Model for humidity-mediated diffusion on aluminum surfaces and its role in accelerating atmospheric aluminum corrosion

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Abstract

Bare aluminum metal surfaces are highly reactive, which leads to the spontaneous formation of a protective oxide surface layer. Because many subsequent corrosive processes are mediated by water, the structure and dynamics of water at the oxide interface are anticipated to influence corrosion kinetics. Using molecular dynamics simulations with a reactive force field, we model the behavior of aqueous aluminum metal ions in water adsorbed onto aluminum oxide surfaces across a range of ion concentrations and water film thicknesses corresponding to increasing relative humidity. We find that the structure and diffusivity of both the water and the metal ions depends strongly on the humidity of the environment and the relative height within the adsorbed water film. Aqueous aluminum ion diffusion rates in water films corresponding to a typical indoor relative humidity of 30% are found to be more than two orders of magnitude slower than self-diffusion of water in the bulk limit. Connections between metal ion diffusivity and corrosion reaction kinetics are assessed parametrically with a reductionist model
based on a 1D continuum reaction-diffusion equation. Our results highlight the importance of incorporating the properties specific to interfacial water in predictive models of aluminum corrosion.

Introduction

Aluminum and its alloys are lightweight metals used in a wide range of applications, but are susceptible to corrosion under a variety of conditions.\textsuperscript{1–3} Corrosion of aluminum occurs even under standard atmospheric conditions and manifests in the form of metal oxide growth and localized surface pitting, with kinetics that increase with increasing temperature and pH,\textsuperscript{4–8} as well as relative humidity (RH)\textsuperscript{9} and concentrations of dissolved oxygen gas.\textsuperscript{8} The first corrosion species formed upon exposure of bare aluminum to the atmosphere is $\gamma$-alumina, which readily forms in presence of both $O_2$ gas\textsuperscript{10,11} and moisture.\textsuperscript{3,6} This oxide layer is more stable than the pure metal beneath it and reduces the rate of subsequent corrosion.\textsuperscript{12–15} Subsequent formation of corrosion pits on the surface typically occurs due to absorption of antagonists such as halides\textsuperscript{14} within the metal oxide layer. These pits can grow from cracking at the oxide surface due to local mechanical stresses and anodic metal dissolution.\textsuperscript{16} Models for corrosion kinetics are desirable as they can inform service lifetime requirements and potentially guide remediation strategies. However, parameterizing these models is complicated owing to the highly coupled nature of the underlying physicochemical processes including (electro)chemistry, material mechanics, and transport, all of which may be modulated by local surface effects.

Thin, nanoscale water films spontaneously condense on oxide surfaces at ambient conditions.\textsuperscript{17} Because aqueous species can significantly accelerate corrosion, understanding the structure and dynamics of water adsorbed onto the oxide surface and how these factors facilitate ion transport is very important. In the initial stages of corrosion pit development, growth is under ohmic control due to the presence of hydrogen gas or salt. However, at longer time scales and higher pH values, pit growth tends to be diffusion controlled owing
to the presence of a developing salt layer over the pit which regulates ion transport.\textsuperscript{14,18} Electrochemical studies have been performed which measured both the local pH and the current density within pure aluminum corrosion pits, where the pH inside the pits was found to be between 1 and 4. The measured current densities were in agreement with theoretical models based on diffusion-controlled dissolution of aluminum.\textsuperscript{19–22} Because the dissolution of metal within an aluminum corrosion pit can exhibit diffusion-controlled behavior, it is important that a corrosion kinetics model have well-calibrated Al\textsubscript{aq} ion diffusivities. Furthermore, because the aqueous environment over the oxide surface is confined under atmospheric conditions, it is also important that the diffusivities correspond to transport along the surface, rather than through bulk liquid water.

Water films on oxide surfaces have been studied experimentally using synchrotron x-rays\textsuperscript{23} and various kinds of vibrational spectroscopy.\textsuperscript{24–32} In particular, the existence of highly structured water at the oxide interface has been identified and attributed to a strong hydrogen-bonding network through the selectivity of Sum Frequency Generation (SFG) spectroscopy,\textsuperscript{26–32} which has been confirmed by atomic-scale modeling.\textsuperscript{33,34} While this structural information provides valuable insight into the chemistry of the water-oxide interface, it does not directly yield the sort of transport data needed to calibrate a corrosion kinetics model. Concentration-dependent Al\textsubscript{aq} ion diffusion coefficients have been mapped out experimentally,\textsuperscript{4,35} but only for bulk liquid solutions.

