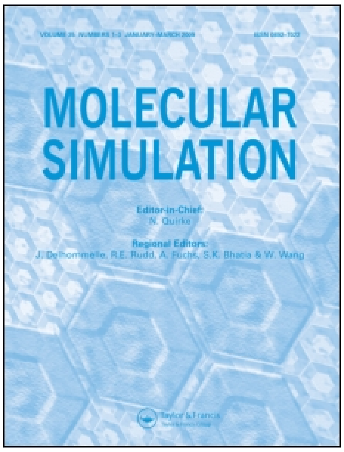

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Trachenko, K. , Dove, M. T. , Salje, E. K. H. , Todorov, I. , Smith, W. , Pruneda, M. and Artacho, E.(2005) 'Radiation damage in the bulk and at the surface', Molecular Simulation, 31: 5, 355 — 359
To link to this Article: DOI: 10.1080/08927020500066825
URL: http://dx.doi.org/10.1080/08927020500066825

Molecular Simulation, Vol. 31, No. 5, April 2005, 355–359

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Radiation damage in the bulk and at the surface

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(Received July 2004; in final form December 2004)

The UK environmental e-science initiative supports the development and modification of simulation tools used to study radiation damage effects. We discuss the development and modification to the DL_POLY molecular dynamics (MD) code. Using the newly developed tools, we study the effects of radiation damage related to the safe encapsulation of highly radioactive materials, including nuclear waste. We address the possible differences between the radiation damage in the bulk and at the surface of a material, and perform MD simulations of energetic events in zircon structure. We find that in the case of readily amorphizable material, the formation of a stable alternative covalent network reduces the possible effect of the surface on the damaged structure.

Keywords: DL_POLY molecular dynamics; Amorphization; Domain decomposition; e-science

PACS numbers: 61.80.-x; 61.82.-d; 62.20.-x

1. Introduction

Long-term safe encapsulation of highly-radioactive materials presents a problem, which includes scientific and technical challenges. One of them is the durability of the encapsulating material (waste form) to serve as an effective barrier to prevent the escape of radioactive isotopes to the environment. These isotopes include highly radioactive nuclear waste or any other radioactive materials that are of no, or limited, use to us, but present environmental and health risk and need to be encapsulated. Depending on the half-lifes, an encapsulating material should remain durable and maintain acceptable diffusion rates on the timescale between hundreds and tens of thousands of years. The diffusion rates are altered by the structural changes caused by irradiation, with the most prominent being the radiation-induced amorphization. The accumulated experimental data shows that materials may possess remarkably different resistance to amorphization, from being readily amorphizable at room temperature, to those that do not show any loss of crystalline order at very high radiation doses even at cryogenic temperatures (for recent review, see [1]).

The origin of this difference in resistance to amorphization is an exciting scientific challenge, and we have recently attempted to propose that the nature of interatomic forces holds the key to the question of resistance of a complex material to amorphization [1,2]. In this paper, we ask yet a different question, namely what are the surface effects of radiation damage. Seemingly different, this question will nevertheless be shown to be closely related to the physics of resistance to amorphization by radiation damage.

The question of surface effects in radiation damage is particularly relevant for waste forms. The most common way of testing the resistance of a material to amorphization is surface irradiation with energetic ions. However, a waste form will experience the damage in the bulk, and hence one needs to understand what are the surface effects of radiation damage. For example, if the surface tends to recover from the damage more efficiently, then the durability of a waste form, based on the surface irradiation experiments, will be over-estimated.

It is not easy to predict the specific effects of surface in radiation damage. For example, previous computer simulations of radiation damage have found that the presence of the surface promotes the damage buildup,

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2005 Taylor & Francis Group Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020500066825

primarily because it is easier to rupture the surface and obtain several additional types of defects not seen in bulk [3–7]. On the other hand, one may expect to find an increased recovery of the damage due to the presence of the surface from a general argument that surface allows for the increased atomic mobility due to the reduced number of constraints.

In this paper, we perform molecular dynamics (MD) simulations of radiation damage events in the bulk and at the surface in zircon, $ZrSiO_4$. This material has been studied recently in the context of waste encapsulation. Whether or not it will be used in practice, there are many mineral forms of zircon, damaged by natural irradiation, which gives experimentalists the opportunity to immediately study the effects of radiation damage.

