

## Radiation damage effects and percolation theory

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### Abstract

We combine theoretical and experimental results to study percolation-driven transport phenomena in an irradiated material. We show that whereas the first transition takes place at the value of amorphous fraction  $p_1 \approx 0.3$ , the second transition corresponds to the percolation of depleted phase. The knowledge of the radius of depletion sphere of the isolated damaged region allows one to predict the radiation dose at which the second percolation transition takes place, with dramatic increase in transport.

Irradiating a material with energetic ions or doping it with radioactive elements results in dramatic changes of its important physical properties. These changes are versatile and include altering such characteristics as transport, density, hardness and conductivity. While in some applications these changes are sought after, other may often appear as undesirable by-products. An example of this situation is using a material as a host, or a waste form, to immobilize highly radioactive nuclear waste and weapons-grade plutonium. Here, an immobilizing waste form is supposed to prevent the radioactive substance from spreading and harming the environment. The crucial question is how effective a waste form will remain over the required period of time, which for various isotopes varies from tens to tens of thousands of years. How does the ability of a waste form to immobilize radioactive substance change as it accumulates the damage?

In this paper we look into how the chemical transport properties of a material change with increasing the degree of self-irradiation. Several materials of different chemistries and structures have been proposed as waste forms [1]. Zircon,  $ZrSiO_4$ , has been proposed to immobilize weapons-grade plutonium, since in nature it can contain radioactive elements for geologic times, although the structure is found to be amorphized [2]. Whether or not it will be used in practice, zircon provides a good case study, due to the availability of natural damaged samples. Here, we combine experimental and simulation results, as well as basic results from

the percolation theory, to propose the criterion for predicting a stability threshold of a waste form that undergoes a transition from a crystalline to an aperiodic state.

Most of the damage comes from heavy energetic recoil atoms in alpha decay, each producing several thousands of permanently displaced atoms [3–5]. These defects that are mostly responsible for the changes in properties can generally be viewed as disorderly introduced points in a lattice. The problem can be reformulated as follows: how do macroscopic properties of the system change as the accumulation of new points (defects) progresses? Percolation theory, developed in the last few decades [6], is a robust mathematical tool designed to analyse precisely this sort of problem in disordered systems. At the heart of the theory lies the result that a system starts to behave qualitatively differently once the percolating cluster is formed, signalling the onset of macroscopic correlations and overall change of system behaviour. Therefore it may seem surprising that percolation theory is hardly used in radiation damage studies at the moment, as one would expect the irradiated material to show remarkable changes of properties at the damage percolation threshold.

Even when percolation is expected, its observation may often be hidden by other intervening phenomena, and require the special attention of an experimentalist. Recently, a typical example of percolative behaviour was found by Geisler *et al* [8] in a hydrothermal experiment performed on the structures of variably damaged zircons. It was found that the diffusion distance, approximated by the thickness of the area affected by chemical alteration, showed a sharp increase at the percolation threshold, corresponding to the concentration of the amorphous fraction  $p_1 \approx 0.3$ , a percolation threshold in the continuous percolation problem [9]. A percolation-type alteration behaviour was also observed in natural zircon crystals from a granite of the Eastern Desert of Egypt [7]. In these crystals, the growth zones that experienced a threshold degree of radiation damage are heavily altered, as indicated by a dramatic enrichment of non-formula elements such as hydrogen, Ca, Al and Fe.

Note that the value of  $p_1$  is usually derived in the system of overlapping equally sized spheres, while in radiation damage one can have overlapping damaged regions of irregular shapes, with isolated amorphous ‘pockets’ etc. Does this preclude us from quantifying the radiation damage in the language of percolation theory? Fortunately, it does not, because it was found that the value of  $p_1$  does not change significantly in the systems that are mixtures of spheres of different sizes [9].

In addition to the transition at  $p_1 \approx 0.3$ , another dramatic increase in diffusion distance was found at  $p_2 \approx 0.7$  [8]. At that value of radiation dose, the diffusion distance was found to be much larger than one would expect from simply assuming a progressive increase of the fraction of connected homogeneous amorphous domains, in which the chemical transport is enhanced. Geisler *et al* therefore suggested that this increase was due to the appearance of high-diffusivity paths of reduced density in the damaged structure. Due to the importance of this effect for other potential waste forms, we revisit this effect here by performing molecular dynamics (MD) simulation.