Investigation of surface-confined transport is a task that is well-suited for atomistic modeling using molecular dynamics (MD) simulations. Explicit all-atom descriptions of the water film and dissolved ions adsorbed over the oxide layer can help to explain how water binds to the surface. Moreover, MD trajectories of atomic motions also enable the direct measurement of species-specific mass transport properties.

There are examples of previous attempts to model the structure and dynamics of surface water with MD, but no models that include the presence of Al\textsubscript{aq} ions. For example, Ikeda and coworkers used \textit{ab-initio} molecular dynamics (AIMD) based on density functional theory
(DFT) to calculate the diffusion coefficient of Al\textsubscript{aq} ions in a 0.8 M bulk AlCl\textsubscript{3} solution.\textsuperscript{36} Martinez and coworkers used classical MD to simulate the diffusion of dilute [Al(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{3+} ions in bulk TIP-4 water.\textsuperscript{37} Faro and coworkers also used classical MD to study the diffusion of [Al(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{3+} ions in bulk water using the extended simple point charge (SPC/E) water model.\textsuperscript{38} Additionally, there has been work to model the dynamics of water films adsorbed on alumina surfaces at various levels of theory, including the investigations by Réocreux et al.,\textsuperscript{34} Argyris et al.,\textsuperscript{33} and Soleymanibrojeni et al.\textsuperscript{39} However, none of these aforementioned studies included dissolved Al\textsubscript{aq} ions within the water film that are expected to be present during corrosion. While Al\textsubscript{aq} ion diffusion through bulk liquid water has been relatively well quantified, the structure and dynamics of confined water is known to significantly diverge from bulk water, so it is not immediately apparent how this might affect ion transport.

We aim to use MD simulations to predict and understand the diffusivity of dissolved Al\textsubscript{aq} ions to provide much-needed constraints on higher-level models of aluminum surface corrosion kinetics. In doing so, we seek to answer the following questions:

- What is the Al\textsubscript{aq} ion diffusivity through water on alumina surfaces and how does it compare to bulk water?

- How do local conditions at the alumina surface such as ion concentration and humidity effect the diffusivity of water and Al\textsubscript{aq} ions?

- How much water needs to be present on the alumina surface to observe transport properties similar to those seen in bulk water?

- How does Al\textsubscript{aq} ion diffusivity effect corrosion kinetics in aluminum oxide surface water, and under what conditions do we find metal dissolution to be diffusion controlled?

Addressing the first three questions requires MD simulations which delicately balance computational efficiency and accuracy while the last requires making physically reasonable connections to higher-level modeling treatments.
All MD simulations rely on a potential energy function to compute atomic forces needed to integrate trajectories. The decision regarding which potential to use for propagating the dynamics must balance competing factors of accuracy and efficiency. Potentials based on quantum chemistry techniques such as DFT can be highly accurate, but are severely limited in terms of system size and trajectory length. AIMD simulations based on DFT are typically limited to a few hundred atoms and trajectories of 10-100 ps, which can preclude studies at low concentrations and may be insufficient to capture slow diffusive motions. Many popular DFT functionals also do a poor job of capturing temperature-dependent properties of water. For instance, the widely used Perdew–Burke–Ernzerhof (PBE) functional predicts bulk water that is under-dense and over-structured at room temperature. Classical non-reactive models enable time scales and system sizes necessary for capturing concentration-dependent mass transport, but at a loss of chemical accuracy. These potentials are unable to capture relevant chemistry that might occur in our system, such as chemisorption, proton transfer, charge transfer, and reactive solute precipitation.