We begin by introducing the MD simulation code used to study radiation damage effects. We have undertaken to adapt the previous MD code DL_POLY [8] to handle large systems, and have implemented several essential features in the code specifically to handle the simulations of radiation damage. The description of these changes forms an important part of this paper, especially because this issue of Molecular Simulations is related to the work of the eMinerals project [9], which in this case supported the code development and implementation. This is followed by presenting the results of MD simulation of radiation damage events and discussing surface effects.

2. Development of the DL_POLY MD code

DL_POLY_3 is a novel general-purpose MD simulation package for large systems [10,11][†]. Until its appearance, MD simulations were limited in realism and accuracy of representation of systems and non-equilibrium processes largely due to size-wise CPU time and memory demand, driven by non-efficient parallelisation utilization. In the following sections, we will briefly describe some key concepts and methods incorporated in DL_POLY_3, the blend, of which contributes to the high performance, scalability and numerical stability of the code. We also give details of two specific options essential for non-equilibrium simulations.

2.1. Parallelisation

DL_POLY_3 is based on a very progressive parallelisation strategy, the Domain Decomposition (DD) scheme. Domain Decomposition is a universal strategy adopted in many areas of mathematical modelling. In MD it is generally adapted from the link-cell method [12–14]. It is appropriate for systems, in which the potential cut-off is very short in relation to the size of the system being simulated, and hence has applications in such diverse areas as: polymers, micro-scale hydrodynamics, phase transitions, surfaces, micelles etc. Parallel adaptations of the link-cell method are particularly powerful as they enable extremely large systems to be simulated very cost-effectively.

The serial form of the algorithm is well documented [13]. It suffices here to outline only the basics. According to the basic strategy, the MD cell is divided into sub-cells, with width slightly greater than the radius of the cut-off. A simple N (number of particles)-dependent algorithm assigns each atom to its appropriate sub-cell and a linked list is used to construct a logical chain identifying common cell members. A subsidiary header list identifies the first member of the chain. This allows all the atoms in a cell to be located quickly. The calculation of the forces is treated as a sum of interactions between sub-cells, in the course, of which all pair forces are calculated. Allowance for periodic boundary conditions is easily made. The algorithm performs well on serial machines because it greatly reduces the time spent in locating interacting particles.

Parallel versions of this algorithm are easily constructed [12,14]. The MD cell is divided into geometrically identical regions (domains) and each region is allocated to a node. Such division is only possible for parallelepiped like MD cells. The mapping of the regions on the array of nodes is a non-trivial problem in general, although specific solutions for machines like hypercubes are much easier to obtain. The region on each node is further subdivided into sub-cells as in the serial algorithm. The coordinates of the atoms in sub-cells adjacent to the boundaries of each region are passed on to neighbouring nodes sharing the same boundaries (exchange of boundary data). After which each node may proceed to calculate all pair forces in its region independently. No further communication between the nodes is necessary until after the equations of motion have been integrated: particles, which have moved out of their node region must be reallocated to a new node.

Regarding the exchange of boundary data, it is crucial that data can only be passed in complementary directions (north-south, east-west, up-down in 3D) at any given instant and in between exchanges, the exchanged data must be re-sorted before the next exchange. This is necessary to ensure the corner and edge sub-cell data are correctly exchanged between regions sharing edges and corners, rather than faces.

Although the DD algorithm is specifically designed for systems with short-range forces, it can also be used for systems with Coulombic forces. Work has been done [15] to produce a new DD adaptation of the Smoothed Particle Mesh Ewald Method (SPME) as devised by Essman *et al.* [16] for calculating long-range forces in molecular simulations. In this adaptation two strategies are employed to optimise the traditional Ewald sum. The first is to calculate the (short ranged) real space contributions to the sum using the DD method as outlined above. The second

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[†] See http://www.cse.clrc.ac.uk/msi/software/DL_POLY/index.shtml

is to use a fine-grained mesh in reciprocal space and replace the Gaussian charges by finite charges on mesh points. The mesh permits the use of 3D fast fourier transforms (3D FFTs) [17]. In DL_POLY_3 we have used the daresbury advanced fourier transform (DAFT) [17], which is a novel, fully distributed, parallel implementation of the 3D FFT that fits well with the DD concept.

