

Molecular dynamics simulation of the (0001) α -Al₂O₃ and α -Cr₂O₃ surfaces

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Abstract

A simple, rigid pair-potential model is applied to investigate the dynamics of the (0001) α -Al₂O₃ and α -Cr₂O₃ surfaces using the molecular dynamics technique. The simulations employ a two-stage equilibration process: in the first stage the simulation-cell size is determined via the constant-stress ensemble, and in the second stage the equilibration of the size-corrected simulation cell is continued in the canonical ensemble. The thermal expansion coefficients of bulk alumina and chromia are evaluated as a function of temperature. Furthermore, the surface relaxation and mean-square displacement of the atoms versus depth into the slab are calculated, and their behaviour in the surface region analysed in detail. The calculations show that even moderate temperatures (~ 400 °C) give rise to displacements of the atoms at the surface which are similar to the lattice mismatch between α -alumina and chromia. This will help in the initial nucleation stage during thin film growth, and thus facilitate the deposition of α -Al₂O₃ on (0001) α -Cr₂O₃ templates.

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1. Introduction

The properties of metal oxides are of considerable interest, e.g. for applications in the surface-coatings industry. Numerous static quantum-mechanical calculations and atomistic simulations have been carried out on surfaces of metal oxides. In contrast, relatively few surface-dynamics studies can be found in the literature. Recently, several dynamics studies (mostly using molecular dynamics simulations) have been performed, e.g. on premelting processes in Cr₂O₃ [1], the (0001) Cr₂O₃ surface [2], the MgO surface [3], the CeO₂ surface [4,5], the α -Al₂O₃ surface [6,7], the (011)CeO₂/(0001)Al₂O₃ interface [8], and the (100), (110) and (111) NiO surfaces [9,10]. These studies have shown that the displacements of the atoms in the surface

region are relatively large, which was also confirmed independently via low-energy electron diffraction measurements [11]. Large, short-lived displacements of the surface atoms may also be important for catalytic processes [8]. As a member of the corundum-type family, α -Cr₂O₃ is widely studied owing to its technological and fundamental scientific importance [12–15]. Our interest in the surface dynamics of α -Cr₂O₃ stems from recent findings that chromia can be used for the templated growth of α -Al₂O₃ thin films at drastically reduced substrate temperatures of 280–560 °C [16,17]. Conventional techniques for the growth of α -Al₂O₃ films, such as chemical vapour deposition (CVD), require substrate temperatures of over 1000 °C [18], which severely limits the range of practical applications. Andersson et al. [16] suggest that the surface mobility is large over the investigated temperature range (280–560 °C) and that the high temperatures used for nonepitaxial α -alumina deposition are primarily needed to promote initial grain nucleation. Surface mobility and migration barriers for a (0001) α -alumina surface were recently

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studied via an *ab initio* molecular dynamics technique by Rosén et al. [19–21].

Using an *ab initio* periodic Hartree–Fock (PHF) method, we have recently investigated the structure and energy of low-index α -Al₂O₃ and α -Cr₂O₃ surfaces, where we found that the {10 $\bar{1}$ 2} and {0001} α -Cr₂O₃ planes are suitable candidates for the templated growth of α -Al₂O₃ thin films [15]. Although there is still some controversy over the termination of the (0001) α -Cr₂O₃ surface [22], most studies provide evidence supporting the Cr-terminated surface [13,14,23,24]. Previous molecular dynamics (MD) simulation studies on the (0001) α -Cr₂O₃ surface mainly focused on the pre-melting processes [1,2]. In Ref. [25], we presented the dynamics of the (0001) α -Al₂O₃ surface calculated with the canonical ensemble at 10 and 100 K, where we found the mean-square displacement (msd) of the atoms to vary non-monotonically as a function of depth into the slab. In the present paper, we will first revisit the (0001) α -Al₂O₃ surface in order to see if these non-monotonic variations persist at higher temperatures. We will then concentrate on the dynamics of the (0001) α -Cr₂O₃ surface.

