Cluster assimilation and collisional filtering on metal-oxide surfaces

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We present the first ab initio molecular dynamics study of collisions between metal-oxide clusters and surfaces. The resulting trajectories reveal that internal degrees of freedom of the cluster play a defining role in collision outcome. The phase space of incoming internal temperature and translational energy exhibits regions where the collision process itself ensures that clusters which do not rebound from the surface assimilate seamlessly onto it upon impact. This filtering may explain some aspects of recent observations of a "fast smoothing mechanism" during pulsed laser deposition.

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The success of pulsed laser deposition of complex oxide films raises the fundamental question of how a disordered distribution of incoming clusters incorporates seamlessly into highly ordered crystals with complex unit cells. In pulsed laser deposition, a laser pulse impinges upon a target and ejects hot material into a plasma plume which then condenses upon a growing substrate[1]. With empirical tuning of parameters such as laser wavelength and energy density, laser pulse width and separation, partial pressure of the ambient gas, and substrate temperature, the resulting film can be made to grow smoothly and nearly defect free[2]. Little is known about what underlies fundamental processes these external parameters control. In recent years, sub-second time-resolved in situ x-ray measurements of growth by this process have become possible[3, 4]. These experiments suggest that incoming clusters from the plume are incorporated into the substrate on sub-millisecond time scales in a "fast smoothing mechanism" which occurs too quickly to be explained by traditional diffusional smoothing[1, 5]. The present work addresses the question of whether smoothing mechanisms exist over the time scale of the actual collisions between the clusters and the surface.

To address the existence of such collisional mechanisms, atomistic, as opposed to continuum, descriptions of growth are most appropriate. Current atomistic studies of crystal growth employ a number of methods, such as kinetic Monte Carlo[6, 7, 8], molecular dynamics based on classical interatomic potentials[9, 10, 11], combinations of the two[12, 13], accelerated molecular dynamics[14], and ab initio calculations of already deposited material[15, 16, 17]. However, kinetic Monte Carlo methods, by their nature, handle only diffusive events, not actual deposition dynamics. Although classical molecular dynamics can address collisions, the use of interatomic potentials raises the issue of accuracy, particularly in oxides, which generally have a number of different atomic species and complex physical chemistry. While ab initio studies of already deposited material give insights into metastable structures and transition states, they do not do so for the kinetic mechanisms active during collisions. To study such mechanisms, this Letter presents the first ab initio molecular dynamics calculations of collisions between metal-oxide clusters and surfaces, with magnesium oxide selected as a simple model system.

Methods — All density-functional theory[18] calculations below employ the local density approximation[19] and use the total-energy plane-wave pseudopotential technique[20] with a 20 hartree (20 H) cutoff. The pseudopotentials include non-local corrections of the Kleinman-Bylander form[21] for the p and d channels.

We represent the MgO (001) surface with a 3 × 3 periodic supercell and three layers of atoms. The surface slabs are separated by 12.10 Å or 18.15 Å of vacuum for cold and hot incoming clusters, respectively. The in-plane lattice constant of the supercell (8.55 Å) corresponds to that of the relaxed bulk crystal. Finally, we integrate over the Brillouin zone for this wide band-gap insulator using a single k-point at the zone center.

For molecular dynamics, we employ the Verlet algorithm[22] using a time step of 2.04 fs. We maintain the electrons within 0.1 mH of the Born-Oppenheimer surface using preconditioned conjugate-gradients within the analytically continued functional approach[23]. These parameters conserve total energy to within 3 mH (0.3% of the collision energy) throughout. The initial condition of the slab is taken to be its fully-relaxed vacuum configuration at zero temperature, with the bottom layer fixed at bulk locations, a constraint also maintained during the molecular dynamics.

To study incorporation of clusters beyond the size of simple molecular units, we study collisions with the eight-atom (N_{cl} = 8) cubic “magic cluster”[24]. To explore the role of internal degrees of freedom, we consider otherwise identical collisions with both “cold” and “hot” incoming clusters. We prepare the cold cluster by full relaxation in vacuum and the hot cluster by adiabatic heating (with no net momentum or angular momentum) to an internal kinetic energy of K_{int} = 0.057 H. This energy corresponds to an internal temperature of T = K_{int}/(3N_{cl}k_B/2) ~ 1500 K, well below the bulk melting temperature, both ab initio (3110 K[25]) and experimental (3250 K[26]). Finally, we give the incoming
clusters a translational kinetic energy representative of the range (\(\sim 10\) to \(\sim 100\) eV) which yields smooth growth in energetic deposition\[1, 27\]. In particular, we choose 1 H (\(\approx 27.21\) eV), near the geometric mean of this range.