We first note that even an isolated damaged region has large density variations, as predicted in our previous MD simulations [5]. This effect is related to the ability of the damaged structure to form stable alternative configurations which can be locally more and less dense than initial structure. In the crystalline structure,  $\text{SiO}_4$  tetrahedra are not connected, but in the damaged structure they form dense polymerized chains of  $\text{SiO}_n$  polyhedra, as seen in the simulation [5, 10] and NMR experiments [3]. Hence the stability of this dense polymerized phase is behind the stabilization of the non-homogeneous density distribution in the damaged region. Recently, large density variations have been confirmed in low-angle x-ray scattering experiments as the presence of regions of depleted matter (rdm) in the damaged structure [8].

A detailed analysis of SAXS spectra shows that several ‘void particles’ of about 8 Å are present in a single damaged region [11].

The percolation transition at  $p_1 \approx 0.3$  marks the point at which the ‘amorphous’ part of the system starts to percolate, but at this point depleted regions in individual damaged regions do not percolate yet. What happens at higher radiation dose, when damaged regions start to overlap significantly? The important question is whether or not rdm annihilate as a result of close overlap. If they do not, then connecting of rdm into a channel due to the overlap can provide a high-diffusivity path for a radioactive substance.

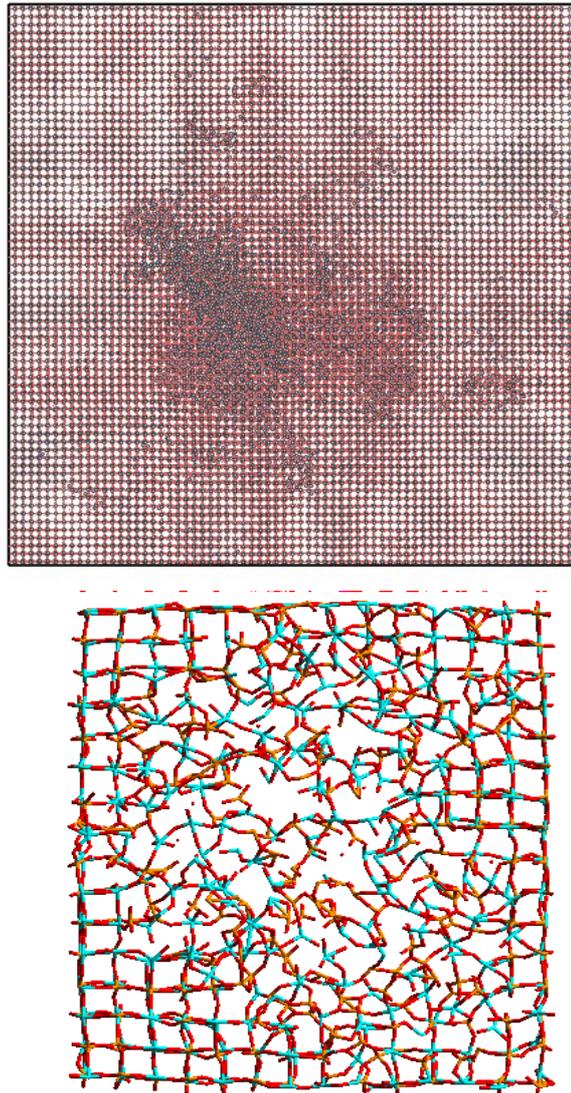
To answer this question, we performed MD simulations of the closely overlapping events, using simulation conditions different to those in [8]. We have used the following interatomic potential for zircon. Zr–O and O–O interactions were taken in the form  $y(r) = A \exp(-r/\rho) - Cr^{-6}$ , with  $A = 1477$  eV,  $\rho = 0.317$  Å,  $C = 0$  for Zr–O and  $A = 9245$  eV,  $\rho = 0.2617$ ,  $C = 100$  eV Å<sup>-6</sup> for O–O interactions. The Si–O interaction was taken in the Morse form  $y(r) = D(\exp(-2\alpha(r - r_0)) - 2\exp(\alpha(r - r_0)))$ , with  $D = 1.252$  eV,  $\alpha = 2.83$  Å<sup>-1</sup> and  $r_0 = 1.627$  Å, and electrostatic interaction. The Zr, Si and O charges were 3.428, 1.356 and -1.196, respectively. Electrostatic interactions were handled by the smooth particle mesh method, which substantially speeds up the simulation of large systems. We find that the above potential reproduces both structural and elastic properties of zircon remarkably well. At short distances, the pair potentials were fitted to the strong repulsive ZBL potentials. We simulated a close overlap of two 50 keV U atoms by implanting the next U event close to the trajectory of a previous event. We employed a constant energy ensemble and a system with 1029 000 atoms. This set of simulation conditions is comfortably accommodated by radiation damage computer simulators. The DL\_POLY MD package was used [12].

