

# Chapter 1

## Introduction

All other atoms ... could be built up from these two units, the final result being not unlike a miniature solar system. The simile suggests in the first place that the atom is to a large extent empty, and that it is likely to be about as difficult to score a direct hit on any part of it as it would be for some far-distant marksman to shoot projectiles at the solar system in the hope of hitting either sun or one of its planets. ... This ... is why atom-splitting is never likely to be an economic method of obtaining cheap energy for industry.

— A.W. Haslett, 1939 [1]

### 1.1 Nuclear Technology in a Modern Society

After more than fifty years of running critical assemblies of nuclear fuel, their inherent atomic processes are still surrounded by many controversies. Furthermore, the

public demand for more and cheaper electric power and the developing environmental awareness seem in conflict.

Media coverage of disasters and epidemics makes us more aware of large scale accidents than of the everyday risk involved in simply living. We are more afraid of flying in an airliner (or even riding an elevator!) than we are of driving a car. The element of risk involved in every human activity has become acceptable in some situations and unacceptable in others.

Nuclear energy has always been associated with nuclear weapons. This is logical, since a type of nuclear reactor is needed to acquire the materials for a state of the art nuclear warhead. Only after the accidents at Three Mile Island did the public become aware of the dangerous possibility of ‘meltdown’ inherent in most reactor designs and the effect of radioactive contamination after such an accident if the reactor is designed without an adequate containment building. The accident at Prypjat reactor park (Chernobyl) showed the public (and the amazed reactor operators) that a reactor can actually explode and contaminate half a continent [2–4]. Western countries claim that such an accident is not possible with their modern reactors, because their reactors and procedures are safe.

## 1.2 Nuclear Fuel

Modern nuclear fuel is usually in the form of uranium dioxide pellets, contained within stainless steel (AGR) or zirconium alloy (PWR) tubes, which are mounted in the reactor in bundles. These tubes are usually called the cladding of the fuel. Traditional nuclear fuel only becomes dangerous after it has undergone irradiation in a reactor, when many radioactive isotopes have accumulated in the fuel matrix.

The use of so called “mixed-oxide” fuels, containing the chemically poisonous element plutonium, makes fuel more difficult to handle even before it has been used in a reactor. Although the use of plutonium is still highly controversial, burning it in a reactor seems to be the only sensible way of disposing of it.

Even if not all the plutonium is burnt in the reactor, weapons grade plutonium is proliferation safe after use in a reactor since extraction and enrichment of plutonium is very difficult.

When a spent pin is taken out of the reactor it still produces a lot of radiation and heat and it is described as “hot”. It is then submersed in water for a couple of months until it has physically cooled down. Nuclear Electric Plc. are concerned with the scenario of a hot bundle that is accidentally dropped during refueling or is punctured during power transients during reactor operation. Some issues are compounded by the fact that reactor operators all over the world are always looking for ways to increase fuel life. As fuel stays in the reactor longer, the concentration of fission products increases, making the effects of pin failure potentially more dangerous.

When a fuel pin breaks and the fuel comes into contact with an oxidizing atmosphere of oxygen, carbon dioxide/monoxide (in AGR reactors) or water (in PWR reactors), the stoichiometry of the fuel can change [5]. Possible associated phase changes greatly change the mechanical properties of the fuel, enhance or degrade the capacity of the fuel matrix to retain fission product ions and change the diffusion behaviour in the lattice (see e.g. Une [6] or Olander [7]). The appearance of different phases over large temperature and stoichiometry ranges makes the uranium-oxygen system particularly interesting.