2.2. *Integration algorithms*

DL_POLY_3 adopts two methods for numerical integration of Newton's equations of motion, that excel in their simplicity of implementation, numerical stability, low memory requirement and satisfactory accuracy; leapfrog Verlet (LFV) [10] and velocity Verlet (VV) [11]. Although VV integration is somewhat slower than the LFV one, it is the default option in DL_POLY_3 since it offers better numerical stability and time-reversible dynamics. These are very important in case of strongly non-equilibrium simulations.

2.3. *Features in aid of non-equilibrium dynamics*

There is a wide variety of simulation control features available in [11]. However, there are two, (i) variable time-step and (ii) density variation bias, that are specifically designed to address the simulation of systems away from equilibrium.

The variable time-step a key feature for simulations of non-equilibrium processes. It is used to ensure that the fastest particle in an MD system travels less than $R_{\max}$ (0.11 Å default) during a time-step of the simulation so that the potential fields of the fastest particle and its neighbouring environment are sampled often enough distance-wise and the dynamics is physically correct. If after a given time-step a particle has exceeded this limit the simulation time-step is decreased by a factor of two and the simulation is continued from the point before this break happened. Similarly, if the fastest particle in the system has travelled less than $R_{\min}$ (0.04 Å default) then the simulation time-step is increased by a factor of two and the simulation is continued from the point before this break happened. In this way, the simulation speeds up time-wise saving on CPU time while the system goes more towards equilibrium. The default values of $R_{\max}$ and $R_{\min}$ can optionally be altered by the user, but in order for the variable time-step algorithm to work correctly the new values must be have a ratio $R_{\max}/R_{\min} > 2.5$.

The density variation bias feature biases the global density of the MD cell by user provided percentage so that larger particle arrays are allocated when the simulation cell is decomposed into domains. This feature is used complementary with the variable time-step, usually as a last resort, in cases when the dynamics is extremely non-equilibrium or drives the system to states where the local density varies much with respect to the global density. A particularly good example of this situation is the simulation of radiation damage events, in which a high-energy recoil creates the regions of depleted and densified matter.

3. MD results of radiation damage events and discussion

The routine set of details in this simulation is as follows. We use the interatomic potential for zircon from [18], which gives an excellent agreement with both structural and elastic properties of zircon. At short distances, this potential is joined to the zbl [19] strong repulsive potential. In this work we study the damage produced by 30 keV U recoil atom. The recoil was implanted after the initial structure was relaxed at room temperature, and we use the constant energy ensemble to propagate the damage. The surface was simulated by connecting the atoms to the vacuum along the z-direction, achieved by simply doubling the length of the unit cell in z-direction and leaving atomic coordinates unchanged. The damage is simulated for about 20 ps. The structures contained 508032 atoms. The simulations were performed on 32 nodes of the Cambridge high performance computing facility (HPCF).

In figure 1 we show atoms that form the damage in the bulk and at the surface. There are several ways to define displaced atoms, and here an atom is defined displaced if it moves to a distance larger than 1.6 Å, the length of Si—O bond. We find that the number of displaced atoms, defined in this way, is 3226 in the bulk and 3270 at the surface, making the difference between them of about 1%. A detailed examination of the overall structure reveals little 'recrystallization', hence figure 1 shows true final damage. Hence one state that no appreciable difference is seen between the bulk and surface in terms of the amount of damage produced.

As far as the qualitative difference between the "radiation cascades" shown in figure 1, we can not be definitive at this point. The damage at the surface looks somewhat more dispersed than in the bulk, but the difference between the two cascades is well within the differences between two different cascades in the bulk we have observed previously [18,20–23]. In the bulk, this difference originated from the different trajectories of the damage in the phase space caused by different recoil velocities. In the present case, the difference in damage shape in the bulk and at the surface may be related to a reconstruction of atoms near the surface (before recoil was implanted), due to surface relaxation. This means that recoil propagated in a different environment than in the bulk and hence the damage propagated on a different phase trajectory. More statistical sampling is needed to reliably conclude whether there is a consistent difference between the damage in the bulk and at the surface in terms of shape.

