

# Atomistic simulations of surface diffusion and segregation in ceramics

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## Abstract

We demonstrate two approaches to studying processes of diffusion and segregation on the surface of oxides and ceramics. When simulating surface diffusion the activation barriers are often so high that the timescales required for direct simulation by molecular dynamics are prohibitive. We show that a combination of the Temperature Accelerated Dynamics (TAD) together with Kinetic Monte Carlo (KMC) methods can reach the timescales required without the necessity of guessing (often incorrectly) which are the dominant processes. We illustrate the power of the methods for surface diffusion and growth of rocksalt oxides. We show that, surprisingly, exchange mechanisms and correlated ion motions are important in surface and near-surface diffusion of those ionic systems. Another approach, Exchange Monte Carlo (MCX), is used to study *equilibrium* segregation in thin ceramic films with application to MgO/MnO. Surface concentrations as a function of temperature and film composition are determined directly from the simulations. For all compositions studied the {001} surface is Mn<sup>2+</sup> rich; the occupancy of sites by Mn<sup>2+</sup> decreases rapidly with depth.

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## 1. Introduction

The last decade has seen the emergence of tremendous interest in the properties of oxide surfaces, stimulated by their commercial potential in a wide range of products including catalysts, optoelectric devices and magnetic storage devices. Key to tailoring both the mechanical and the chemical behaviour of their surfaces

is doping with impurity cations or anions. Despite this, relatively little effort has been devoted to the theoretical study of grossly non-stoichiometric oxide surfaces.

Well-defined layers of crystalline oxides on semiconductors are candidate materials for gate dielectrics in solid state electronics [1]. Such oxide layers are often grown using molecular beam epitaxy, and are usually required to be atomically smooth. The commonest smoothing mechanism is surface diffusion. This surface motion must not involve exchange between surface layers. Atomically sharp interfaces will be impossible to produce if the atoms of the upper surface layer swap places with those in the substrate below. High activation energies make investigation of surface diffusion processes especially difficult. Whilst it is possible to simulate

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the behaviour of superionic conductors directly using molecular dynamics [2,3], the migration barriers in simple refractory oxides, in contrast, are so high that the timescales required for direct simulation are prohibitive.

In this paper we demonstrate application of three novel methods to study long-timescale processes of surface diffusion and segregation between bulk and surface in rocksalt oxides. First, we show how combination of temperature-accelerated dynamics and Kinetic Monte Carlo allows us to model diffusion processes on the surface of BaO and SrO, occurring on a long timescale. Second, we apply Exchange Monte Carlo to investigate segregation between surface and bulk in MgO/MnO solid solution.

## 2. Methods

### 2.1. Temperature-accelerated dynamics

TAD calculations aim to increase the number of transitions undergone by the system by carrying out the simulations at a higher temperature,  $T_{\text{high}}$ , and extrapolating their rate to a lower temperature of interest,  $T_{\text{low}}$ . No prior information concerning mechanisms is required. The system is free to explore the local potential surface and find its own route from one potential minimum into another. We start with the system in the basin on the potential energy surface corresponding to a particular local potential minimum. When the system undergoes a transition out of the basin, the saddle point (the highest point on the minimum energy path) is found using the nudged elastic band method [4] and the corresponding static barrier height recorded. The trajectory is then reflected back into the initial basin, the simulation continues and the particle searches for another way out of the basin.

The TAD method assumes harmonic transition-state theory and thus the exponential dependence of rates on temperature. Using the static barrier heights, each escape time is extrapolated from  $T_{\text{high}}$  to find the corresponding time at  $T_{\text{low}}$ . It is possible [5] to define a time at which the simulation from the basin can be stopped such that the probability that any transition observed after that time would replace the first transition at  $T_{\text{low}}$  is less than a predefined confidence level  $\delta$ . Typically boosts of the order of  $10^2$ – $10^6$  were obtained for a given simulation.