No less interesting is the huge stoichiometry range of the single  $\text{UO}_2$  phase and to some extent the hexagonal  $\text{U}_3\text{O}_8$  phase (see Figure 1.1). At high temperatures the

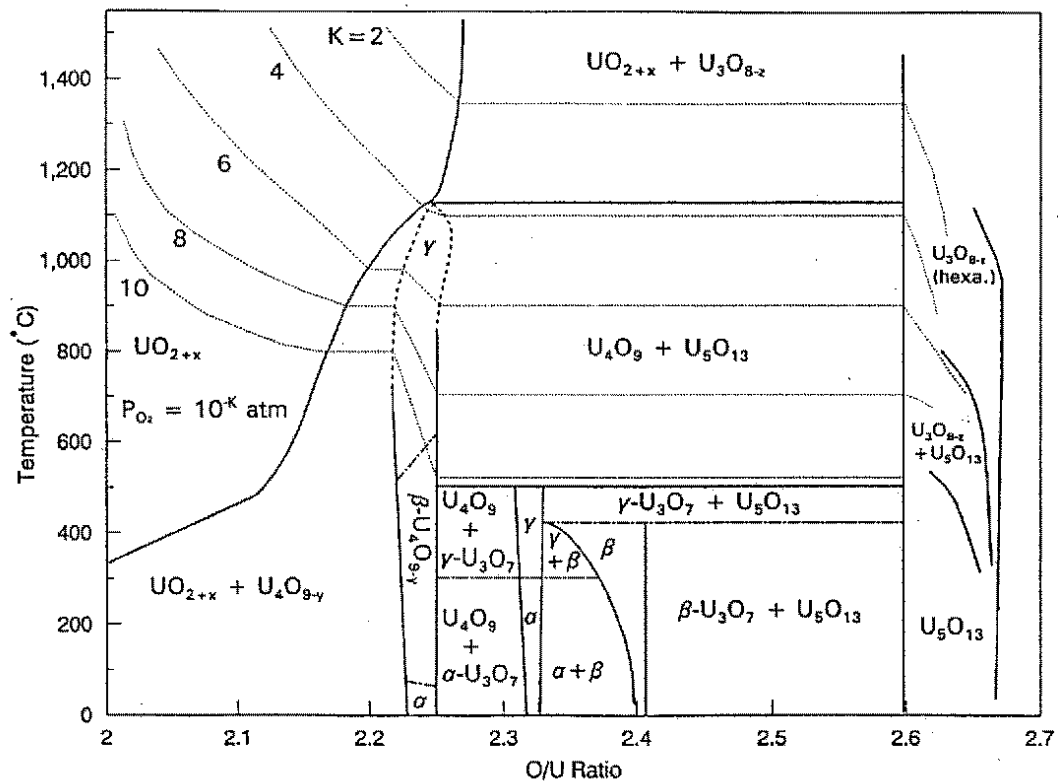


Figure 1.1: Uranium-Oxygen phase diagram taken from Naito *et al.* [8] and Bradford [9].

$UO_2$  lattice seems to be able to suppress the phase change to the  $U_4O_9$  structure completely, and  $U_3O_8$  is only formed after the oxygen-uranium fraction becomes greater than 2.25.

It is the stoichiometry range and the high melting point (approx. 2880 °C) of ceramic  $UO_2$  which makes it a very good reactor fuel. The disadvantages of  $UO_2$  are the low thermal conductivity and the high heat capacity. The advantages of a high melting point are clear, hot reactors are thermodynamically more efficient; the importance of the stoichiometry will become apparent below.

## 1.3 Safety Issues

The nuclear industry employs three methods to make nuclear power as safe as possible. The first one is, of course, to build a device which does not fail and is safe to operate. This is achieved by carefully choosing the construction materials to match the properties demanded by the engineering design. Technologically this is already a challenge, because neutron radiation affects most structural materials (hydrogen/helium embrittlement in steel, activation in certain types of concrete and steel, etc.). The operational procedure also belongs in this first category, as it is a part of the system that aims to keep the reactor in a safe state.

The second method is to ensure that when a part of the reactor fails, the reactor remains in a safe state due to physical aspects of the design (e.g. when the main circulation pumps fail, natural convection keeps the coolant flowing at a sufficient rate). The human intervention usually makes accidents worse and most critical systems and procedures are designed to be “walk away” systems.