In both simulations of the damage in the bulk and at the surface, we find that the damaged structure is stabilized by the presence of disordered Si—O—Si chains. This is consistent with our previous modelling and experimental

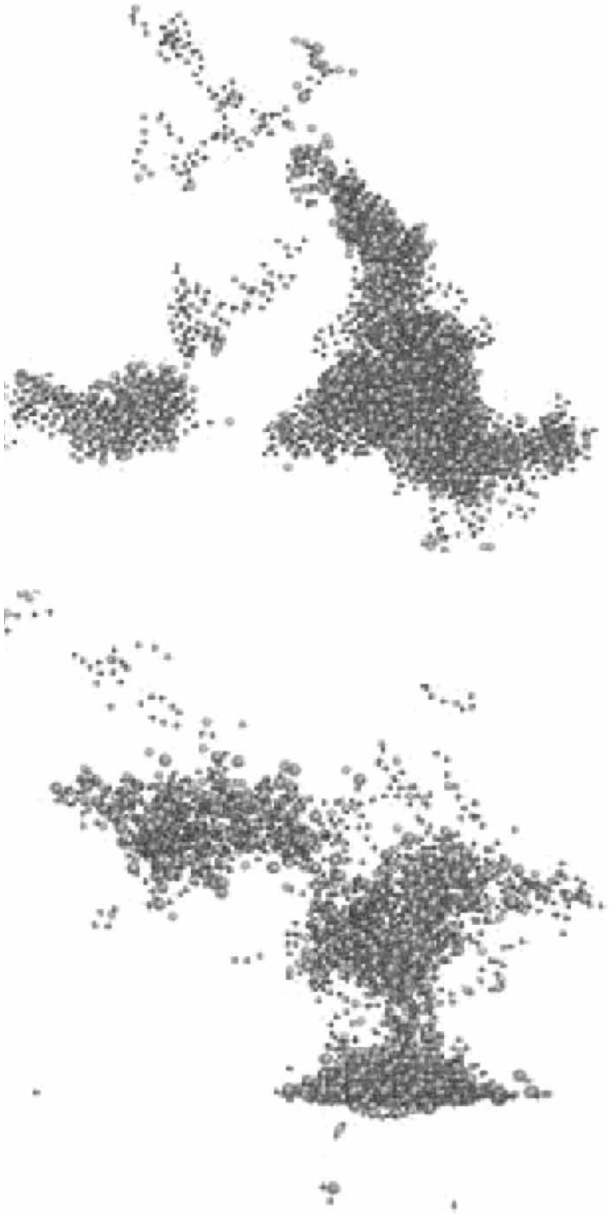

Figure 1. Displaced atoms in zircon structure damaged by 30 keV event in the bulk (top) and at the surface (bottom). The initial direction of the recoil is up and slightly to the left in both pictures.

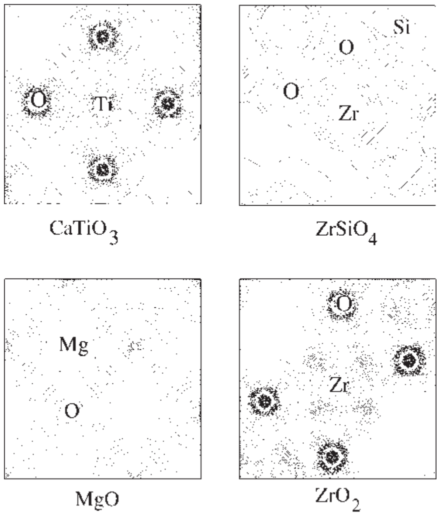

Figure 2. Contour plots of deformation density $\delta\rho$, calculated for radiation amorphizable materials ($CaTiO_3$ perovskite and $ZrSiO_4$ in the top), and highly resistant systems (MgO and ZrO_2, in the bottom). The plots are drawn for the cation-anion planes, between − 0.25 and 0.25 e, and each line corresponds to a step of 0.006 e (we have checked that the shape of the electronic density is not altered by changing the numerical values of the contours). Dashed and solid lines correspond to negative and positive values, respectively). Note that the electronic charge around the Ti—O and Si—O bonds is directional. In contrast to this covalent character of bonding in the top plots, no directionality is seen in $\delta\rho$ in the highly ionic MgO and ZrO_2 (there is certain deformation of the electronic density of Zr atom, however it is not in the direction of neighbouring O atoms).