To overcome these challenges, we develop a modeling framework based on classical MD with a reactive force field (i.e., potential energy function) to predict the structure and transport properties of aluminum ions in water on alumina surfaces. Physical accuracy of the underlying force field is first validated against AIMD simulations. A range of experimental data are then used to design an atomic model of a pristine alumina-water interface that relates water film thickness to the RH of the environment. We apply this framework to map out factors governing the rate of aluminum ion diffusion and obtain quantitative inputs for a reductionist 1D continuum-based model of an aluminum corrosion pit. Our MD results indicate that surface effects can reduce ion diffusion rates by several orders of magnitude, which our continuum model in turn shows plays a strong role in governing overall corrosion kinetics.
Methods

Classical Molecular Dynamics Simulations

All classical MD simulations in this work were performed using the reactive force field model ReaxFF.\textsuperscript{42} The total energy is calculated in Equation 1 as

\[
E_{\text{total}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{tor}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{over}} + E_{\text{under}} + E_{\text{specific}},
\]

where \(E_{\text{bond}}\), \(E_{\text{angle}}\), and \(E_{\text{tor}}\) are bond, angle, and torsional energy terms, \(E_{\text{vdWaals}}\) and \(E_{\text{Coulomb}}\) are pairwise van der Waals and Coulombic terms, \(E_{\text{over}}\) and \(E_{\text{under}}\) are energy penalties for over- and under-coordination of atoms, and \(E_{\text{specific}}\) is an empirical energy correction term. Each energy term other than Coulomb and van der Waals are bond order dependent, with the bond order computed in Equation 2 as

\[
BO'_{ij} = BO'_{ij} + BO_{ij}^\pi + BO_{ij}^\pi^\pi = \exp \left[ p_{bo1} \left( \frac{r_{ij}}{r_{0}^{\sigma}} \right)^{p_{bo2}} \right] + \exp \left[ p_{bo3} \left( \frac{r_{ij}}{r_{0}^{\pi}} \right)^{p_{bo4}} \right] + \exp \left[ p_{bo5} \left( \frac{r_{ij}}{r_{0}^{\pi\pi}} \right)^{p_{bo6}} \right].
\]

Here \(ij\) index atom pairs, and is summed over \(\sigma\), \(\pi\) and \(\pi\pi\) bond types, \(r_0\) is the equilibrium bond distance for atoms \(i\) and \(j\) for the corresponding bond type, and \(p_{bo}\) are empirically determined parameters. Additional details of the ReaxFF method can be found in the literature.\textsuperscript{42–44}

We used the ReaxFF model that was previously used by Soleymanibrojeni and coworkers\textsuperscript{45} for studying aqueous aluminum systems and confined water films.\textsuperscript{39} This parameterization merges the O and H atom terms (plus O-O, H-H, and O-H interactions) from the water/hydrocarbon ReaxFF model developed by Zhang and van Duin\textsuperscript{46} with the Al atom terms (plus Al-Al, Al-O, and Al-H interactions) from the Al/O/H ReaxFF model developed by Zhang and coworkers.\textsuperscript{47} Validation testing of this parameterization against AIMD
simulations is discussed in detail in section .

Molecular dynamics trajectories were integrated using the ReaxFF implementation in the LAMMPS software package\textsuperscript{48,49} with 3D periodic boundary conditions. Isochoric-isothermal ($NVT$) and isothermal-isobaric ($NPT$) simulations were performed at various points in this study using a Nosé-Hoover-style thermostat and barostat.\textsuperscript{50} We note that using a non-stochastic thermostat such as Nosé-Hoover is important in the present application to avoid breaking time-correlated properties such as mass transport through diffusion.\textsuperscript{51} A 0.1 fs time step was used for all simulations and the thermostat and barostat coupling constants were set to 100 fs and 1000 fs, respectively. Partial atomic charges were determined at each time step using the $Q_{eq}$ charge equilibration procedure implemented in LAMMPS\textsuperscript{49} with the relative accuracy threshold set to $10^{-6}$.

Schematics for the two different types of system configurations considered in this work are shown in Figure 1. These configurations include “bulk” liquid water in the condensed phase and a thin “film” of water that is pooled on the naturally occurring aluminum oxide ($\gamma$-alumina) surface.

Simulations of bulk liquid water were performed at 300 K and 1 atm using a cubic cell containing 8,000 water molecules at an initial density of 1.0 g·cm$^{-3}$. The equilibrium density predicted by ReaxFF was determined through a two-step process starting with an initial 100 ps $NVT$ thermalization followed by $NPT$ dynamics performed with an isotropic barostat. The $NPT$-averaged cell vectors converged within 100 ps yielding a density of 0.999 g·cm$^{-3}$. For each Al$_{aq}$ ion concentration of interest, aluminum atoms were then randomly added in a uniformly distributed manner to the simulation cell, avoiding close atom-atom contacts of 2 Å or less. The minimum and maximum numbers of Al atoms were 1 and 725, corresponding to concentrations of 0.05 M and 1.0 M, respectively.