Finally, by studying accident scenarios (see e.g. ref [10] ), we can predict events, and take measures to minimize the effects of such an accident. The (usually spherical) containment building is, for instance designed to absorb the shock wave energy which might be exerted by a steam explosion, caused by an overheated reactor core.

This study can be regarded a part of this third category of accident management, as this thesis predicts the behaviour of fission products in oxidizing fuel thereby providing information for the improved fuel and operating designs.

## 1.4 Nuclear Fission

Uranium fission by neutron bombardment was discovered by Frisch [11] and Meitner in 1939, only seven years after the discovery of the neutron itself. The appearance of nuclei with a much lower mass after neutron irradiation puzzled chemists at first, but the correct interpretation of the appearance of barium in neutron irradiated samples [12] was given by Lise Meitners' visual model of a liquid drop separating into two parts. The term fission comes from "binary fission" of cells in biology.

### 1.4.1 Fission energy

When a  $^{235}\text{U}$  nucleus splits into two smaller nuclei, approximately 200 MeV is released. Most of this energy can be found in the kinetic energy of the fission products. The neutrons which are released with this reaction leave the fuel pin and cause fission in other  $^{235}\text{U}$  nuclei (hence the term 'chain' reaction) or leave the reactor core. A gram of  $^{235}\text{U}$  will produce  $8 \times 10^7$  kJ which corresponds to  $2 \times 10^4$  kWh. In the nuclear industry the unit of MWd (Mega-Watt day) is often used; one gram of  $^{235}\text{U}$  generates about 1 MWd of energy, so a 1GW power station with a 30% thermal efficiency will use about 3 tonnes of uranium-235 annually.

Nuclear operators will also use the term "burnup" which is the percentage of uranium isotopes that have changed due to fission or neutron capture. The "burnup" is used as a measure of the fuel age. A burn up of 1% corresponds to 10 GWd/t of generated heat.

Finally there is a quantity called the fission rate,  $F$ , which is measured in fissions per  $\text{cm}^3\text{s}$  ( $[\text{fcm}^{-3}\text{s}^{-1}]$ ).

### 1.4.2 Fission products

In a reactor pile, many isotopes of common periodic table elements may be formed by fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . Some of fission product nuclei are still unstable and undergo spontaneous nuclear reactions or capture neutrons or electrons to form more stable nuclei.

Uranium and plutonium nuclei in nuclear reactors do not break up into two equal parts. This is not a quantum mechanical, but a geometric phenomenon. Liquid drop models predict this behaviour when oscillation is the cause of fission. Only when fission is caused by particles carrying a large amount of momentum, does a nucleus break up in equal parts. However, even fast neutrons in nuclear reactors do not carry enough momentum to split nuclei in this fashion. Slow neutrons captured by a uranium nucleus merely bring the nucleus into an unstable configuration, causing the nucleus to oscillate and break up into unequal parts. Therefore, the fission yield spectrum of uranium is a curve known as the “Camel Curve”. The fission yield spectrum of uranium-235 (taken from van den Bosch and Huizenga [13]) split by thermal neutrons is shown in Figure 1.2.

Many of the atoms shown in Figure 1.2 are in fact not important as they are highly radioactive and decay to a more stable configuration in a matter of seconds or minutes. Less active nuclei with half life times of several hours up to thousands of years hinder reactor operation and safety in two ways.

Isotopes of xenon and samarium with a half life of several hours cause reactor poisoning, because of their high cross section for neutron capture. Reactor safety is usually not impaired as the phenomenon is well known. However, the persistence of the chief engineer to continue a test on a  $^{135}\text{Xe}$  poisoned core was an important factor in the 1986 Chernobyl accident [2–4].