results [20,21,24]. In order for the damaged structure to regain coherence with the crystalline lattice, this polymerised silica phase needs to be re-arranged, with involves overcoming high energy barriers due to the need to break bonds. It appears that the stability of this polymerised phase stabilizes the damage as efficiently at the surface, as it does in the bulk [20,21]. In other words, whatever the difference between the damage at the surface and in the bulk may be, it is suppressed by the formation of this stable polymerised phase.

It is interesting to take this point further and to relate the formation of covalent polymerised phase to a general question of what makes material amorphizable by radiation damage. We have recently suggested that the nature of interatomic forces is the relevant physical parameter, and proposed that a material is amorphizable by radiation damage if its chemistry allows it to form a covalent network. On a more detailed level, we proposed that the resistance to amorphization is defined by the competition between the long-range (ionic) and short-range (covalent) forces. We have demonstrated how this theory works for more than 100 different materials [1].

The nature of interatomic forces can be reliably deduced by inspecting the electronic density maps. In figure 2 we show the electronic density maps for readily amorphizable zircon, perovskite, $CaTiO_3$, together with highly resistant MgO and ZrO_2. These maps have been calculated using SIESTA density functional method. Details of the method and calculation have been presented elsewhere [2,25]. What is evident in figure 2 is the strong covalency of bonding in readily amorphizable zircon and perovskite, and ionicity in highly resistant MgO and ZrO_2. This is seen as the directionality of the electronic density and its significant value in the plane perpendicular to the line connecting the centres of two atoms, and its absence in the latter case. The analysis of Mulliken population shows the significant value of overlap between Si and O atoms, as well as between Ti and O atoms, confirming substantial covalency of bonding. On the other hand, overlap Mulliken populations are considerably smaller between Mg—O, as well as between Zr—O atoms. These points, as well as other measures of ionicity/covalency are discussed in more detail elsewhere [26].

Because the amorphizability is directly related to the nature of interatomic forces as discussed above, figure 2 demonstrates that zircon has the ability to form stable covalent alternative network, which stabilizes the damaged state. The stability of this network drives amorphization in both bulk zircon and at the surface, and reduces the possibly existing difference of the damage in the bulk and at the surface. Hence the general scientific conclusion of this work echoes the introduction: generally, it is not easy to predict what are the surface effects in radiation damage. If a material is readily amorphizable like zircon, the strong driving force for damage stabilization may reduce the possible difference between the damage at the surface and in the bulk. This should hold true for readily amorphizable materials like silicate and titanate oxides (see [1] for review). In this case the prediction of the structural changes of a waste form due to irradiation, based on the surface bombardment results, is probably reasonably justified. However, if a material is resistant to amorphization, one can speculate that effects of the surface may play a more visible role.

4. Summary

We have presented the modifications made to the MD code aimed at handling large systems required in radiation damage simulations, and discussed the modifications that we implemented to handle the simulations of radiation damage more efficiently. These developments have allowed us to address a question, important both scientifically and practically, of what is the possible difference between the damage in the bulk and at the surface. We proposed that in the case of readily amorphizable materials like zircon, a possible difference between the damage in the bulk and at the surface is suppressed due to the formation of the stable polymerised covalent network that drives amorphization in both cases. Larger statistical sampling of events may help to answer whether there is a consistent difference of the damage in the bulk and at the surface in terms of its shape and dispersion.

Acknowledgements

We are grateful to NERC, EPSRC, CMI and BNFL for support. KT is grateful to Darwin College, Cambridge for support and acknowledges useful discussions with K Nordlund. Simulations were performed on Cambridge HPCF.

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