2. Computational details

In our previous work [25], we developed an empirical model for α -Al₂O₃ in which the atomic interactions are described by a Buckingham potential plus a Coulomb term. In Ref. [26], we transferred this potential to α -Cr₂O₃ which has the same corundum-type structure and similar lattice constants to α -Al₂O₃. For both material systems it was found that the repulsive interactions between cations are negligible and the resulting potential takes the form

$$V(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} - \frac{C_{OO}}{r_{ij}^6} + A_{OO} \exp\left(-\frac{r_{ij}}{\rho_{OO}}\right) + A_{MO} \exp\left(-\frac{r_{ij}}{\rho_{MO}}\right) \quad (1)$$

where O represents oxygen and M = Al or Cr. The potential parameters for α -Al₂O₃ are $A_{AlO} = 3411.118$ eV, $\rho_{AlO} = 0.244549$ Å [25], and for α -Cr₂O₃ they are $A_{CrO} = 2362.905$ eV, $\rho_{CrO} = 0.270628$ Å, with $A_{OO} = 91.55955$ eV, $\rho_{OO} = 0.547148$ Å and $C_{OO} = 32.32$ eV Å⁶ [26]. Cations and anions take their full formal charges. As was shown in Refs. [25,26], this empirical model is able to describe the structural properties of alumina and chromia very well. The calculated lattice constants for α -Al₂O₃ are $a_0 = 4.773$ Å and $c_0 = 12.990$ Å (experiment $a_0 = 4.760$ Å and $c_0 = 12.993$ Å [27]), and for α -Cr₂O₃ they are $a_0 = 4.987$ Å and $c_0 = 13.558$ Å (experiment $a_0 = 4.951$ Å and $c_0 = 13.556$ Å [28]). In contrast to the shell model [29], the present model ignores polarization effects. Including these effects makes not only the parameterisation more difficult but also the MD equilibration process much more time-consuming. In this context, we note that Barrera et al. [1] have shown that polarization effects are negligible

in some melting processes. However, these effects are also reflected in the high-frequency dielectric constant ϵ_∞ and become more important for large differences between ϵ_∞ and unity.

Since rigid models, whose potential parameters are usually obtained from fitting bulk properties, cannot self-consistently adjust to a new environment, they may not be adequate to describe surfaces and defects [30]. Whether a rigid model can be applied to the surface depends on how different the charges that the ions carry at the surface are from the bulk. Recently, *ab initio* Hartree–Fock calculations [31] showed that Cr carries only slightly less charge at the surface (2.13 |e|) compared to the bulk (2.31 |e|), with a concomitant decrease of the nearest Cr–O separation from 1.99 Å in the bulk to 1.80 Å at the surface. Thus, we anticipate that the error introduced by a rigid model is relatively small.

In the present work, the surface relaxation at zero temperature is carried out by a static calculation using the computer code METADISE [32]. For non-zero temperatures, we employ the MD computer code DL_POLY (Version 2.15) [33] with a slab model to calculate the surface dynamics. Here we choose an orthorhombic simulation cell (with periodic boundary conditions) of 960 particles with cell faces (11 $\bar{2}$ 0), (10 $\bar{1}$ 0) and (0001), measuring $V = X \times Y \times Z = 19.949 \times 17.276 \times 27.116$ Å³ at zero temperature. Since the cell expands with temperature, it is necessary to find the new dimension of the simulation cell for a specific temperature before the surface relaxation can be studied. Consequently, it is important to employ appropriate thermodynamic ensembles to conduct the equilibration procedure. We equilibrate the bulk system as follows: first, we choose the constant-stress ensemble (Berendsen thermostat and barostat [33]) to find the cell dimension at a specific temperature; we relax the simulation cell for at least 80 ps with a time step of 0.4 fs; we then replace the constant-stress ensemble with the canonical ensemble (Evans thermostat [33]) and relax the system with the new dimension again for at least 64 ps, and finally perform a production run of 32 ps. For the calculations pertaining to surfaces, a slab (which is cut directly from the equilibrated bulk) is equilibrated further for at least 64 ps, and then a production run of 32 ps is performed with data output every 4 fs. Fig. 1 shows snapshots of the equilibrated bulk (a) and equilibrated slab (b) of the chromia crystal (at $T = 500$ K) employed in the present work. The mean-square displacement in the z -direction for the j th ion is defined as $\text{msd}_{zj} = N^{-1} \sum_{i=1}^N (z_{ij} - \bar{z}_j)^2$ with $\bar{z}_j = N^{-1} \sum_{i=1}^N z_{ij}$, where i denotes the i th output data and N represents the total number of data outputs (in our calculations $N = 8000$); the other components of msd are defined in the same way. Finally, the msd_j values are averaged over each plane (the assignment of atoms to planes is still meaningful over the temperature range investigated in the present study). We have checked the statistical fluctuations of the mean-square displacements and for all cases these are smaller than 4% (8%) for atoms in the bulk (surface).