Results — Figure 1 presents snapshots of our raw results at representative times. The central result for the cold cluster (top row) is that it rebounds and does not bind to the surface. Initially (\(t = 0.05\) ps), the cold cluster approaches the surface. After contact of the electron clouds, the cluster compresses while pushing atoms on the surface into the slab (\(t = 0.20\) ps). The cluster then rebounds into the environment (\(t = 0.35\) ps) and does not contribute to growth of the surface.

In marked contrast, the hot cluster binds to the surface. Initially (\(t = 0.05\) ps), it approaches the surface with \(\sim 1500\) K of internal kinetic energy and the same impact parameters and velocity as the cold cluster. After contact, this cluster also compresses while pushing atoms on the surface into the slab (\(t = 0.20\) ps). The cluster then rebounds into the environment (\(t = 0.35\) ps) and does not contribute to growth of the surface.

Despite the small number of atoms in the cluster, thermodynamic concepts provide a useful framework for these observations. If we describe the disordering of the hot cluster as “melting,” then the translational energy which the hot cluster is unable to recover is analogous to the latent heat of fusion. We then expect the melted cluster to equilibrate with the underlying surface — first by maintaining a constant temperature while releasing the heat of fusion into the surface, and then by cooling until its temperature matches that of the surface.

The internal temperature of the hot cluster (Figure 2) arguably shows just this behavior. During the impact

FIG. 1: (color) \textit{Ab initio} molecular dynamics snapshots of hot and cold clusters in collision with magnesium-oxide surface: Mg cores (red), O cores (blue), electron-density isosurfaces (white), coordinate axes (upper right panel).

FIG. 2: (color online) Cluster (solid curve) and surface (dotted curve) temperature versus time: impacting, freezing, cooling intervals (left to right, demarked by dashed vertical lines). Dashed horizontal and diagonal lines are guides to the eye.
in the first interval \((t < 0.20 \text{ ps})\), the internal energy of the hot cluster rises to approach the bulk melting point (3100 K). In the second, “freezing,” interval \((0.20 \text{ ps} < t < 0.50 \text{ ps})\), the temperature shows fluctuations around a relatively constant value (horizontal dashed line in Figure 2). Consistent with this, the snapshot from the center of this interval \((t = 0.35 \text{ ps})\) shows a cluster in the midst of changing its topology to conform to the underlying surface. In the third interval \((0.50 \text{ ps} < t)\), the cluster cools while the surface heats as the two equilibrate to a common temperature. Snapshots from this interval \((t = 0.65 \text{ ps} \text{ and } t = 0.80 \text{ ps})\) show the cluster assimilated into the surface, with only thermal vibrational motion remaining.

Within the preceding framework, we make the following predictions. First, the temperature of a cluster which ensures melting upon impact should decrease with increasing incoming translational energy. There thus should be a melting curve in the phase space of incoming cluster temperature versus incoming translational energy, above which the cluster melts upon impact. This curve has a horizontal asymptote at the melting temperature of the cluster for low translational energies, with a horizontal intercept where the translational energy alone is sufficient to melt the cluster. Second, the cluster temperature which ensures binding after impact should increase with increasing translational energy because internal temperature promotes absorption of mechanical energy. There thus should be a binding curve in the phase space above which the cluster binds. This curve has a horizontal intercept at the incoming energy below which the attraction between cluster and surface always suffices to bind the cluster, followed by a vertical asymptote at the translational energy above which the cluster never absorbs sufficient energy to allow binding. Due to the ratio of bulk to surface bonds in the cluster, the translational energy above which the cluster always melts should be greater than the energy below which it always binds, so that, in general, the melting and binding curves cross. Finally, we expect that collisions will begin to disrupt the topology of the surface for translational energies somewhere near the point where there is enough energy to melt cold clusters upon impact, thus defining a disruption curve.

Figure 3 shows this phase space. In particular, Figure 3(a) illustrates a melting curve, binding curve and disruption curve, and indicates points corresponding to the above ab initio molecular dynamics calculations. (The specific placement of the curves and background coloring derive from classical molecular dynamics simulations described below.) The melting and binding curves define four regions in the phase space: assimilation, reflection, tumultuation, and sedimentation. In the region above both curves, clusters bind and melt and subsequently deform and assimilate seamlessly onto the surface upon impact. In the region below both curves, clusters neither bind nor melt and thus reflect intact from the surface.