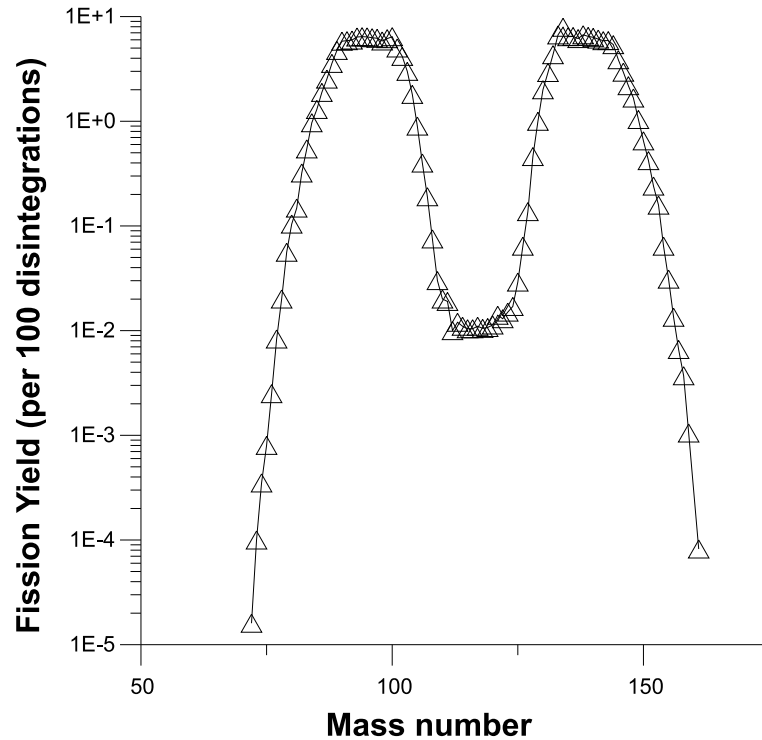


Figure 1.2: Fission yield spectrum (per 100 disintegrations) of uranium-235 interacting with thermal neutrons.

The fission products of interest from the point of view of radioactive contamination have much longer half lives, and although they are less radioactive than the nuclei mentioned above, they remain radiotoxic for a long time. Furthermore, radioactive isotopes of iodine, tellurium and caesium can be very dangerous when ingested, because the body readily absorbs and concentrates them in vital organs. Some fission products, for example ruthenium, have long living radio-active isotopes *and* are chemically toxic.



## 1.5 Trapping of Fission Products

Figure 1.3 shows the fission products present in the  $\text{UO}_2$  fuel after 2.9% burnup and a cooldown period in the pond. The fission yield was calculated for Grimes and Catlow [14] using the “FISPIN” code [15]. The graph also shows in which state the fission products are found in the  $\text{UO}_2$  fuel. Solubility data was taken from Kleykamp [16, 17]. In real nuclear reactors, all fission products start out in solution in the matrix, since they are the result of random fission of matrix uranium atoms. In this sense, the data assembled in Figure 1.3 may be somewhat unrealistic, since the solution experiments are done by mixing  $\text{UO}_2$  and another oxide and observing which phases appear at elevated temperatures.

In a reactor, the process works the other way round. Atomic diffusion of the fission products causes precipitation of gas, metal and oxide clusters. As such, the fuel history is a very important parameter in deciding the characteristics of precipitation. For example, short thermal ramps and local over-heating drastically change the distribution of the fission products. Also, the centre of the fuel pellets erode much faster than the cooler outside, because there is a large thermal gradient across the fuel pellet. To counter this erosion, smaller pellets can be used with a hole in the middle (i.e. as in fast breeder reactors). Precipitation of metals at high burnup often happens within fission gas bubbles [18]. Figure 1.4 shows an example of a metal precipitate in a large void or bubble.

The ability to accommodate fission products is not only a topic of study in fuel technology. The long term storage of actinides has similar solubility requirements [19] to fuels albeit on a much longer time scale and in a different temperature regime.