Simulations of surface water involved a more complicated construction. First, a unit cell for $\gamma$-alumina was taken from Krokidis et al\textsuperscript{52} and was oriented such that the (110) facet was aligned in the $+z$ direction. The (110) facet was chosen because of its relative abundance
at room temperature due to low surface energy and because of its high capacity for surface hydroxylation.\textsuperscript{53–55} The cell was then replicated to a size of $4 \times 4 \times 1$ and equilibrated with a 250 ps $NPT$ trajectory using an anisotropic barostat at 300 K and 1 atm. The resulting equilibrium cell vectors were $50.806 \times 47.719 \times 11.094$ Å$^3$, corresponding to an oxide layer with a thickness similar to experimental samples.\textsuperscript{10,11,11,56–58} Afterwards, a vacuum space of 108.906 Å was added to expose the (110) surface normal to the $+z$ direction and the bottom half of the slab was held fixed to simulate the effect of the bulk crystal.

The surface was passivated with hydroxyl groups according to alumina surface hydration studies by Weschert et al.\textsuperscript{59,60} Water molecules were then randomly distributed over the passivated surface and equilibrated with $NVT$ dynamics for 100 ps, yielding a water film that was $\Delta z \approx 5$ Å thick. After equilibration, additional monolayers ($\Delta z \approx 3$ Å) of water molecules were added above the existing water film and re-equilibrated for 100 ps as necessary to reach the desired water film thicknesses of approximately 5 Å and 22 Å. These water film thicknesses correspond to 30% and 90% relative humidity (RH) conditions respectively,
according to x-ray photoelectron spectroscopy (XPS) analysis performed by Deng et al.\textsuperscript{17}

Configurations with solvated Al atoms were prepared from this state following the same approach as described for the bulk liquid water system. Initial concentrations were set assuming that the Al was uniformly distributed in the surface water film.

In all simulations of surfaces, a harmonic wall was placed at the upper $z$-edge of the simulation cell to prevent any water vapor from potentially binding to the bottom of the alumina slab across the periodic boundary. The harmonic wall has the form shown in Equation 3

$$E = \begin{cases} 
\varepsilon(z - z_0)^2 & z \geq z_0 \\
0 & z < z_0 \end{cases}$$

(3)

where $\varepsilon$ is the spring constant of the wall, $z$ is the distance between an atom and the periodic boundary along the $z$-direction, and $z_0$ is the cutoff distance along $z$ for the interaction.\textsuperscript{61} The harmonic wall parameters $\varepsilon$ and $z_0$ were chosen to be 500 kcal-mol$^{-1}$ and 2.5 Å respectively.

Diffusion coefficients for a given chemical species (H$_2$O or Al$_{aq}$) were calculated from mean-squared displacements (MSD) as defined in Equation 4 using the so-called Einstein formula\textsuperscript{62}

$$\text{MSD}(t) = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$$

(4)

for all atoms averaged over the spatial region of interest and over time origins. To efficiently calculate the MSD over all possible time lags, we used a fast Fourier transform approach treating the MSD as an autocorrelation function for the position of the particles.\textsuperscript{63} Diffusion coefficients were calculated from the MSD using Equation 5

$$D = \lim_{t \to \infty} \frac{\text{MSD}(t)}{2nt},$$

(5)
Figure 2: Overview of the block-bootstrapping procedure used to calculate uncertainty in diffusion coefficients for Al\textsubscript{aq} ions in bulk water at $T = 300$ K, $C = 0.1$ M. (a) Representative Al\textsubscript{aq} ion MSD curves for each 100 ps block of the 1000 ps trajectory. (b) Sampling distribution of the mean Al\textsubscript{aq} ion diffusion coefficient calculated by bootstrap resampling of the 10 diffusion coefficients obtained from the MSD curves in panel (a).

where $D$ is the diffusion coefficient and $n$ is the number of dimensions in which the particles can diffuse ($n = 2$ for surface diffusion and 3 for diffusion in bulk water).

