core 3.00
Yb core 3.00
Lu core 3.00
ends

buckingham
La core F core 2817.74 0.2980 0.0 0.0 20.0
Ce core F core 2627.13 0.2980 0.0 0.0 20.0
Pr core F core 2453.39 0.2980 0.0 0.0 20.0
Nd core F core 2488.27 0.2950 0.0 0.0 20.0
Sm core F core 1764.57 0.3064 0.0 0.0 20.0
Eu core F core 2085.74 0.2950 0.0 0.0 20.0
Gd core F core 1667.02 0.3037 0.0 0.0 20.0
Tb core F core 1541.15 0.3065 0.0 0.0 20.0
Dy core F core 1536.68 0.3037 0.0 0.0 20.0
Ho core F core 2590.91 0.2809 0.0 0.0 20.0
Er core F core 1880.44 0.2920 0.0 0.0 20.0
Tm core F core 1390.19 0.3037 0.0 0.0 20.0
Yb core F core 2381.55 0.2808 0.0 0.0 20.0
Lu core F core 1448.23 0.2990 0.0 0.0 20.0
ends

ends
```

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Appendix 4

J B Amaral A C Lewis, M E G Valerio and R A Jackson J. Phys.: Condens. Matter 16 (2004) 8733–8741

poten

species

Li	core	1.00
Al	core	3.00
Ca	core	2.00
Sr	core	2.00
Pb	core	2.00
Co	core	2.00
Ni	core	2.00
Cr	core	3.00
Fe	core	3.00
Y	core	3.00
Si	core	4.00
Ti	core	4.00

ends

Buckingham

Li	core	F-	core	443.8	0.2714	0.0	—
Al	core	F-	core	1400.0	0.2571	0.0	—
Ca	core	F-	core	3400.0	0.2661	0.0	—
Sr	core	F-	core	3400.0	0.2906	0.0	—
Pb	core	F-	core	400.0	0.4115	0.0	—
Co	core	F-	core	1613.5	0.2668	0.0	—
Ni	core	F-	core	1599.7	0.2626	0.0	—
Cr	core	F-	core	949.7	0.2895	0.0	—
Fe	core	F-	core	1993.0	0.2620	0.0	—
Y	core	F-	core	1650.0	0.3020	0.0	—
Si	core	F-	core	1773.4	0.2571	0.0	
Ti	core	F-	core	3500.0	0.2570	0.0	

ends

ends