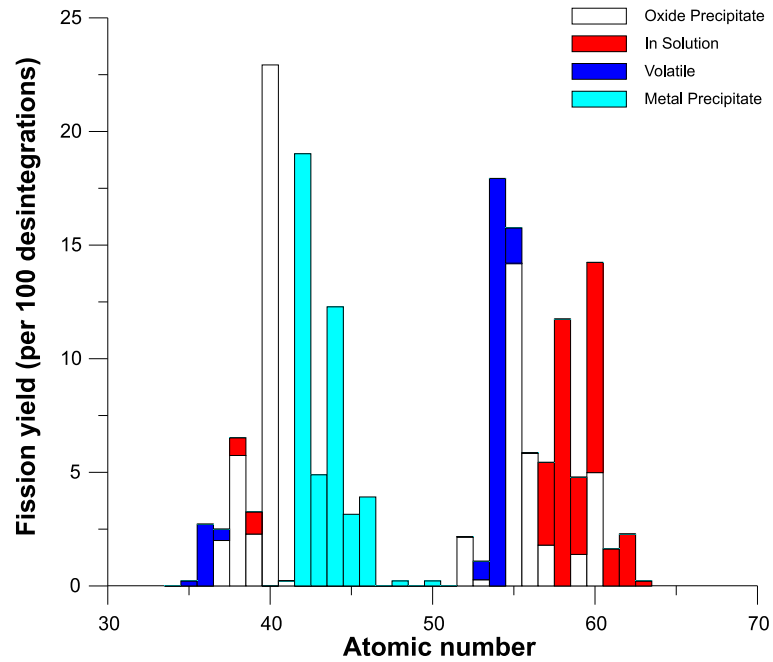


Figure 1.3: Fission products in the  $\text{UO}_2$  fuel after 2.9% burnup and a cooldown period in the pond. This figure also shows the state of the fission products in the fuel matrix: the volatiles precipitate in bubbles; the metals form the 5-metal inclusions often found inside fission gas bubbles. Atoms in solution usually take up a cation position, which can often be observed with x-ray diffraction, because solution affects the lattice parameter. The fraction of zirconium (element 40) in solution in the matrix is highly dependent on temperature, and is therefore not shown.

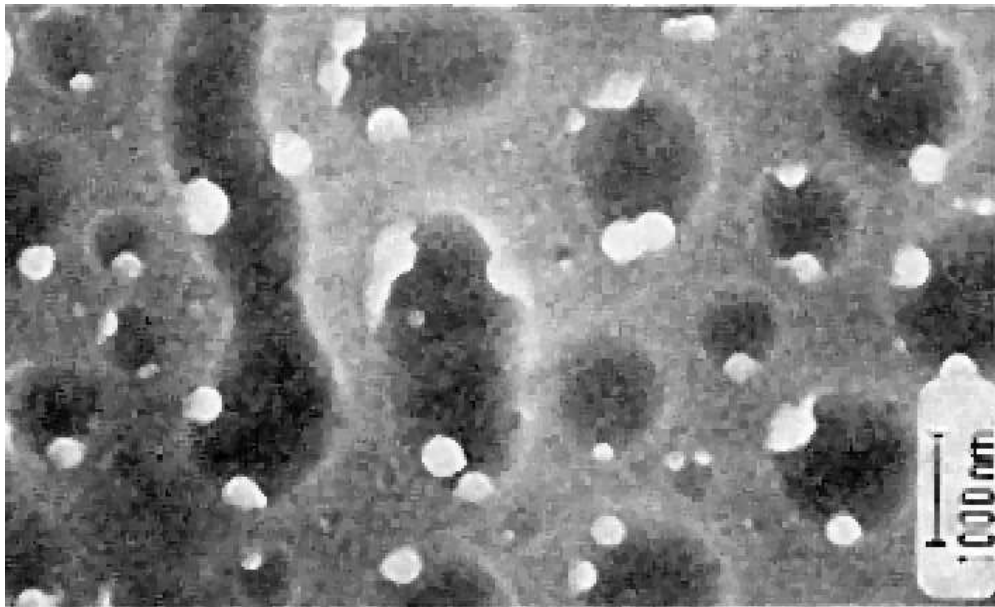


Figure 1.4: 5-metal beads inside a helium bubble at the grain boundary (Taken from *Fundamental Aspects of Inert Gases in Solids* [18]).