Our TAD calculations have been carried out using rigid ion potentials based on the well-established model of Lewis and Catlow [6]. Models of this kind give excellent results for the surface energies and structures of oxides of simple closed-shell ions, defect energies and activation energies for ion transport. Comparisons with quantum calculations show good agreement where redistribution of the electron density is not large [7]. Cal-

culations were performed in the canonical  $NVT$  ensemble. The surface was represented by a slab of ions ( $\approx 400$  ions), typically containing four layers to ensure negligible interaction between the top and bottom layers of an individual slab.  $T_{\text{high}}$  and  $T_{\text{low}}$  were set to 1200 K and 300 K, respectively.

### 2.2. Kinetic Monte Carlo

The set of possible movements of molecules on the surface and between the surface and the bulk, together with the corresponding activation energies from TAD calculations, allows us to run the KMC simulations. For each configuration of molecules on the surface, a set of possible events is established. The following were taken into account:

- Initial stage of the exchange jump - displacement of an ion (anion or cation) from the adsorbed layer towards the surface with simultaneous displacement of another ion of the same type from the surface towards the adsorbed layer. After this step both displaced ions occupy interstitial sites between the surface and the adsorbed layer;
- final stage of the exchange jump—movement of one of the displaced ions into the surface, and the other into the adsorbed layer;
- movement of an ion pair on the surface as a single species.

Activation energies for these events differ for movement near a step and away from it, in accordance with the TAD results. The rate of an event is related to its activation energy according to  $\Gamma = \Gamma_0 \exp(-E_a/kT)$ , where  $\Gamma_0$  is a characteristic vibrational frequency (taken to be  $10^{13} \text{ s}^{-1}$ ),  $E_a$  the activation energy and  $T$  the temperature. At each step, one of the possible events is randomly chosen with a probability proportional to its rate. The system is changed accordingly, and the time counter incremented [4] by  $\Delta t = -\ln \mu / \sum_i \Gamma_i$ , where  $\mu$  is a random number between 0 and 1, and  $\sum_i \Gamma_i$  is the sum over all possible events. The size of the surface in the KMC simulations was  $20 \times 20$  (i.e. 400 ions), with periodic boundary conditions applied. A typical simulation included  $4 \times 10^6$  events.

### 2.3. Exchange Monte Carlo

In simulations of non-stoichiometric ionic materials and solid solutions using ‘standard’ MC, kinetic barriers prevent sampling the whole of the configurational space since almost always only one cation arrangement—the initial configuration—is sampled. We have described elsewhere [8] Exchange Monte Carlo (MCX) simulations in which *both* the atomic configuration *and* the atomic coordinates of all the atoms are changed. Each

production simulation involves  $10^4$  cycles, where each cycle allows for both the displacement of all the ions and an exchange of ionic configuration. The system was allowed to equilibrate for  $5 \times 10^3$  cycles. Allowing random moves of randomly selected atoms takes account of both surface relaxation and vibrational effects. To determine whether the change is accepted or rejected, the usual Metropolis algorithm is applied [9]. The maximum change in the atomic displacement for each ionic species,  $r_{\max}$ , is variable; its magnitude is adjusted automatically during the simulation to maintain an acceptance/rejection ratio of approximately 0.5. Changes in ionic configuration are attempted by exchanging the position of a  $\text{Mn}^{2+}$  ion and a  $\text{Mg}^{2+}$  ion, both chosen at random. Again, the Metropolis algorithm is used to accept or reject any attempted exchange. The surfaces are assumed to be planar, semi-infinite and periodic in two dimensions [10]. We have neglected segregation to kink steps or dislocations which real crystals undoubtedly possess. All thin film calculations were undertaken on 4MnO–MgO layers comprising 576 ions ( $12 \times 12 \times 4$ ), on an MgO substrate of 2880 ions ( $12 \times 12 \times 20$ ). The lattice parameters for the MgO substrate were held fixed at those obtained in a previous bulk MC simulation using an *NPT* ensemble at the appropriate temperature. In order to represent the deposition of a film on an inert substrate, only the atoms within the four layers of the thin-film were allowed to intermix. This allows us to discriminate between the effects of the substrate on the overlying film and processes operating within the film. The number of atoms in each layer of the film is moni-

tored as the simulation proceeds, and an average is calculated during the simulation.

