REPLY

Reply to comment on 'Large swelling and percolation in irradiated zircon'

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Abstract
The authors of the comment (Corrales *et al* 2003 *J. Phys.: Condens. Matter* **15**
6447) on our paper (Trachenko *et al* 2003 *J. Phys.: Condens. Matter* **15** L1)
suggested that different simulation conditions *could* result in different results,
including a wider spread of the damage. To show that this is not the case, we have
repeated the simulations, exactly as proposed by the authors of the comment,
using new potentials with ZBL short-range terms and with potentials proposed
by the authors of the comment (Park *et al* 2001 *Phys. Rev.* B **64** 174108).
We find that, contrary to the suggestions of the authors of the comment, the
damage is well localized in the simulation box and is generally similar to that
found in the original paper. We find that, similar to our previous results, the
damage has a depleted region in the centre and is more dense at the boundaries.
We show that the suggestions of the authors of the comment, that the damage
should be more spread in our simulations, probably originate from unphysical
results derived in their previous simulation work.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently there have been a number of published simulation studies of the formation of structural
damage in zircon and other materials due to the motion of recoil atoms following radioactive
alpha decay. Many of these have been carried out with recoil energies that are much lower
than the experimental recoil energies. Among the studies of low-energy recoil processes on
zircon are the studies of Park *et al* [3], with recoil energies of 0.2 keV, Crocombette and
Ghaleb [4, 5] with recoil energies between 2 and 5 keV, and our own earlier work [6], with an
energy of 2 keV. By contrast, the recoil energy of a decaying Pu atom embedded in the zircon
structure is 70 keV. The reasons for the use of low energies in these simulations may include
the fact that higher energies require the use of simulation samples that are too big for the
available computing resources, or difficulties that the simulation algorithms may encounter
handling atoms with widely different kinetic energies. We have now managed to perform

simulations of alpha decay processes in zircon and perovskite at realistically high energies, either 30 or 70 keV (the former being lower to account approximately for electron energy loss mechanisms) [2, 7]. From this work we have come to realize that there is a significant difference between the outcomes of simulations using low and high energies, which is why we use the phrase 'realistic' when describing the use of high energies in [2]. Our feeling now, based on the comparison between the different simulations, is that there is hardly any significant information or insight to be gained by studying low-energy events. Thus we now need to face the issue of how best to make progress in the simulation of realistically high recoil energies. The authors of [1] are pessimistic that progress can be made. We will argue here that such pessimism is wrong.

The authors of [1] have made a number of remarks about our simulations of radiation damage in zircon [2]. The main purpose of the work in [2] was to propose a possible mechanism for the 20% volume swelling found in highly damaged samples of zircon. The central idea of the model was that the volume expansion can be seen as arising from a percolation of damaged regions, with a large non-elastic quadratic behaviour at high defect concentration [2]. On the microscopic level, the model is based on the non-homogeneous distribution of density in the damaged structure, which causes deflection of the subsequent damage due to the different number of scattering centres on both sides. The existence of the non-homogeneous density distribution is now beyond doubt and has been shown to exist in recent low-angle x-ray scattering experiments (SAXS) [8]. The SAXS experiments have confirmed the existence of depleted regions on the nanoscale, as we predicted in our earlier simulations [7]. It should be understood that, in our work on the percolation model for the volume expansion [2], the heterogeneity of the damaged structure could merely have been assumed, without needing any backing from simulations. In fact, this was how we developed the argument in [2] and the simulations were used only to provide a *rough* confirmation of the one fitted parameter in the model (they could only provide 'rough' rather than 'exact' confirmation because it was too difficult to perform enough simulations to get quantitative statistical accuracy). We note that the authors of [1] make no comment on the percolation model *per se*. All their comments are aimed at questioning the validity of our molecular dynamics simulations.

In this reply we demonstrate that the results of the simulations of high-energy radiation damage in zircon are not strongly dependent on the details of the interatomic potentials, and that there are no problems with the sizes of the simulations we run or our methodology. What surprises us is that there are, in fact, more significant faults with some of the earlier work from the authors of the comment [1]. For example, we show in this reply that the model of zircon used in the work of Corrales and Weber [3] is inherently unstable in simulations, which in part is likely to be due to an elastic instability in their model which gives a negative value of the elastic constant c_{66} (for some reason this value is not reported in their own publication).

2. Interatomic potentials

2.1. General considerations

The issue of interatomic potentials can be rather more subjective than one would hope. Ideally a good interatomic potential model will allow a simulation to reproduce a wide range of structural, thermodynamic and physical properties of the equilibrium crystal phase. In many cases, it may be assumed that these are the key factors. However, in simulations of radiation damage, the issue of how good a model will reproduce equilibrium properties is rather less important than some other factors, because the important processes in these simulations probe the behaviour of the material at conditions that are very far away from equilibrium. Tests of crystal structure and elasticity probe the behaviour of a model against infinitesimal atomic

displacements within a local potential energy minimum. These have some impact on the behaviour of the collision process around the perimeter of the damaged region, but at the heart of the cascade the atoms are in a high-temperature fluid state, where the primary interatomic interactions will mainly have ballistic rather than bonding characteristics. A suitable model of the interatomic potential energy has to properly model this state and the way that the structure relaxes as the system cools from this state. We note that one of the authors of the comment [1] has performed simulations of radiation damage in zircon [4, 5] with an interatomic potential model that is 25% too soft, without any apparent concern.