## 1.6 Structural Property Changes During Reactor Operation

Unirradiated fuel for LWR reactors contains about 3-5 vol % voids (this increases to approximately 15 % for FBR reactors) to accommodate the fission products which will be produced during fission. The first stages of the fuel life show a fuel crimp as the fuel sinters at high temperature. The crimp effect increases the space between the fuel and the cladding and, as a consequence of the decreased thermal conductivity, ultimately increases the fuel temperature.

Fortunately, the formation of fission products and radiation damage counters the crimp effect after about 2% burnup, causing the fuel to swell again. This persistent swelling of the fuel is the main reason why fuel has a limited life time.

The non-uniform thermal neutron flux inside the fuel pellets causes anisotropic expansion. This is the reason why fuel pellets show extensive macroscopic damage in the form of cracking and segregation after fission yields greater than 30.000 MWd/t (approximately 3% burnup).

## 1.7 Pellet-Cladding-Interaction (PCI)

Pellet-cladding-interaction (PCI) includes all mechanical and chemical interactions between the fuel pellets and the cladding. Differences in expansion coefficients cause local stress. Stress corrosion cracking is caused by the combination of this effect and the availability of oxygen. Formation of zirconium-uranates, caesium-uranates and zirconium-hydrides also weakens the cladding. Finally, at high burnup  $> 5$  %, the formation of plutonium in the RIM layer ( $\approx 10\mu m$  of the outer diameter of a pellet)

causes a local increase of fission gas pockets and fission products, which further corrode the cladding.

A good measure against many cladding problems is the deposition of pure zirconium on the inside of the cladding before it is charged with fuel.

## 1.8 Fuel Oxidation

The change in the fuel oxygen potential, induced by the accumulation of charged fission products, is buffered by the stoichiometry range of the  $\text{UO}_2$  lattice. The desired situation is that the uranium oxide will remain in the fluorite structure, with fission products in solution or precipitated within the matrix.

When the fuel is exposed to an oxidizing agent, the  $\text{UO}_2$  may undergo a phase change. The fuel properties change, and fission products may be released into the environment. Experimenting with fuel at this stage is very difficult, and does not clearly reveal which mechanisms are responsible for the release of certain fission products. Controlled experiments with ion implanted non-radioactive fuel (SIM-FUEL) are simpler and allow examination of a single fission product in the fuel. Of course, this approach therefore ignores potentially important mixed ion and intrinsic post irradiation effects.

## 1.9 Non-fertile fuel

Part II. of this thesis is a study of the solution behaviour of dopant ions in  $\text{Y}_2\text{O}_3$  [20]. Although not directly relevant to fission products in uranium oxides at this moment, it provides a glimpse of a possible future material, where fissile material is dissolved in a ceramic host lattice.

The cold war has left us with an enormous stockpile of weapons grade plutonium which amounts to a global total of 245-265 tonnes. In addition to this, the worlds nuclear power stations add another 60-70 tonnes of (non-weapons grade) plutonium annually. The cumulative worldwide plutonium production of nuclear power stations totals about 1000 tonnes today [21]. Fortunately plutonium produced by normal power stations cannot be used to fabricate a nuclear weapon.

There are two interesting problems in the management of the plutonium stockpile. Although the nuclear industry is interested in the use of plutonium in nuclear reactors, the only use of plutonium at this moment is via mixed-oxide fuels. Mixed-oxide fuels are normal uranium-oxide fuels with a percentage of plutonium-oxide mixed in. Unfortunately mixed fuels do not reduce the total amount of plutonium, as plutonium is still being produced via the fast neutron capture of  $^{238}\text{U}$ . However, weapons grade plutonium in the mixed-oxide fuel is rendered useless as a weapons material.