In the region above the melting but below the binding curve, clusters melt but do not bind and thus tumult from the surface in a deformed state. In the region above the binding but below the melting curve, clusters bind but do not melt and thus sediment intact on the surface. Finally, the disruption curve defines the region where the surface topology is disrupted. The ab initio results conform to this demarcation of phase space, with the translational energy of 1 H such that the cold cluster (lower purple star in Figure 3(a)) reflects and the hot cluster (upper purple star in Figure 3(a)) assimilates.

To test whether these conclusions are general and insensitive to details of the underlying interactions, we construct a simple interatomic potential model of a generic divalent ionic crystal in the form of a Coulomb interaction and a pairwise short-range repulsion,

\[
U = \frac{1}{2} \sum_{i \neq j} \left[ \frac{q_i q_j}{r_{ij}} \left( 1 - \text{erfc} \left( \frac{r_{ij}}{a_{ij}} \right) \right) + A_0 e^{-\left( r_{ij}/a_{ij} \right)^2} \right],
\]

where we work in atomic units, \(U\) is the total energy of the crystal, \(q_i = \pm 2\) are the ionic charges, \(r_{ij}\) is the distance between atoms \(i\) and \(j\), \(A_0 = 7 \text{ H}\) (fit to compromise between the lattice constant and bulk modulus of MgO) measures the strength of the repulsion between ionic cores, and \(a_{ij}\) is a range parameter defined as the mean ionic radius of atoms \(i\) and \(j\) \((R_{Mg} = 0.66 \text{ Å}, R_O = 1.32 \text{ Å})\). The “erfc” term is part of the short-
range repulsion between ionic cores and serves to remove
the Coulomb singularity when the ionic cores overlap.
This simple model material prefers rock-salt over the
cesium-chloride structure, as does magnesium oxide, and
has a lattice constant and bulk modulus of 5.0 ˚A and
240 GPa, both significantly larger (20% and 50%, re-
spectively) than the corresponding experimental quanti-
ties for magnesium oxide.

Using the above model, we repeat the procedure of the

*ab initio* molecular dynamics calculations in the same
time three-layer 3×3 supercell, but now map the phase space
in detail: on a grid of 40 values of incoming tempera-
ture and 50 values of translational energy, sampling 25
collisions at each phase-space point, for a total of 50,000
trajectories. To explore convergence with system size, we
also study a five-layer 6×6 supercell using 100,000 trajec-
tories. Figures 3(a,b) summarize these results. The blue
intensity of each pixel encodes the probability of melting;
the green encodes that of binding; and the red channel
encodes disruption, overriding blue and green regardless of
cluster behavior. Points where clusters disrupt the
surface thus appear red, whereas points where clusters
assimilate appear cyan, reflect appear black, tumult ap-
pear blue, and sediment appear green. The pixelization of
the figure reflects the discreteness of the sampling and the
fluctuations reflect Poisson statistics (±20%).

Remarkably, the data in both Figures 3(a,b) corre-
spend precisely to the expectations of the physical pic-
ture developed above. In particular, we find the ex-
pected five regions of behavior separated by the anti-
pated curves. Even quantitatively, within the correspond-
ing supercell, the *ab initio* results fall correctly into the
assimilation and reflection regions, despite the relatively
small area of these regions and the quantitative differ-
ces between the *ab initio* and model materials. The
larger supercell results show the same overall behavior,
with quantitative correspondence for the internal tem-
peratures and some rescaling of the translational energy.
The latter effect, we believe, results from a deeper surface
providing a more “cushioned” impact.

**Conclusion** — We present the first direct Born-
Oppenheimer *ab initio* molecular dynamics calculations
to demonstrate that metal-oxide clusters can assimili-
ate seamlessly onto metal-oxide surfaces during the col-
loisonal time scale (~1 ps) — far shorter than diffus-
ional time scales. These calculations, along with exten-
cive classical molecular dynamics simulations and general
physical considerations, support the novel picture that
the internal degrees of freedom of the incoming clusters
play an important role in deposition. The phase space of
incoming temperature and translational energy sum-
maries important features of collision outcome, distin-
guishing regions of melting and binding in terms of curves
whose behavior is easily understood.

The resulting phase diagram leads to new insights into
pulsed laser deposition. Each laser pulse produces an en-
semble of clusters scattered across the phase space. For
translational energies typical of experimental conditions
for smooth growth, the arrangement of regions in the
phase diagram indicates that the collision process itself
provides an effective filter to ensure assimilation of clus-
ters onto the surface *upon impact*. For translational en-
ergies above the crossing of the melting and binding curves,
incoming clusters which manage to bind also melt, and
thus assimilate rather than sediment. We believe that
this result may relate to observations of a “fast smoothing
mechanism” in growth by pulsed laser deposition[11][5].

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