In this sense, one can identify three key features for any interatomic potential energy model. The *first* is that the model should simulate the energies of atoms with very short contact distances, which are much shorter than those found in equilibrium structures. Many authors have suggested the use of ZBL short-range potentials [9]: we used a more ad hoc method to avoid problems with the $-r^{-6}$ potentials in our earlier work [2, 7], but below we will show that there is little difference in the sizes of the damaged regions when using either our *ad hoc* method or the ZBL potentials. To some extent there is some insensitivity to the exact details of the short-range ballistic interactions, particularly for glancing incidence, as outlined in appendix A.

The *second* feature of an interatomic potential energy model for simulation of radiation damage is that it should properly reproduce the structural stability of atomic arrangements. This is so that the simulation reproduces the correct behaviour of the atoms as the simulation relaxes following the initial high-energy impulse of the recoil atom. It is in this sense where the assessment of a potential energy model can be subjective. For example, one of the authors of the comment [1, 10] remarked that his own models gave a lower energy for $ZrSiO_4$ in the scheelite structure than in the zircon structure (by 0.6 eV/formula unit). We find that the potential energy model of the authors of [1, 3] suffers from the same deficiency (by 0.875 eV/formula unit; we show below that this model has even worse deficiencies), as does that of Meis and Gale [11] (by 0.8 eV/formula unit). Crocombette and Ghaleb [10] made the subjective judgement that this does not matter. Experimentally it is known that the regions of zircon damaged through radiation events contain a high degree of polymerization of SiO_4 polyhedra [12]. A good model for simulations of radiation damage in zircon needs to be able to properly reproduce this behaviour.

The *third* key feature is that the model should be stable in large scale molecular dynamics simulations under the operation of normal thermal motion, even without the effects of radiation damage. Large simulations are less constrained by the existence of the periodic boundary conditions than small simulations; in particular, small simulations have only a restricted range of wavevectors and do not allow for the existence of long wavelength fluctuations. Hence a model that is unstable in large simulations can appear to be stable when only tested in small samples. We always test for structural stability in large simulations before introducing a radioactive decay event. In this regard it should be noted that the interatomic potential model used by the authors of [1, 3], is structurally unstable in large scale molecular dynamics simulations, even under the effects of a mere 300 K temperature. This may in part be associated with the failure of the model to reproduce the relative energies of the zircon structure against the scheelite structure; it is likely that it is also associated with the inherent shear instability in their model, as discussed below. Figure 1 shows a slice of a simulation produced using the model of [3]. It can be seen that there is a huge number of spontaneous defects and shear deformations forming at an early stage in the simulation. We show below that the shear deformations arise from an inherent elastic instability in the model.

What is clear from this discussion is that there are *many* criteria against which a model interatomic potential for simulations of radiation damage in ceramics can be assessed, and not
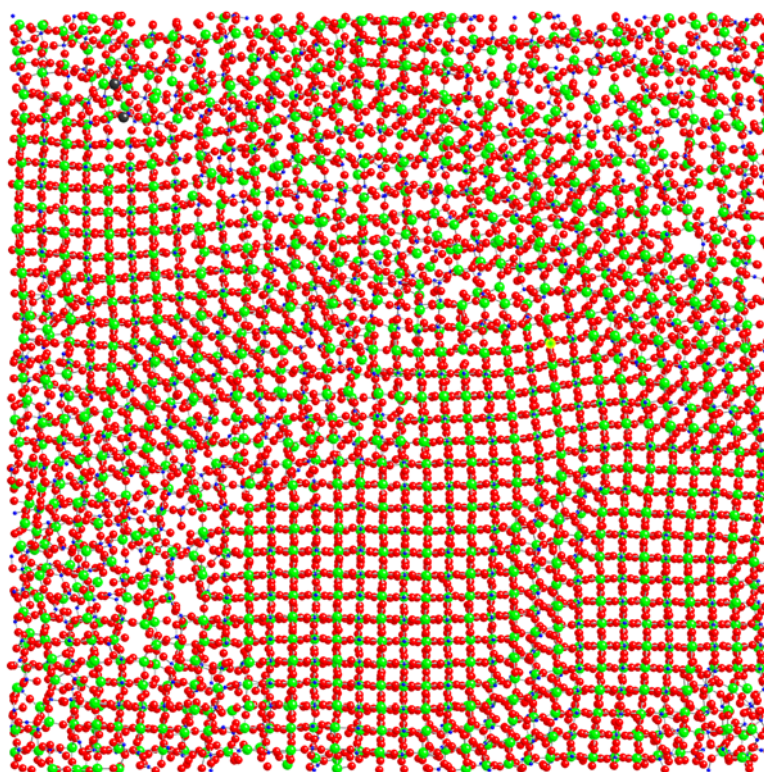
Figure 1. Results of a standard molecular dynamics simulation performed using the model of Park *et al* [3] at 300 K, following a standard equilibration and before the simulation of an alpha decay process. The slice of the configuration shows the large extent of structural disorder introduced by the thermal motions.

all criteria can be met simultaneously. Our choice is for a model that is stable against thermal fluctuations, and which has lower energy than other possible polymorphs. One could argue that to get equilibrium thermodynamic and physical properties correct is more important, but we are not so minded.