The only method to ensure a decrease in the amount of plutonium produced in the reactor is the use of a fuel which does not breed plutonium [22]. This means a fuel which does not contain  $^{238}\text{U}$ . Although economical and engineering considerations tell us that  $\text{Y}_2\text{O}_3$  is unlikely to be the right host material, Chapter 6 shows how we can predict the solution behaviour of other ceramic materials via atomistic simulation.

## 1.10 Atomic Scale Simulation

Today, we often rely heavily on computational facilities to explain our experimental results. It has become possible to predict the outcome of limited experiments, and

test our basic ideas through simulation.

The nuclear industry has always been interested in atomistic simulation, because direct experimentation is difficult with radioactive materials. Many of the relevant computer codes in use today have been developed by, or in collaboration with, the nuclear industry. Originally their purpose was to investigate defect processes in fuel, but now they find employment in many other fields.

In this thesis, the “CASCADE” code [23], which was mainly developed at Harwell Laboratory, is used to simulate processes in the uranium dioxide fuel. The simulated atoms are described by interatomic potentials, which are derived from either quantum mechanical procedures or by fitting to experimental data (or both). Our individual ions contain a shell and a core [24], which takes polarization effects into account.

Atom positions are determined via a process of energy minimisation. That is, atoms are moved iteratively until further movement no longer changes the total energy of the system by more than a certain prescribed amount.

In the last ten years the Atomistic Simulation methodology has been used to study many different systems other than those covered in this thesis. Chemical and structural properties of catalytic materials such as zeolites have been studied. Large scale defect structures of electronic materials used in varistors and capacitors have been studied and compared with microscopic studies [25–28]. Defect properties of other types of materials have also been simulated. Recently cellular automata methods based on rules derived from atomistic simulations have been studied in an attempt to predict large scale effects [29].

The calculations in this report should be considered as computer “experiments”. Our experiments supply us with the enthalpies of solid state reactions and ion migra-

tion activation enthalpies. The prediction of diffusion behaviour is based on finding all possible diffusion mechanisms and choosing the most favourable.

## 1.11 Molecular Dynamics

In contrast to the method described above (ie. energy minimisation), the Molecular Dynamics methodology (MD) can be employed to make predictions concerning diffusion processes of ions in a sample of material at elevated temperatures without the need to select the mechanisms or pathways that underlie diffusion behaviour. An additional advantage of MD is that the study of ion migration yields absolute diffusion coefficients rather than activation energies. A disadvantage of the MD treatment is that due to computational restrictions it can only effectively be used to study the diffusion behaviour of relatively fast diffusion processes such as the diffusion of oxygen ions in  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ . Cation migration is presently too slow to study with this technique.

The results of MD simulations are presented in Chapter 7. For this the penicillin code [30] was used and the intrinsic defect behaviour in  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  studied. Two parallel algorithms were developed and included in penicillin to increase the simulation timescales. In addition tools developed by Bulatov [31] were extended to study diffusion behaviour in more detail. Some documentation on the current toolset can be found in Appendix A.

## 1.12 Visualisation of Atomistic Simulation Data

There are many reasons to add methods for visualising both input and output data to the current set of tools used in the atomistic simulation arena.



Firstly, the understanding of defect processes in a lattice can be improved by actually seeing and being able to manipulate an image of the relaxation effect of a host lattice after inclusion of a defect. Secondly, common errors caused by conceptually difficult structures can be reduced dramatically. Finally, the ability to make presentation quality pictures of defect structures is useful for explaining complex defect structures.

During this study visualisation codes were developed to investigate CASCADE and penicillin output. Both codes are described in the Appendix A. In addition many static visualisation methods are investigated and used in Appendix B: “Visualisation of Atomic Scale Simulations”.