In the simulations of Al\textsubscript{aq} ions in surface-adsorbed water thin films, $z$-dependent diffusion coefficients were computed by averaging over the MSD for particles restricted to spatial $z$-bins with a width of 2.5 Å. The origin for the bins started from the alumina-water interface and ended at the water-vacuum interface. Only particles which resided within the $z$-bin over the entire time lag were averaged into the MSD for that bin. We computed separate spatially resolved diffusion coefficients for water and Al\textsubscript{aq} ions and the Al\textsubscript{aq} diffusion coefficient was treated as undefined for spatial bins with no ions present.

The 95% confidence interval on each diffusion coefficient was calculated from a block-bootstrapping approach as outlined in Figure 2. The bootstrapping procedure was as follows:

1. Each 1000 ps MD trajectory was separated into 10 non-overlapping blocks of 100 ps.

2. An MSD curve was generated for each 100 ps block out to a 50 ps time lag averaging
over all particle types of interest. Separate MSD curves were generated for water and Al\textsubscript{aq} by tracking positions of water oxygen and Al ions.

3. A diffusion coefficient was calculated from each MSD curve from the slope obtained through a linear regression over the time interval $5 \leq t \leq 50$ ps. This yielded a set of 10 independent evaluations of the diffusion coefficient.

4. From the set of 10 diffusion coefficients, we randomly resampled with replacement $10^5$ times to obtain a bootstrap sampling distribution of the mean diffusion coefficient.

5. The 95% confidence interval was computed from the top and bottom 2.5% percentiles of the sampling distribution.

Figure 2(a) shows a representative set of 10 MSD curves and Figure 2(b) shows the resulting bootstrap sampling distribution of the mean diffusion coefficient obtained from those curves. We note that even with only 10 independent samples, the resulting sampling distribution exhibits approximately normal characteristics.

All trajectory snapshots were rendered using OVITO.$^{64}$ OVITO was additionally used to analyze the partial radial distribution functions (RDFs) and perform spatial property binning. RDFs were analyzed with a bin size of 0.04 Å, spatially resolved diffusion coefficients were computed over atoms in bins of 2.5 Å, and all other spatially resolved properties were binned in increments of 0.1 Å.

**Ab Initio Molecular Dynamics Simulations**

Ab initio molecular dynamics (AIMD) simulations were performed in order to benchmark the ReaxFF model. All AIMD simulations were performed with CP2K$^{65}$ using the DZVP-MOLOPT-SR-GTH basis set and either PBE$^{66}$ or Becke-Lee–Yang–Parr (BLYP)$^{67,68}$ density functionals with a D3 dispersion correction.$^{69}$ Calculations were spin-polarized using Γ-point sampling with the orbital transformation $^{70}$ and Gaussian plane wave$^{71}$ methods. A 400 Ry
cutoff was used for the finest grid with a relative cutoff of 40 Ry. The SCF convergence threshold was set to $1.0 \times 10^{-6}$ H.

Simulations of charge-neutral bulk liquid water were performed using a 3D periodic cubic simulation cell with 100 water molecules and side lengths of 14.423 Å such that the density was 1.0 g·cm$^{-3}$. In simulations of Al$_{aq}$, one water molecule was replaced with an Al metal center, leading to an effective concentration of 0.55 M. All AIMD trajectories were integrated using a coarse 1.0 fs time step owing to the computational cost of the simulations; these AIMD simulations were only used to predict non-reactive structural properties of water and Al$_{aq}$ systems. An initial $NVT$ equilibration was performed with a Langevin thermostat$^{72,73}$ for a minimum of 20 ps with the $\gamma$ parameter set to 0.005 fs$^{-1}$. Production runs of 100 ps were performed using a Nosé-Hoover thermostat with a time constant of 41.696 fs.