Although the model we have used previously [2, 6, 7] is stable and captures the experimental behaviour associated with the radiation damage remarkably well (see the last section), we have now developed a new model, which we will discuss in the following section. This model is designed to properly reproduce the equilibrium properties and to use the ZBL short-range interactions as advocated by the authors of [1], thereby meeting all the criticisms of [1]. Our motivation for this is to demonstrate that the model of our earlier work [2, 6, 7] gives results that are not significantly different from those with a model free from some of the criticisms of [1], and to demonstrate that our sample sizes are adequate for this work. We similarly use the model of the authors of the comment [1, 3], in spite of its inherent instabilities, to demonstrate that the same picture emerges, but with the production of many thermal defects it is less straightforward to separate out the true radiation damage.

2.2. A new interatomic model

We have developed a new model interatomic potential for $ZrSiO_4$, consisting of a new component to describe interactions over equilibrium distances coupled with the ZBL model for

Table 1. Comparison of the predictions of the equilibrium properties of the zircon crystal calculated using our new model ('Calc.') with experimental data ('Exp.'). Δ is the percentage difference between the experiment and calculation. We also show the results of the calculations of [3], showing the level of agreement obtained by the authors of the comment [1]. Our new model is not significantly any worse than that of [3] for any of the parameters; on the other hand, the two major discrepancies of the model of [3] are that the c/a ratio is the wrong side of unity and the value of c_{66} indicates an inherent elastic instability in the model.

Property	Exp.	Calc.	Δ (%)	[3]	Δ (%)
a (Å)	6.604	6.660	+0.85	6.342	−4.0
c (Å)	5.979	5.907	−1.2	6.511	+8.9
Si–O (Å)	1.623	1.58	−2.6	1.632	+0.6
Zr–O1 (Å)	2.128	2.158	+1.4	2.059	−3.2
Zr–O2 (Å)	2.267	2.311	+1.9	2.422	+6.8
O–Si–O (1)	97°	102°	+5	92°	−5
O–Si–O (2)	116°	113°	−2.5	119	+2.5
Bulk modulus (GPa)	225.2	220.0	−2.4	259	+15
c_{11} (GPa)	424	428	+0.9	505	+19
c_{33} (GPa)	490	523	+6.7	522	+6.5
c_{44} (GPa)	114	109	−4.4	119	+4.4
c_{66} (GPa)	49	31	−37	−0.2	−100.5
c_{12} (GPa)	70	46	−34	72	+3
c_{13} (GPa)	149	148	−0.7	172	+15
C_V (300 K) (J mol^{-1} K^{-1})	98.6	93.7	−5	91.9	−7
S (300 K) (J mol^{-1} K^{-1})	84.4	75.7	−10	80.9	−4

short-range interactions. Our starting point was the model developed by Mittal *et al* [13] based on their measurements of phonon dispersion curves. This model is not ideal for molecular dynamics simulations, partly because it contains a shell model for the oxygen atom and we therefore re-tuned the model without including the oxygen polarizability.

For the Zr–O potential we used a Born–Mayer function:

$$\phi(r) = A \exp(-r/\rho). \tag{1}$$

For the O–O interaction we used a Buckingham potential:

$$\phi(r) = A \exp(-r/\rho) - Cr^{-6}. \tag{2}$$

We used a Morse function for the Si–O interaction, without switching off the Coulomb attraction between the bonded atoms (which was found to be significant in the fitting procedure):

$$\phi(r) = D(\exp(-2\alpha[r - r_0]) - 2\exp(\alpha[r - r_0])). \tag{3}$$

We included Coulomb interactions and allowed the ionic charges to vary in the fitting procedure. All calculations were performed using the GULP code [14].

The model parameters were adjusted by fitting against the crystal structure, elastic constants and some phonon frequencies, keeping the value of the O–O C parameter fixed at a value of 100 eV Å^{-6}, and the values of ρ for the Zr–O and O–O interactions set at the values 0.317 and 0.2617 Å (these values had previously been determined by Mittal *et al* [13]). The best set of parameters deduced by comparing simulation with experiment gave charges for the Si, Zr and O ions of +1.356$|e|$, +3.428$|e|$ and −1.196$|e|$, respectively ($|e|$ is the magnitude of the electronic charge), values of A of 1477 and 9245 eV for the Zr–O and O–O ion pairs, respectively, and values of D and α of 1.252 eV and 1.252 Å, respectively, for the Si–O atom pairs. The comparison of the predictions of the new model with experimental data are given in table 1. It can be seen that the new model gives excellent agreement with experimental data

for the structural and elastic properties. In the same table we also compare the predictions of the model used by the authors of the comment [1], as reported in [3]. It can be seen that our new model gives generally better agreement with experiment; we comment on two particular problems with the model of [3] below. We also note that our model gives the energy of the zircon structure that is 0.554 eV per formula unit *lower* than that of the scheelite structure, in contrast to the models used by the authors of the comment [1], as discussed above.

For the simulation runs, we mix the short-range potentials with the ZBL functions [9]:

$$\phi_{\text{ZBL}}(r) = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r} \sum_{i=1}^{4} a_i \exp(-b_i r/r') \tag{4}$$

where the values of coefficients a_i and b_i are obtained from [9]:

$$r' = \frac{0.885\,34 a_{\text{B}}}{\sqrt{Z_1^{2/3} + Z_2^{2/3}}} \tag{5}$$

and a_{B} is the Bohr radius with value 0.529 Å. The ZBL potentials and the short-range interactions are mixed with a switching function $f(r)$ to give

$$\phi_{\text{mix}}(r) = f(r)\phi_{\text{ZBL}}(r) + (1 - f(r))\phi(r) \tag{6}$$

with

$$f(r) = \begin{cases} 1 - \exp(-(r_{\text{m}} - r)/\xi)/2 & r < r_{\text{m}} \\ \exp(-(r - r_{\text{m}})/\xi)/2 & r > r_{\text{m}}. \end{cases} \tag{7}$$

Values of both r_{m} and ξ were adjusted for each atom pair in order to produce the smoothest mix, ensuring that $r_{\text{m}} + \xi$ always lay below the equilibrium interatomic distance in the crystal structure.