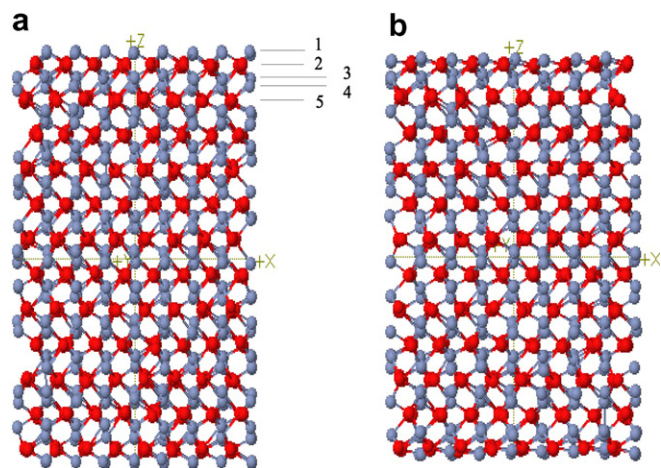


Fig. 1. Equilibrated bulk (a) and equilibrated slab (b) of α -chromia ($N_p = 960$, $T = 500$ K, (0001) Cr-terminated slab; the labels refer to the numbering used in Table 2).

3. Results and discussion

3.1. Thermal expansion coefficients

Before focusing on the surface properties of (0001) α - Al_2O_3 and α - Cr_2O_3 , we briefly discuss the thermal expansion of bulk α -alumina and chromia. The thermal expansion coefficient β , defined by $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$, is used to express the volume change of a substance due to a temperature change [34]. Strictly speaking, the simulation cell for the system considered here is not exactly orthorhombic any more at non-zero temperatures, but the deformation is negligible at low to intermediate temperatures. As a first approximation, we assume that the volume depends linearly on temperature. Consequently, the new cell volume can be calculated by $(X + \Delta X) \times (Y + \Delta Y) \times (Z + \Delta Z)$, and the thermal expansion coefficient β can be approximated by

$$\beta = \frac{1}{V} \frac{\Delta V}{\Delta T} \bigg|_P \quad (2)$$

The calculated thermal expansion coefficients for α - Al_2O_3 and α - Cr_2O_3 are summarized in Table 1, together with the available experimental data taken from Refs. [35,36]. As can be seen, the present model is able to reproduce the thermal expansion coefficients for α -alumina reasonably well, while the corresponding values for α -chromia

are significantly overestimated. This is hardly surprising, since the parameterisation was carried out for α -alumina and then transferred to α -chromia, and the experimental thermal expansion coefficients did not enter the cost function during the parameterisation procedure. Nevertheless, as far as the accuracy of the dynamical data are concerned, we note that the error introduced by this uncertainty in the chromia potential is significantly smaller than the statistical fluctuations of the mean-square displacements of the atoms. In contrast, we have found that it is important to take the thermal expansion of the system into account (via the equilibration procedure described in Section 2 above) in order to obtain accurate values of the mean-square displacements.

3.2. Surface relaxation

We now apply the present model to investigate the relaxation of the (0001) α - Cr_2O_3 surface. The obtained percentage changes in the interplanar spacings after full relaxation are summarised in Table 2. As can be seen, the present calculations agree reasonably well with the experimental results of Rohr et al. [23] using low-energy electron diffraction (LEED). Our calculations are also consistent with previous theoretical works in that all of these studies predict a large surface relaxation, i.e. the top Cr layer moves inward quite substantially while the second layer relaxes relatively little. However, the present model predicts a (0001) α - Cr_2O_3 surface energy of 0.9 J m^{-2} , which is considerably lower compared to other studies; e.g. Rohrbach et al. [14] predict a value of 1.4 J m^{-2} using density functional theory, while Rowley et al. [37] obtained 4.8 J m^{-2} with an aspherical ion model (AIM).