### 3. Results

#### 3.1. Diffusion and growth of rocksalt oxides

We consider first the diffusion of BaO (SrO) ion pairs along the (100) surface of a BaO (SrO) substrate. The TAD calculations show clearly that the diffusion mechanism with the lowest energy barrier involves both cation and anion exchange with surface ions. Each jump involves one of the ions in the adsorbed ion pair exchanging with an ion of the same charge in the surface while the other atom of the adsorbed pair remains above the surface, held in place by the Coulombic binding. The ion pair is thus reoriented by  $90^\circ$  or by  $180^\circ$ , depending on which of the three possible nearest-neighbour adsorption sites is occupied by the exchanged ion. The ion pair can then move by exchanging the counter-ion with a counter-ion in the surface in an analogous step. Diagrams of the exchange mechanism for oxygen diffusion are shown in Fig. 1. The cation diffusion process is similar. The migration energies for the cation and anion exchanges are very close: 0.35–0.46 eV for the cation, 0.37–0.44 eV for the anion. This is less than the activation energy to move the BaO pair across the surface as a single adsorbed species ( $\approx 0.6$  eV) and comparable with the activation energy for similar movement of an SrO ion pair at the same surface ( $\approx 0.4$  eV). Despite

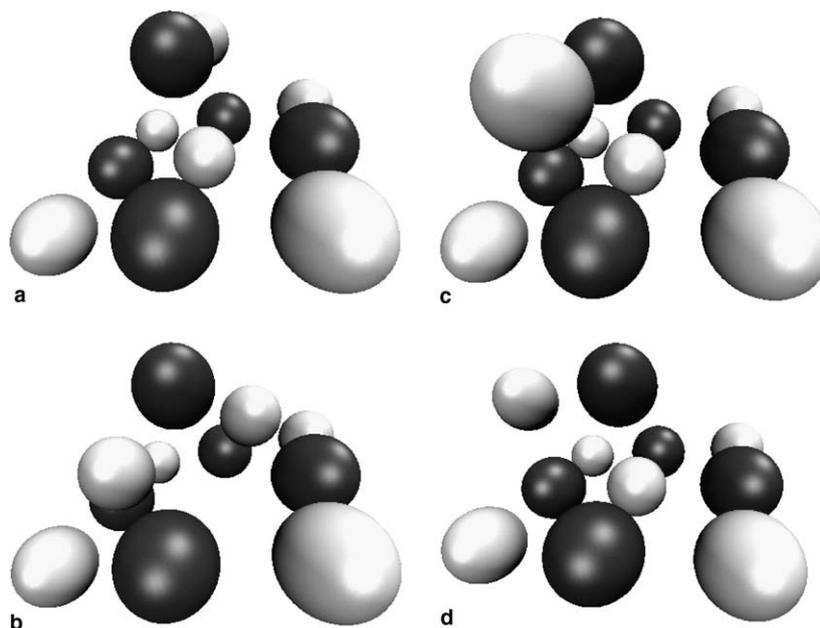


Fig. 1. Exchange mechanism of the surface diffusion for the case of oxygen diffusion. Dark spheres: cations; grey spheres: oxygen ions. We show the initial position (a), middle of the transition (b) and the two possible final positions, after the exchange has taken place (c-d). As a result of the transition, the ion pair is reoriented by  $90^\circ$  (c) or by  $180^\circ$  (d).