2.3. New cascade simulations

We have used this model in new simulations of the radiation damage. A sample image of a cascade is shown in figure 2. This simulation was performed using the DL_POLY code [15, 16]. The sample contained 192 000 atoms. Many of the details are as reported in an earlier paper [7]. In this case we used a recoil uranium atom of energy 30 keV, which interacts with other atoms through appropriate ZBL potentials.

The cascade is shown in figure 2. In this case, though, we show the entire simulation, whereas in our previous papers [2, 7] we have only shown the damaged regions. The purpose of now showing the whole simulation is to demonstrate that the extent of the cascade does not propagate beyond the limitations of the periodic boundary conditions. The size of the damaged region can be characterized in two ways. The *first* is to estimate the mean radius of the damaged region. The event shown in figure 2 is around 5 nm, similar to that produced in our earlier work [2, 7]. The *second* method of characterizing the scale of the damage is to calculate the final displacement of the recoil atom. For our new potential this is 8.5 nm, which is the same as we obtained with our original potential. Of course, these numbers are slightly dependent on the direction of the recoil, and the accuracy of the mean value is limited by the fact that we cannot perform enough simulations to compute a proper statistical average.

From these simulations, and subsequent analysis of the damaged regions, we conclude that our new model gives results for the damage that are not significantly different from our original work, which has been criticized in the comment [1]. Yet the new model should now be free of all the criticisms that were levelled at our original model. We would argue on this basis that the fine details of the short-range interactions are not significant in the ballistic limit
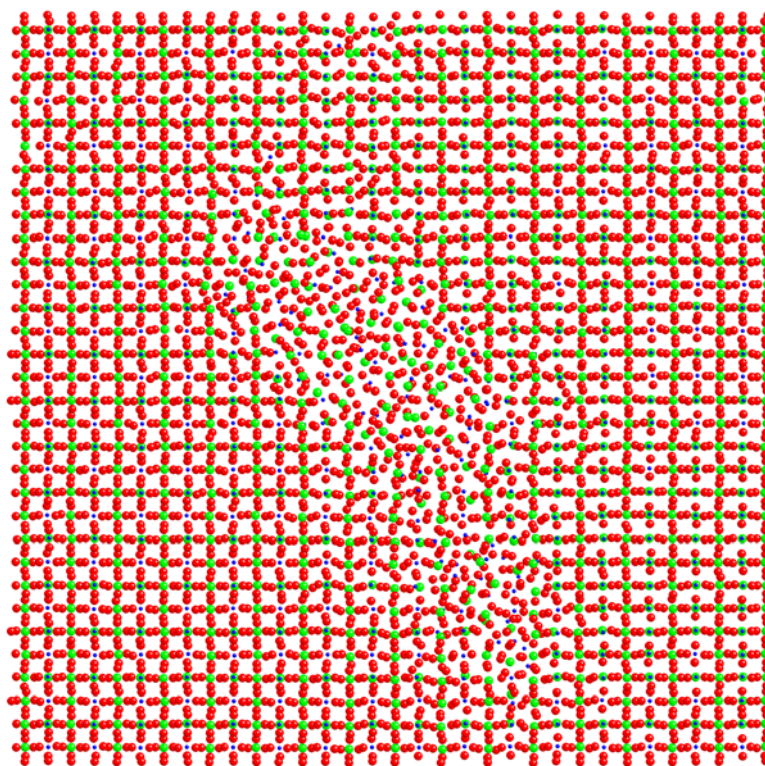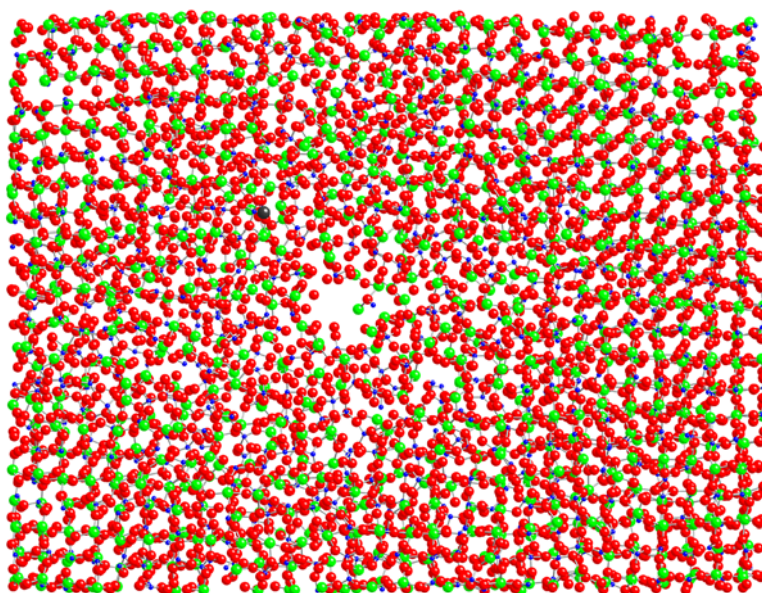
Figure 2. Results of a cascade simulation performed using our new model, viewed from above and showing the entire width of the simulation sample. It is clear that the cascade is completely contained within the sample of 192 000 atoms.

found in the fluid state around the initial recoil. Similarly, the effects of elasticity are also not significant in the damage caused by the recoil atom.