3.3. Surface dynamics

Before discussing the dynamics of the (0001) α - Al_2O_3 and α - Cr_2O_3 surfaces, we briefly describe the calculated average bulk mean-square displacement (msd) values. The latter are summarised in Table 3 together with the experimental data of Lewis et al. [27] and the MD simulation results of Baudin et al. [6]. As can be seen, our calculated msd values are in reasonable agreement with the available experimental data for α - Al_2O_3 . All of these studies predict that the msd_z values are larger than the corresponding msd_{xy} values, and that the msd values for

Table 1
Calculated and experimental thermal expansion coefficients (in 10^{-6} K^{-1}) for α - Al_2O_3 and α - Cr_2O_3 at different temperatures T

T (K)	Calculated	Experimental	Calculated	Experimental
	α - Al_2O_3	Ref. [35]	α - Cr_2O_3	Ref. [36]
100	22.8	–	21.6	–
300	22.6	23.0	25.6	16.0
500	24.5	24.5	27.1	18.5
700	28.9	25.5	25.3	19.5

Table 2
Percentage changes in interplanar spacings (see Fig. 1) at the surface of a fully relaxed (0001) slab of α - Cr_2O_3

Method	d_{12}	d_{23}	d_{34}	d_{45}	Reference
Exp (LEED)	–60	–3	–21	6	[23]
AIM	–40	6	–30	11	[37]
Shell	–59	13	–54	31	[38]
GGA + U	–60	12	–44	9	[14]
PHF	–49	3	–47	11	[15]
Static	–62	0	–51	23	This work

Table 3

Average mean-square displacement of atoms (in 10^{-3} \AA^2) for bulk $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$ at various temperatures ($M = \text{Al, Cr}$)

T (K)	$\overline{\text{msd}}_{xy}^M$	$\overline{\text{msd}}_z^M$	$\overline{\text{msd}}_{xy}^O$	$\overline{\text{msd}}_z^O$	Reference
$\alpha\text{-Al}_2\text{O}_3$					
300	2.8	3.2	3.3	3.7	Exp [27]
300	1.6	1.8	2.3	2.9	MD [6]
300	2.2	2.6	2.3	2.9	This work
500	3.8	4.5	3.9	5.0	This work
$\alpha\text{-Cr}_2\text{O}_3$					
100	0.8	1.0	0.8	1.2	This work
300	2.4	3.2	2.6	3.5	This work
500	4.5	5.3	4.7	5.9	This work
700	6.2	8.2	6.7	8.8	This work

oxygen ions are slightly larger than those for metal ions. However, it has to be noted that the calculations are not compatible with the results of the X-ray diffraction study of Ishizawa et al. [39] on $\alpha\text{-Al}_2\text{O}_3$ who predict that $\text{msd}_{xy} > \text{msd}_z$ with relatively large msd_{xy} values (of $5.1 \times 10^{-3} \text{ \AA}^2$ at room temperature). Considering the fact that an aluminium atom is about 1.5 times heavier than an oxygen atom and a chromium atom is more than 3 times heavier than an oxygen atom, we do not observe any significant mass dependence of the msd values. However, as can be seen from Table 3 and the results presented in Ref. [25], the msd values for $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$ are almost directly proportional to temperature.

Fig. 2 shows the normalised msd values of Al and O ions (i.e. divided by the corresponding average bulk values) for the (0001) $\alpha\text{-Al}_2\text{O}_3$ surface as a function of depth z into the slab at temperatures of 300 and 500 K. As can be seen, the main features observed in Ref. [25] at 10 and 100 K also

appear at these higher temperatures: namely, the Al msd values vary highly non-monotonically as a function of z in the surface region; the outermost Al layer (having bulk alumina on one side and vacuum on the other side) exhibits the largest msd value, while the outermost O layer (sandwiched between the top two Al layers) has a much smaller msd value than the second O layer. Our normalised msd_z values for Al and O at the surface are smaller than those obtained by Baudin et al. [6] but are in good agreement with the quasiharmonic lattice dynamics results of Marmier and Finnis [7].