the apparent similarity to the metal exchange reaction, there is a *crucial* difference—the necessity for the counter-ion to remain close to the exchanging ion. This suggests that extended subsurface diffusion mechanisms such as those proposed for metals [11,12] are unlikely for ionic surfaces. Motion of ion pairs along a step at the (001) surface of BaO also proceeds by an exchange mechanism. However, the edge complicates matters because of the drastically reduced symmetry. The second stage of the exchange can move the ion pair towards, away from or parallel to the step. The energy barrier to moving the ion pair away from the step is slightly higher than the barrier to moving towards it, whilst the energy to move along the step is midway between these two. Ions in contact with the step edge are bound to the step. As a result, clusters of ions or islands on the surface are very stable, and their evolution proceeds on much longer timescales compared to the initial formation of proto-steps.

The activation energies for all of the processes studied have been used as input to Kinetic Monte Carlo simulations. First the resulting isotropic two-dimensional diffusion coefficients can be extracted from these simulations from the standard result  $\langle r^2 \rangle = 4Dt$  where  $D$  is the diffusion coefficient. Diffusion coefficients are plotted as a function of inverse temperature in Fig. 2. The larger value of  $D$  is for the diffusion of SrO on SrO as would have been expected from the activation energies data. In order to demonstrate the importance of the exchange mechanism, we show in Fig. 2 the diffusion coefficient for the motion of BaO on BaO but *excluding* the exchanges. This results in a reduction of  $D$  by between one and three orders of magnitude, depending on temperature. A similar effect was found for SrO on SrO.

An important consequence of the possibility of exchange of atoms between the surface and the adsorbed

layer is that attempts to grow sharp interfaces between different oxides may be complicated if the exchange mechanism is still active in these structures. The existence of this low-energy mechanism in some cases (e.g., SrO on BaO) suggests that ionic materials may not be grown on a substrate with a similar structure without significant intermixing.

### 3.2. Segregation on the MgO/MnO surface

Fig. 3 displays the fractional surface coverage of  $\text{Mn}^{2+}$  ions at the {001} surface as a function of the overall mole fraction  $\chi$  of  $\text{Mn}^{2+}$  present in the film over a range of temperatures. Due to the small thickness of the films, it is not straightforward to define a so-called ‘bulk’ composition and so we have found it more useful to plot quantities of interest as a function of the total mole fraction of  $\text{Mn}^{2+}$ . The straight line in Fig. 3 shows the behaviour expected if there were no segregation to or from the surface. The surface concentration of  $\text{Mn}^{2+}$  increases sharply as a function of overall concentration, with enrichment of the surface layer by the larger  $\text{Mn}^{2+}$  ion at all temperatures for *all* compositions.

At other than the highest  $\text{Mn}^{2+}$  concentrations, the surface concentration varies strongly with temperature, as also clearly shown in Fig. 3, with a marked decrease in the surface enrichment by  $\text{Mn}^{2+}$  with increasing temperature. For example, for an overall 20%  $\text{Mn}^{2+}$  composition ( $\chi = 0.2$ ), the fractional surface coverage decreases from  $\approx 0.7$  to  $\approx 0.4$  as the temperature increases from 600 to 2400 K.

The ratio  $\text{Mn}^{2+}:\text{Mg}^{2+}$  decreases rapidly as a function of depth. Only in the outermost two layers does the  $\text{Mn}^{2+}$  occupancy exceed 50%. As the temperature