We have also carried out some large-scale simulations using the model advocated by the authors of [1] as reported in Park *et al* [3], even though we have shown above that this model is unstable in large-scale simulations. Although there is little scientific advantage in using unstable models, it is important to benchmark our models against the model advocated by the authors of [1], namely that described in [3]. We show the results of one cascade simulation using the model of [3] in figure 3. We have performed a number of other simulations, including a series of runs with varying sample sizes, and all give similar behaviour. It has to be appreciated that part of the sample that is not directly in the cascade region appears damaged because of the inherent instabilities of the simulation model against shear and defect formations. The rough dimension of the damage due to the cascade is 6 nm, which is slightly larger than with either of our models, but this difference can easily be accounted for by the enhanced ease of defect formation in the model of [3] and because the thermal defects make it less straightforward to define the edge of the damaged region. In this model the displacement of the recoil atom is 11 nm, slightly larger than in either of our two models, but again easily accounted for by the inherent instability of the model.

What the comparison between the three runs shows is that the size of the cascades is not as extensive as assumed by the authors of the comment [1]. This point is particularly relevant for the discussion in the next section.

Figure 3. Results of a cascade simulation performed using the model of Park *et al* [3]. This shows a slice of the configuration. The boundary structure is not included in order to assist visual separation of the damage to the structure caused by the recoil atom from damage to the structure that arises from the instability of the model against thermal fluctuations, as discussed in the text. The key point to observe is the low-density code surrounded by the higher-density shell.

2.4. Some general comments on the issue of interatomic potentials in reply to remarks made in the comment [1]

We append to this section some specific remarks on points made in [1]. The issue of the agreement with experimental data will be discussed in the last section and the issue of agreement with thermodynamic data is discussed in appendix B.

 (i) The authors of [1] spend some time discussing the factor of $1/2$ in the three-body term used to describe the bending of the O–Si–O bond. The initial paper from which this potential was taken [17] did not include this factor, but our work, in common with all other studies that use this potential, included the factor of $1/2$ without changing the parameter value. This is because the absence of the factor of $1/2$ in [17] is a mistake and the parameter reported there does take account of the factor of $1/2$. Hence we were justified in our treatment of this function and its parameters. There is a point to be made about the sociology of the workings of the scientific community; a simple contact with one of the authors of [17] would have clarified the situation!

 (ii) For our molecular dynamics simulations, we used a full Ewald summation with truncations set by the DL_POLY code within a prescribed accuracy chosen by the user. There were no artificial cut-offs as implied in the comment [1].

(iii) The main concern expressed in the comment [1] about the model interatomic potential used in our original work is that the short-range interactions are too stiff, resulting in a bulk modulus that is too large by a factor of 2. The question is whether or not this is significant (we note above that the authors of the comment do not consider a significant underestimate of the bulk modulus to be important). We would argue that an overstiff potential model would, to first order, correspond to running a simulation at a lower temperature; similarly

a soft model would correspond to running at a higher temperature. This can be seen in the calculations of the heat capacity given in appendix B. It is seen there that the additional stiffness of the potential energy functions corresponds to a temperature renormalization of around 20%. Thus we would not expect that the enhanced stiffness of our model to have any significant effect on the simulation of radiation damage.

(iv) We would have hoped that the authors of the comment [1] would have previously proposed models that were free from the sort of criticisms they were making of our own models. We noted above that their models used in [3–5] give the wrong relative energies of the zircon and scheelite phases of $ZrSiO_4$, and that the model of Crocombette and Ghaleb [4, 5] is elastically soft compared to the experimental data. We have also remarked that the model of the main authors, Coralles and Weber [3], is unstable in the molecular dynamics simulations. In part this may be traced to a shear instability inherent in their model. In table 1 we show the elastic constants calculated using the model of [3]. In most cases there is good agreement with experiment. The one exception is for c_{66}. The model of [3] gives a small negative value for this elastic constant, which implies a shear instability in the $x-y$ plane. This instability can be seen in our simulations using this model, figure 1. We remark that our calculations of the other elastic constants from this model are in close agreement with the calculated values reported in [3]; inexplicably the value of c_{66} is not reported in [3], even though the information about the full elastic constant tensor would have been given in the output of the calculation. We also remark that the c/a ratio, which has an experimental value of 0.905, and is calculated in our previous and new models to have values of 0.935 and 0.890, respectively, is calculated to have a value of 1.027 in the model of [3]. We would have expected any reasonable model for zircon to give a calculated value of c/a to be the correct side of unity! We also calculated the elastic constant tensor using the model of another of the authors of the comment [1, 11]. In this case the calculated value of c_{66} is as low as 25% of the experimental value, which is stable at least, but with a clear softness against the corresponding strain. The values of four of the elastic constants are given in [11], but again the value of c_{66} is not among them.