Next, we focus on the dynamics of the (0001) Cr_2O_3 surface. The normalised Cr and O msd values for this surface are shown in Figs. 3 and 4, respectively, at temperatures of 100, 300, 500 and 700 K. As can be seen, the dynamics of the (0001) $\alpha\text{-Cr}_2\text{O}_3$ surface region displays similar features to its $\alpha\text{-Al}_2\text{O}_3$ counterpart: the Cr msd_z values of the outermost six layers exhibit highly non-monotonic variations as a function of depth z into slab; inside the sixth Cr layer the Cr msds are essentially equal to the corresponding bulk values. As expected, the Cr ions in the outermost surface layer exhibit the largest displacements since there are no neighbouring atoms on one side of the layer to constrain their movements. In contrast, it is somewhat unexpected that the Cr ions in the third and fifth Cr layers have similar msd_z values, while the Cr ions in the fourth Cr layer have very low msd_z values (even slightly smaller than the corresponding bulk values). The latter can be attributed to the relatively large expansion of the fourth interplanar spacing d_{45} (see Table 2). Overall, the msd versus z curves for Cr at the (0001) $\alpha\text{-Cr}_2\text{O}_3$ surface have a very similar shape over the whole investigated temperature range. Similarly, both components of the O

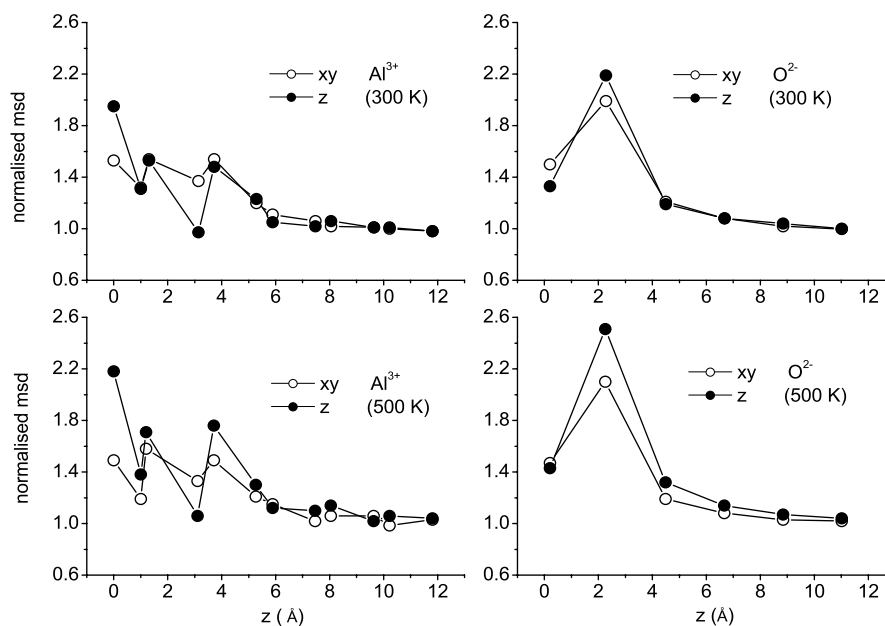


Fig. 2. Normalised mean-square displacements of oxygen and aluminium ions in a slab of (0001) $\alpha\text{-Al}_2\text{O}_3$ as a function of depth z into the slab ($T = 300$ and 500 K). The msd values are divided by the corresponding average bulk msd values (see Table 3). The figure shows only one half of the slab; the curves are essentially symmetrical with respect to the centre of the slab.