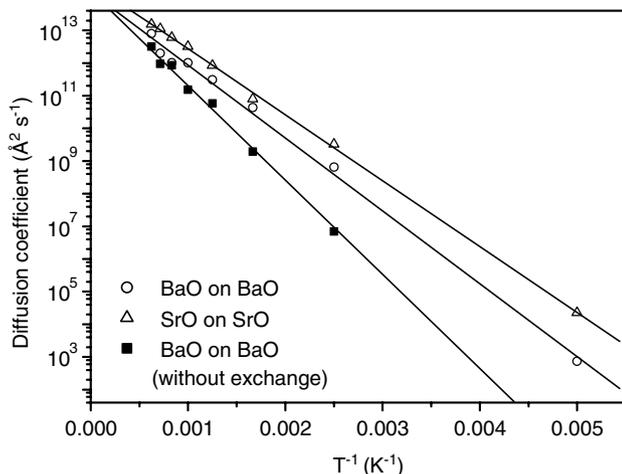


Fig. 2. Diffusion coefficients for oxide ion pairs on (100) surface of oxides as a function of inverse temperature: BaO on BaO and SrO on SrO. The diffusion coefficient for BaO on BaO excluding the exchange mechanism is also shown for comparison.

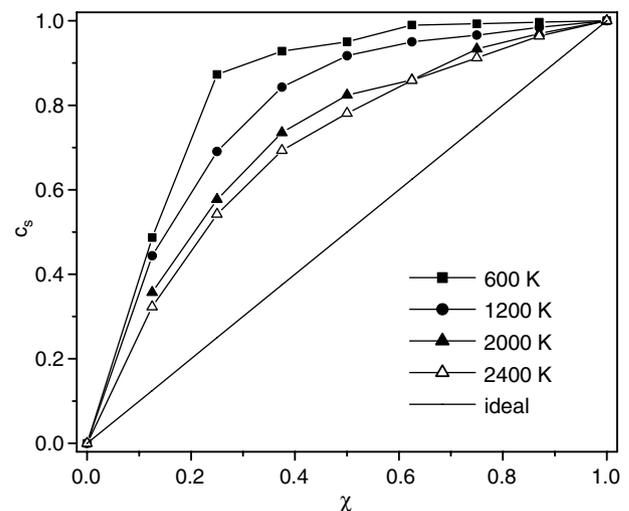


Fig. 3. The fractional surface coverage of  $\text{Mn}^{2+}$  ions  $c_s$ , plotted as a function of the overall Mn mole fraction  $\chi$  in the thin-film at different temperatures.

increases, consistent with Fig. 3, intermixing of all the layers increases with the occupancy of the lower two layers by  $\text{Mn}^{2+}$  increasing significantly. We do not see any oscillatory subsurface behaviour as noted by Battaile et al. in their mean-field simulation studies of similar systems [13].

In Fig. 4 we display snapshots of the surface structure at 800 K for total  $\text{Mn}^{2+}$  mole fractions  $\chi$  in the film of 0.125 (Fig. 4a) and 0.25 (Fig. 4b). The surface structure for  $\chi = 0.125$  is dominated by the formation of islands of  $\text{Mg}^{2+}$  ions. These islands are separated by lines of  $\text{Mn}^{2+}$  ions, which are aligned along the [110] direction (Fig. 4a). In contrast, when  $\chi = 0.25$  the surface occupancy by  $\text{Mn}^{2+}$  is 0.87 and the remaining  $\text{Mg}^{2+}$  ions tend to form chains along the [110] direction (Fig. 4b). For overall compositions with  $\chi > 0.375$  the surface cations are almost all  $\text{Mn}^{2+}$ .