3. Simulation cell sizes and extent of cascades

It is argued in [1] that the simulations we have reported are too small for the recoil energy, and by extension it is argued that our results may be influenced by finite-size effects. We have three remarks with respect to the simulations we have performed. *First*, we experimented with several different sizes and found that the resultant cascade damage was not noticeably affected by the sample size. We reported this point in [7]. To our minds this is a clear demonstration that our results are not affected by sample size. *Second*, as documented in the previous section, and seen in figure 2, we have shown that the size of the cascade is only weakly dependent on the details of the short-range potentials, being mostly determined by the energy of the recoil atoms. *Third*, as documented in section 5 below, the size of the cascade we generate in our models is fully consistent with a wide range of experimental results. The authors of the comment [1] acknowledge this point, but attempt (unreasonably in our view) to dismiss the significance of the agreement between the simulation results and the experimental data. Since we know the size of the damaged regions in the experiments, and we know that our simulation samples are substantially larger than the experimentally determined sizes of the cascade-induced damaged regions, we believe that it cannot be argued that our simulation samples are too small.

There are two main thrusts to the argument in the comment [1] with respect to the size of the simulations we use, and neither have reference to experimental data or to detailed tests. The *first* is with respect to the rules of thumb developed for simulations of irradiation processes

in metals. We see little point in citing simulations of metals in preference to the comparison with experimental data or detailed checks on internal consistency. In particular, the bonding characteristics of metals and silicates are very different, with the latter showing a much wider range in the strength of bonding (e.g. Si–O bonds) and having directional covalent bonds that are absent in metals. Indeed, one of the authors of the comment himself has noted that the damage produced in a ceramic, such as zircon, is qualitatively different to that produced in a metal [4]. The *second* thrust of the argument of [1] relies on the application of SRIM calculations, which may only give a rough guide because they do not include any information about the structural information or local bonding. We note that the issue of bonding is considered to be important by the authors of [1] elsewhere in their comment. Neither of these arguments stand up against the internal consistency checks and the tests against experiment which are documented in our papers on our simulations [2, 7]; indeed, we are amazed that the authors of the comment [1] should pay such scant disregard to the importance that simulations should agree with experimental data!

It is clear that the authors of [1] have no substantial evidence against the validation of the sample sizes used in our work, nor any evidence to refute the tests we carried out which showed that our samples are sufficiently large to be unaffected by their finite sizes. We make some additional remarks about the SRIM calculations in appendix B.

4. Simulation methods and temperature scaling

The comment [1] contains a section discussing the way we dealt with the dissipation of the thermal energy deposited into the simulation by the recoil atom, but the comment makes a number of incorrect assumptions. We used the standard Nosé–Hoover constant-temperature algorithm rather than the *ad hoc* temperature rescaling method assumed by the authors. This is an appropriate algorithm because formally it represents the statistical mechanical coupling of the system to a heat bath held at a preset temperature. We note that it has been suggested that this is likely to be the only way to simulate electron energy loss effects [18]. We used time constants between 1 and 3 ps and found that the exact value had no noticeable effect on the cascade simulation. It should be noted that the time constant we have chosen is longer than the basic timescale of the cascade—the thermal spike lasts for around 0.2–0.3 ps—and the polymerization around the edges of the damaged region form immediately after this time interval. Thus, we are not taking energy out of the cascade region until well after there has been significant dissipation into the rest of the sample. In our opinion, this is rather more realistic than to have an absorbing outer layer of atoms, as advocated by the authors of the comment [1], not least because it leads to a true thermodynamic equilibrium consistent with a canonical ensemble. We do not believe that it has been demonstrated that there is any problem with this approach.

We also investigated the use of constant energy (NVE) ensembles and found that the samples we are using are large enough to absorb the energy sufficiently not to change the basic behaviour of the cascade. However, we only ran the NVE simulations to investigate whether there are differences, and all our reported results were obtained with the Nosé–Hoover constant-temperature ensembles. The key point is that, with large samples, the problem of energy dissipation is much less of a problem than for the small samples of, for example, [3–5].

We also used constant stress algorithms in conjunction with the Nosé–Hoover constant-temperature algorithm in order to allow for the relaxation of shear and volume stresses. The time constant for the strain relaxation in the algorithm was of the same size as the time constant for the Nosé–Hoover algorithm.

The authors of the comment mention the importance of allowing the sample to equilibrate between cascade events. We typically allowed several tens of ps between events, certainly long

enough for us to be able to check via inspections of animations produced from the simulation trajectories that all motions larger than thermal motions had ceased.

It was also noted that the use of periodic boundaries can lead to artificial effects through waves propagating through the boundaries and impacting on the replicated image of the initial source of the waves. This is a particular problem for sound waves, where the group velocity is equal to the phase velocity. The recurrence time, τ, for our simulation sample of zircon, with a speed of sound of $v = 6900$ m s^{-1} (estimated from the bulk modulus and density via $v^2 = B/\rho$) and linear dimension $L = 13$ nm (as for our simulation with 192 000 atoms) would be $\tau = L/v = 1.9$ ps. This is longer than the basic timescale of the production of the damaged region, as noted above, and is roughly in line with the basic time constants of the thermal and strain relaxations in the simulation algorithms.

We conclude that our simulations do not suffer from any problems associated with temperature rescaling and we note that the comment [1] offers no substantiated challenges to our methodology.

Finally, it should be noted that we see similar cascades in CaTiO$_3$ perovskite using samples of 300 000 atoms and potentials tuned against quantum mechanical calculations (to be published). Similar effects were also seen by Purton and Allen in their simulations of pyrochlores [19].