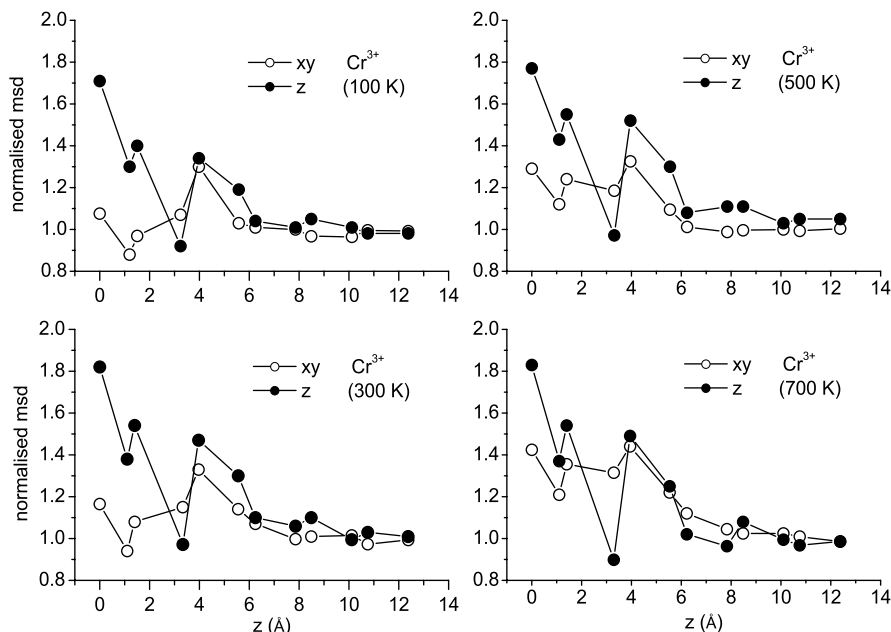


Fig. 3. Normalised mean-square displacements of chromium ions in a slab of (0001) α -Cr₂O₃ as a function of depth z into the slab ($T = 100, 300, 500$ and 700 K). The msd values are divided by the corresponding average bulk msd values (see Table 3). The figure shows only one half of the slab; the curves are essentially symmetrical with respect to the centre of the slab.

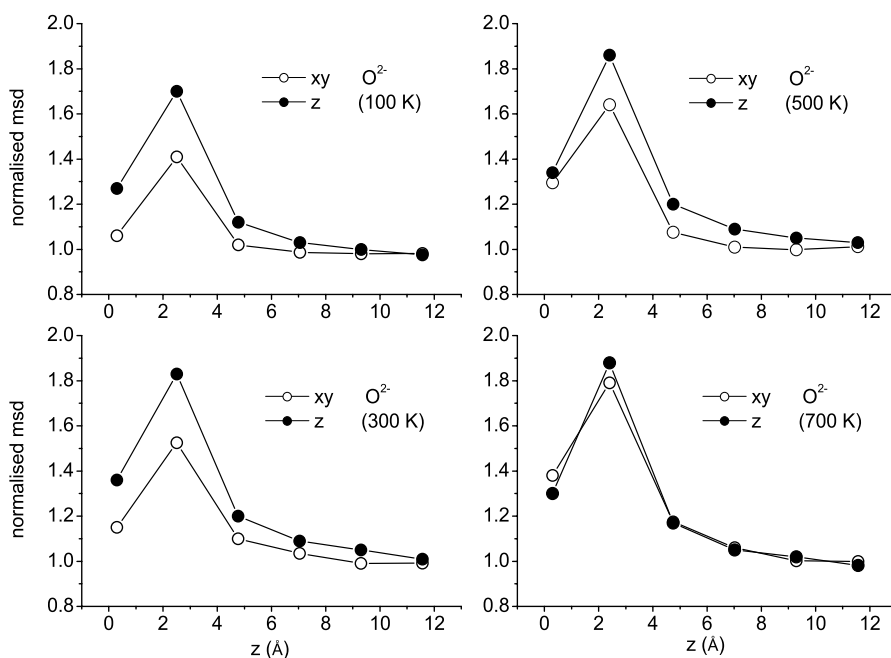


Fig. 4. Same as Fig. 3, except that the msd values are for oxygen ions.