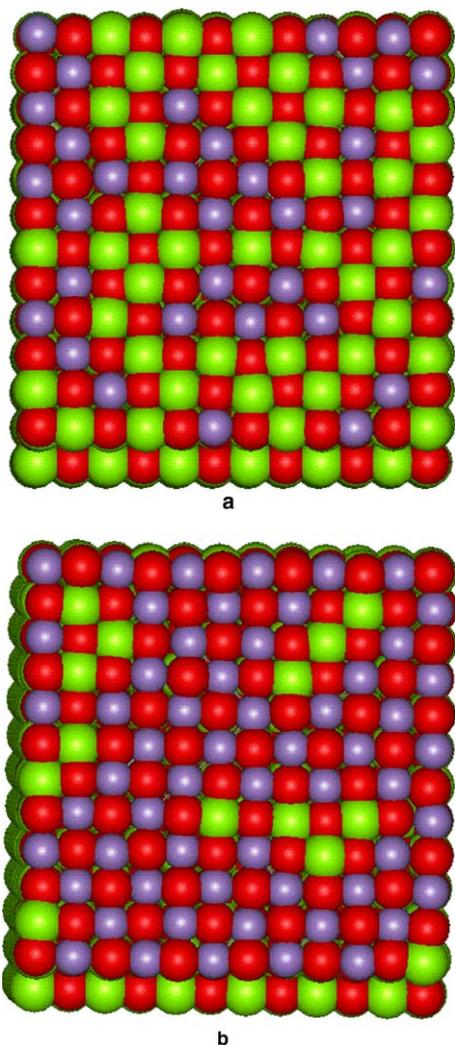


Fig. 4. Snapshots of the surface structure at 800 K for total Mn mole fractions (a)  $\chi = 0.125$  and (b)  $\chi = 0.25$ . Black, light-grey and dark-grey represent oxygen, magnesium and manganese ions respectively.

#### 4. Discussion and conclusions

Interstitialcy mechanisms, the class into which the exchange mechanism of surface diffusion essentially falls, are unusual in most bulk ionic materials. However, this is often because the Frenkel formation energies in the bulk are large, rather than because the interstitialcy migration energy itself is high. For an ionic pair at a surface, the initial condition for an interstitialcy mechanism is provided—there is no formation energy. The co-operative nature of the mechanism ensures that the Coulomb barrier to migration is low. The high energy cost of one ion climbing out of the Madelung well, which is a major factor in the high barriers to migration for ionic crystals, is largely offset by the energy gain of the other ion falling into the well as the first ion vacates it. Despite the similarity to the metal exchange reaction, there is an important difference—the necessity for the counter-ion to remain close to the exchanging ion.

We have shown the importance of exchange mechanisms in a variety of surface diffusion processes in simple oxides. The possibility of this kind of mechanism has been neglected in the past, despite the importance of well-defined layers of crystalline oxides in solid state electronics [1]. More generally, molecular beam epitaxy is currently being used to create layered structures of ferroelectric, ferromagnetic and dielectric oxides [14]. The question of whether the exchange mechanism is still active when a molecule of an oxide diffuses on a different oxide substrate is of fundamental importance for creating sharp interfaces in such structures. The existence of this low-energy mechanism in some cases suggests that ionic materials may not be grown on a substrate with a similar structure without significant intermixing. Further investigations of this effect for the perovskite structures are in progress.

We have employed the Monte Carlo Exchange technique to calculate directly the surface concentration of  $\text{MnO}/\text{MgO}$  thin-films on a  $\text{MgO}$  substrate as a function of temperature and bulk composition. The concentration of  $\text{Mn}^{2+}$  ions decreases rapidly with depth. At low temperatures and low concentrations  $\text{Mn}^{2+}$  ions form chains along the [110] direction in an  $\text{Mg}^{2+}$  matrix, whilst at higher concentrations the opposite is true. At high temperatures the  $\text{Mn}^{2+}$  ions are more dispersed throughout the film. It is worth stressing that we have studied a *thin-film* of  $\text{MnO}-\text{MgO}$ , rather than the surface of a much larger sample of solid solution; preliminary results indicate some similarities between the {001} surface of a bulk sample and the {001} surface of the thin film. Differences are due to the availability of  $\text{Mn}^{2+}$  ions for segregation as a function of overall composition in the two cases.

Finally, we have shown that temperature-accelerated dynamics, Kinetic Monte Carlo and Exchange Monte Carlo can be used for modelling surface processes and

equilibrium surface concentrations. We have found new exchange mechanism of surface diffusion in ionic solids and have shown that for all compositions studied the {001} surface of MgO/MnO solid solution is  $\text{Mn}^{2+}$  rich.

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