5. Validation of results

The authors of the comment [1] make a number of vague comments under the theme of 'validity of results' and grudgingly admit that our simulation results on the cascades agree with experiments in a number of important areas. These include the size of the damaged region caused by the cascade simulation, which is in remarkable agreement with NMR [12] and TEM results, and the observation of polymerization of the silicon and oxygen atoms, which is also in agreement with NMR results. We note also that the polymerization is also observed in the simulations of some of the authors of the comment [1, 4, 5], although they have not carried out as detailed a study of the polymerization as we have reported; presumably the authors of the comment [1] would therefore agree that our interatomic potentials are capturing this important part of the real system. The good agreement between our simulation and experiments has been stated in [1] to be 'fortuitous', but no justification is given for this. Nor is any evidence given that both our simulations and the experimentally damaged regions are smaller than real cascades.

In addition to the experimental evidence cited above, we have also shown that our simulation is fully consistent with recent small-angle x-ray scattering studies of irradiated zircon [8]. These new results give an independent quantitative measure of the length scale of structural inhomogeneities, which correspond to the low-density cores and higher-density polymerized shells.

The authors of the comment [1] obliquely bring in the issue of comparing simulations, which are necessarily carried out over a very short interval of time, with experimental results from samples that have been treated over much longer periods of time. This is always a problem in any simulation study of non-equilibrium processes, and the best that anyone can do (including the authors of the comment [1, 3–5]) is to run the simulation for as long as it takes for all changes to slow down to imperceptible rates. We have run our cascade simulations for over 100 ps after the cascade, well beyond the time after which the thermal energy of the recoil has dissipated. We appreciate that over long periods of time there will be rebonding, but we doubt if this is significant, due to the protection afforded by the polymerized shell we detect in our simulations. This shell is critical to the properties of zircon and we do not believe that any

deficiencies in our potentials invalidate our observation of this shell because it is in agreement with NMR and because we see the same shell in our simulations performed with our new potential and that of Park *et al* [3], albeit in an otherwise unstable structure (see above).

6. Conclusion

The main points made in the comment [1] on our paper relate to the simulation potentials and the simulation method. We anticipate that we will not convince those who want to disagree, but we would claim that there is adequate experimental evidence to support the view that both of our models, namely that in our original publications [2, 7] and the one presented here, correctly reproduce the important features of real cascade events (length scales, polymerization of silicon and oxygen atoms and structural inhomogeneities). We have shown that the model of the main authors is inherently unstable against finite fluctuations such as the normal thermal fluctuations. Even though our original model did not reproduce properties such as the bulk modulus as well as the model of [3], we would prefer to work with a stable potential which reproduces the main behaviour and accept that some of the numbers are not spot on, rather than a potential that gives a simulated structure that simply falls apart under a mere 300 K of thermal energy. We presume that the authors of the comment [1] would agree with us on this point, in spite of their advocacy of the use of an unstable potential. Whilst we accept that the interatomic potential in our earlier work [2, 7] is slightly too stiff in places, we believe that it captures a lot of the behaviour observed in real cascades, including the polymerized shell and the low density core, and we note that these conclusions have not been in any way challenged by the comment. In this reply we have demonstrated that the use of a potential that reproduces the equilibrium structure and properties, and which contains very short range interactions of the form advocated by the authors of the comment [1], does not produce results that are significantly different from our earlier work [2, 7].

We note that the authors of the comment [1] have not challenged the observation of a deflection from the polymerized shell. We believe that one could expect this to happen based on the existing experimental results. In this case the unknown quantity would be the extent of deflection, and we believe that our simulations provide some insights into this. Moreover, the authors do not comment on the main point of the paper [2], which is the proposal for a mechanism for the volume swelling in irradiated zircon. The model we proposed did not use data from the simulation—instead, the simulation was used as a check that the one free parameter in the model, namely the average extent of the deflection whose value was obtained by comparison with experimental data, is realistic. We do not believe that the authors of the comment have provided any challenge against this.

We offer our model for the volume swelling in irradiated zircon [2] in the spirit of much of theoretical physics, as a model that can now be tested against experiments, other simulations and more detailed theory. We are encouraged by the way that the model gives a swelling curve that agrees with experiment. In particular, we are encouraged by the fact that our model explains the increase in the swelling around the percolation point and the quadratic dependence of the swelling on the degree of damage at higher levels of damage. We note that there is no discussion of the model for swelling in the comment [1]—we presume that the authors do not find fault with this.

Finally, we are amazed that the authors of the comment are so pessimistic about the prospects for simulations of several million atoms in their final section of [1]. They claim [1] that these are 'too costly, even with the use of cutoffs for the Coulomb interactions'. In fact we are closer to being able to perform such large simulations. The latest generation of high-performance computers now allow us to run simulations with a million atoms using the Ewald

summation to handle the electrostatic interactions without the need for reduced cut-offs. We are collaborating with the authors of the DL_POLY code on the development of particle–mesh methods for handling the electrostatic energies. These allow for improved performance scaling with sample size, without sacrificing any accuracy. We believe that the authors of [1] are being unnecessarily pessimistic in their outlook on the immediate prospects for large-scale cascade simulations. At the very least, our work [2, 7] has the significant advantage over other studies [3–5] in driving forward the development of technologies towards the many million atom cascade simulations, work that will ultimately benefit even the authors of the comment [1].