msd versus z curves for (0001) α -Cr₂O₃ (shown in Fig. 4) display nearly the same behaviour over this temperature range (the msds for the higher temperatures converge to their bulk value slightly deeper in the slab). The paramount feature of these curves is that the msd value of the oxygen ions in the second O layer is largest, while the msds in the outermost oxygen layer are significantly reduced. This arises from the large relaxation of the outermost Cr ions, which essentially sink into the first oxygen layer (see d_{12}

in Table 2). Since the O ions are close packed on the (0001) oxygen planes, the movement of these ions in this plane is quite restricted and therefore the msd_{xy} values are smaller than the msd_z values. As pointed out above, the first O layer is sandwiched between the first and second Cr layers, the second O layer is sandwiched between the third and fourth Cr layers, and the third O layer is sandwiched between the fifth and sixth Cr layers. We notice from Fig. 3 that the msd_z value of the Cr ions in the fourth

Cr layer is relatively low, while the other Cr surface layers have relatively large msd_z values. Similarly, from Fig. 4 it can be seen that only O layer number two has a significantly enhanced msd value, while the other surface O layers have moderate msd values. We attribute this behaviour to the overall dynamical balance of the system, which favours the stabilization of the surface. For instance, if the msd values of O ions in a certain layer are high, then the metal ions in the neighbouring layers have relatively low average msd values. Figs. 3 and 4 show that the maximum value of the normalised msd_z for (0001) $\alpha\text{-Cr}_2\text{O}_3$ is around 1.8. Compared to surface and bulk root mean-square displacement ratio data of metals compiled by Somorjai [40], this value is relatively low. For instance, the ratio of the msd_z value for the metallic (110) Cr surface to bulk Cr is 3.2. As Somorjai [40] pointed out, the mean-square displacement of surface atoms is very sensitive to changes in the number and type of neighbouring atoms. The coupling strength between neighbouring atoms also affects the phonon density of states. A recent layer-by-layer analysis of the local phonon density of states for (100) and (110) NiO [10] seems to corroborate the present results. Finally, we have evaluated the mean displacement of the Al and Cr surface atoms in the basal plane. We have found that, at a temperature of $\sim 400^\circ\text{C}$, the combined mean displacement ($\text{md}_{xy}^{\text{Al}} = 0.09 \text{ \AA}$ and $\text{md}_{xy}^{\text{Cr}} = 0.09 \text{ \AA}$) is similar to the difference in the lattice constants a_0 between α -alumina and α -chromia ($\Delta a_0 = 0.19 \text{ \AA}$). This will help in the initial nucleation stage during thin film growth and aid the formation of small islands. We also believe that the mean-square displacements are intimately related to surface mobility, i.e. the larger the msd values the larger the surface mobilities. Incidentally, such a temperature of $\sim 400^\circ\text{C}$ is also consistent with the experiments of Andersson et al. [16,17] who employed substrate temperatures of 280–560 $^\circ\text{C}$ for the successful overgrowth of $\alpha\text{-Al}_2\text{O}_3$ on $\alpha\text{-Cr}_2\text{O}_3$ templates.

4. Conclusions

Molecular dynamics simulations of the (0001) $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$ surfaces have been carried out. Over the investigated temperature range the magnitude of the mean-square displacement values for the atoms in the bulk was found to be nearly linearly dependent on temperature, while the normalised mean-square displacements at the surface of the slabs are almost independent of temperature. The calculations also revealed that the mean-square displacement values of the anions are slightly larger than those of the cations, but essentially independent of ionic mass. The msd_z values of the cations were found to vary non-monotonically as a function of depth z into the slab, with a maximum ratio of msd_z at the surface to bulk of about 2.1 for Al and 1.8 for Cr. The O ions in the outermost oxygen layer were found to have much smaller msd values than in the second oxygen layer. Overall, the dynamics of both the (0001) $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Cr}_2\text{O}_3$ surfaces show a very similar behaviour, which should favour the tem-

plated growth of $\alpha\text{-Al}_2\text{O}_3$ on the (0001) $\alpha\text{-Cr}_2\text{O}_3$ surface. One of the problems for the templated growth of α -alumina on chromia is the large strain due to the lattice mismatch between the two materials. A moderate increase in temperature to $\sim 400^\circ\text{C}$ gives rise to an increase in the mean displacements of the atoms at the surface which is similar to the lattice mismatch between α -alumina and chromia. This will help in the initial nucleation stage and the formation of small islands, and thus facilitate the growth of $\alpha\text{-Al}_2\text{O}_3$ on (0001) $\alpha\text{-Cr}_2\text{O}_3$ templates.

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