In figure 1 we show the close overlap of two radiation events, with a 1 nm slice of the region damaged by two events. It is clearly seen that the structure damaged by overlapping events contains several depleted regions (voids) with characteristic sizes of about 1 nm. As the front from the next implanted event moves into the previously implanted damaged region, rdm do not annihilate as a result of this overlap, and one can view the damaged structure from the overlap as one damaged region that has depleted matter inside it (see figure 1). In other words, close overlap of two events produces locally a new quality, a channel of depleted matter between two overlapping damaged regions. This means that we can again use percolation theory to describe this effect on the macroscopic level, because at some value of amorphous fraction  $p = p_2$ , depleted channels connect into the percolating cluster.

We can introduce  $R_{\text{dep}}$  as the effective radius of depletion sphere that contains all rdm in a single damaged region, such that outside  $R_{\text{dep}}$  there are no rdm. Figure 2 schematically illustrates this. How is  $R_{\text{dep}}$  related to the radius of the whole damaged region  $R$ ? It may seem surprising, but the knowledge of  $p_1$  and  $p_2$  (or radiation doses, that give  $p_1$  and  $p_2$ ) is all one needs to answer this question. Indeed, if  $N$  is the number of objects (damaged regions),  $V$  is the system volume and  $v$  is the volume of an individual object, the amorphous fraction  $p$  is given as

$$p = 1 - \exp(-vN/V). \quad (1)$$

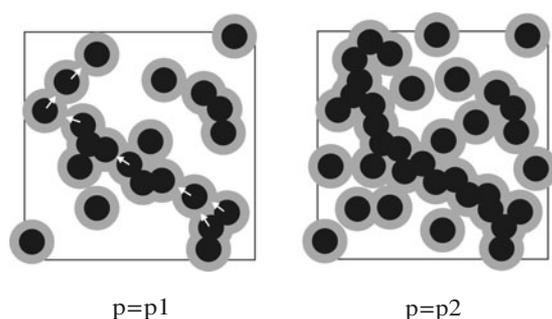
At  $p = p_1$ , overlapping spheres with radius  $R$  percolate (see figure 2). Assuming that  $p = p_2$  corresponds to the percolation of depleted phase, one can ask what increase of  $N$  is needed to cause percolation of spheres with radius  $R_{\text{dep}}$ . The volume fraction of these smaller spheres at the percolation threshold is still  $p_1$  (see figure 2); therefore, according to equation (1),  $N_2/N_1 = v_1/v_2 = (R/R_{\text{dep}})^3$ , where  $v_1$ ,  $v_2$ ,  $N_1$  and  $N_2$  are the volume and numbers of spheres with radius  $R$  and  $R_{\text{dep}}$ , respectively. At the same time, from equation (1) it follows that  $N_2/N_1 = \ln(1 - p_2)/\ln(1 - p_1)$ , and therefore  $(R/R_{\text{dep}})^3 = \ln(1 - p_2)/\ln(1 - p_1)$ .



**Figure 1.** Close overlap of two events (top), and a slice of the damaged structure in the vicinity of strong overlap (bottom). The top graph was prepared using the Atomeye software [13].  
(This figure is in colour only in the electronic version)

From the experimental values  $p_1 \approx 0.3$  and  $p_2 \approx 0.7$ , we estimate  $R_{\text{dep}}/R \approx 0.7$ . We find that this ratio is consistent with our previous simulations [5], as well as with the picture of the damaged region from this simulation.

We noted above that percolation of depleted regions can be an effect in other irradiated materials, including waste forms. Indeed, density fluctuations in irradiated materials are not uncommon, and in many cases appear as a result of material's ability to form stable local structures with density varying across a damaged region. Therefore, one can use the same equations as above: as discussed,  $N_1/N_2$  gives  $R_{\text{dep}}/R$ . On the other hand, the knowledge of



**Figure 2.** A schematic representation of percolation of spheres with radius  $R$  at  $p = p_1$  and  $R_{\text{dep}}$  at  $p = p_2$ .

$R_{\text{dep}}/R$  from the simulation or, for example, a diffraction experiment allows one to calculate the dose at which the depleted phase starts to percolate. This, together with  $p_1$ , can provide an important benchmark for the acceptable load of radioactive substance in a waste form: at  $p = p_1$  and  $p_2$  one should expect large increases of transport, which should be considered when predicting the performance of a waste form over time.

We conclude by suggesting that there may be percolation phenomena in the radiation damage area to be uncovered yet. We hope that this work will stimulate larger discussion and experiments aimed at looking for percolation effects in irradiated materials.

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