Appendix A. Importance of the potential energy function in high-energy glancing collisions

In this appendix we demonstrate that for glancing incident collisions the detailed form of the interatomic potential is not critical. The energy transferred between an impact atom and a target atom, E_{transfer}, has a simple dependence on the angle of deflection of the impact atom, θ (defined such that $\theta = \pi$ for complete back scattering):

$$E_{\text{transfer}} = \frac{4E_0 m_1 m_2}{(m_1 + m_2)^2} \sin^2(\theta/2) \tag{8}$$

$$\theta = \pi + 2 \int_R^\infty \frac{p}{r^2(1 - p^2/r^2 - V(r)/E_i)^{1/2}} \, dr \tag{9}$$

where r is the distance between atoms, $V(r)$ is the potential energy between the two atoms, p is the closest distance between the trajectory of the impact atom and the target atom if $V(r) = 0$, E_i is the kinetic energy of the impact atom, m_1 and m_2 are the masses of the two atoms and R is the distance of closest contact, equivalent to the point when $V(R) = E_i$ for a direct impact. Masses and energy are defined in the centre of mass for the collision process. The key point of this equation is that, if $V(r) < E_i$, which is the case for glancing impacts, the scattering angles are relatively insensitive to the form of $V(r)$. Moreover, in the case of a direct impact ($p = 0$, giving $\theta = \pi$) there is no dependence on the interatomic potential. On this basis, we would claim that the exact details of the short-range potentials are not overly important in determining the initial behaviour of the cascade simulation.

Appendix B. Comparison of calculated thermodynamic properties against experimental data

Room temperature is a difficult point at which to compare thermodynamic properties for materials with strong covalent bonds, because frequently this is the point where the thermodynamic functions change most rapidly. Around this point, small changes in vibrational frequencies will have the effect of causing large changes in the thermodynamic properties. In figure B.1 we show the heat capacity calculated by our new and original [2, 6, 7] models and that calculated using the model of Park *et al* [3], the model used by the main authors of [1].
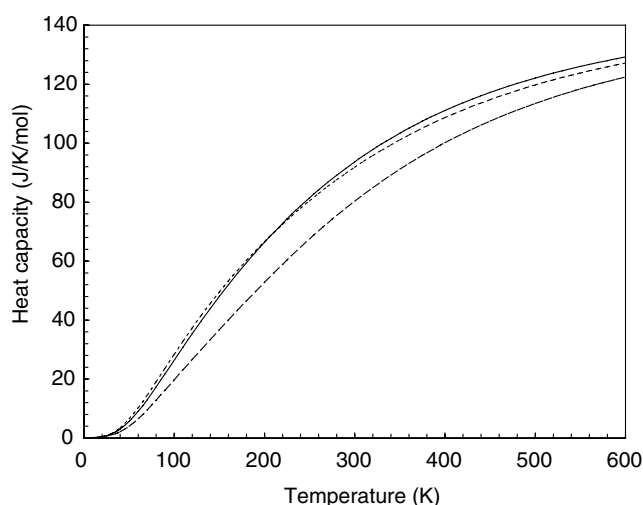
Figure B.1. Comparison of the hear capacity calculated using our new model (full curve), the model of [3] (dotted curve) and our original model [2, 6, 7] (broken curve).

The results of the new model are very similar to those given by the model of [3]. It is clear that our original model corresponds to a simple temperature rescaling.

Appendix C. SRIM calculations

The authors of the comment [1] try to contrast SRIM results with our results. We have performed SRIM calculations of a 30 keV U atom (which is equivalent to a Zr atom in our previous simulations, since the U short-range repulsive potential was assigned to a Zr atom), using threshold displacement energies of 129, 53 and 64 eV for Zr, Si and O atoms, respectively (these were determined by the main authors of the comment in [3] and we have averaged them over all directions), and gives the recoil range of about 10 nm. This is in good agreement with the value of 11 nm found in the simulation using the potential energy model of [3], and with 8.5 nm found in simulations with our earlier model [2, 7] and with our new model.

It is interesting that the methodology that the authors of the comment [1] advocate has been applied by the main authors to yield an obviously wrong result in their previous work [3]. There it was found that a 0.2 keV recoil could not be contained in the simulation box with 5 nm dimensions. We have performed SRIM calculations of 0.2 keV Zr recoils using the threshold displacement energies determined by these authors [3] and found the recoil range to be at most 1 nm. Moreover, we have performed MD simulations of 0.2 keV Zr atom recoils, using the potentials of [3] and ZBL interatomic potentials. We have found that, for three different initial directions, a Zr atom with recoil energy 0.2 keV has a range of no more than 1 nm, consistent with SRIM calculations.

It is therefore clear that there is a serious fault in the simulation performed by the main authors of the comment in [3], which can affect or invalidate the results in that work and any future results. This will be discussed elsewhere in more detail, since it appears to be important to explain the qualitative differences in the simulation results and their interpretation. One possible reason for the unrealistically large recoil range found in [3] is that a strong short-range repulsion was included only between Zr–O, Si–O and O–O atoms, whereas such a repulsion also exists between Zr–Zr, Si–Si and Zr–Si atoms at short distances. Inclusion of

such a repulsion would localize the damage and make it more realistic, but there may be more hidden faults in the simulation in [3].

It becomes clear now that the concerns of the authors of the comment [1], namely that our damage should be much more widespread, may in fact be related to their previous results which showed unrealistically dispersed damage, with a 0.2 keV recoil travelling more than 5 nm, as discussed above.

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