**1D Diffusion-Reaction Model**

We constructed a reductionist model of an aluminum corrosion pit to assess the impact of ion diffusivity on corrosion kinetics. This model was based on a discretized form of the 1D diffusion-reaction partial differential equation$^{74}$

$$\frac{\partial}{\partial t} C(x_i, t_n) = D \frac{\partial^2}{\partial x^2} C(x_i, t_n) + R(C_0^n).$$  \hspace{1cm} (6)

In Equation 6, $C$ is the concentration of Al$_{aq}$ ions, $D$ is the Al$_{aq}$ ion diffusion coefficient, $R$ is a reaction term acting as a source of Al$_{aq}$ ions, and $x$ and $t$ are position and time domains, respectively. Our model considered two cases for a corrosion pit and schematics of the initial-boundary-value problem are shown in Figure 3. In one case, the corrosion pit was immersed in water (left). In the other case, the pit was non-immersed and the only water available to mediate ion transport was that arising from exposure to humid air leading to the development of a thin water film on the surface (right). Corrosion was assumed to occur at a “crack” in the alumina surface at the interior-most point of the pit and was modeled
as an inexhaustible source of Al\textsubscript{aq} ions. The spatial domain was 1 \( \mu \text{m} \) long with a closed boundary at \( x = 0 \) and an open boundary at \( x = 1 \mu \text{m} \).

The diffusion-reaction equation was solved numerically on a grid using an Euler-type propagator\textsuperscript{75}

\[
\frac{C_i^{n+1} - C_i^n}{\Delta t} = D \frac{C_{i+1}^n - 2C_i^n + C_{i-1}^n}{\Delta x^2} + R_i^n
\]  

with a Dirichlet boundary condition such that Al\textsubscript{aq} ions could diffuse out of the system (Equation 7). Here \( i \) indexes the \( x \) dimension and \( n \) indexes time. The time step was set to 1 fs and the grid spacing was set to 0.033 \( \mu \text{m} \), which were verified to yield good conservation behavior. The diffusion coefficient \( D \) was set to values predicted for Al\textsubscript{aq} ion transport in bulk liquid water or surface water as calculated from the atomistic simulations in this work. For a given simulation, \( D \) was treated as a constant whose value was set based on the temperature, humidity/pooling conditions, and for the maximum possible ion concentration (\( C = 1.0 \text{ M} \), see below).

To incorporate a corrosive process, a point source of Al\textsubscript{aq} ions was added at \( x = 0 \) in the
form of a concentration-dependent reaction term $R$\textsuperscript{76,77}.

$$R(C^n_0) = k \left(1 - \frac{C_0^n}{C_{eq}}\right).$$  \hspace{1cm} (8)

Here $R$ is the reaction rate at the ion source and $C_0^n$ is the ion concentration at the first spatial mesh point (i.e., $x = 0$). Parameters $k$ and $C_{eq}$ are empirically derived constants, where the base metal loss rate $k$ was chosen to be $1.0 \times 10^{-10}$ mol·L$^{-1}$·s$^{-1}$ based on the mass loss of an aluminum alloy from accelerated aging experiments\textsuperscript{78} and the equilibrium saturation concentration $C_{eq}$ was chosen to be 0.1 M based on multi-phase field modeling results\textsuperscript{79}. The initial concentration of Al$_{aq}$ ions in all simulations was set to zero and the simulations were propagated in time until a steady state was reached.

It should be noted that simulations corresponding to the immersed and non-immersed cases were performed in an entirely decoupled manner using the same basic equations. In our 1D model, the concept of “bulk” and “surface” are necessarily abstract and correspond only to the choice for the diffusion constant and whether its value derived from a “bulk” or “surface” MD simulation. This choice lends itself to a bounding study, but does not consider situations in which the pit is partially filled with water nor does it allow for features of 2D or 3D flow, such as simultaneous transport through the bulk and along a surface.

Results

Validation of ReaxFF model

The ReaxFF model chosen for this work is likely among the best performing models for aqueous aluminum systems\textsuperscript{45} and has been used previously to study strongly confined water adsorbed on alumina surfaces\textsuperscript{39}, but it has not been extensively validated. Before applying this model to study Al$_{aq}$ ion transport and solid aluminum-containing systems, we first performed a number of benchmark calculations to assess its accuracy in describing the
structural properties of condensed phases. Below we compare the structural properties of pure water and water containing Al$_{aq}$ ions at a concentration of 0.5 M as obtained from NVT simulations performed using ReaxFF and with AIMD using two different DFT functionals (PBE-D3 and BLYP-D3). We also assess the equilibrium structures of aluminum and γ-alumina crystals.

Focusing first on pure water, Figure 4 shows the O-O, O-H, and H-H partial RDFs obtained at 300 K using ReaxFF, with comparisons to DFT-based AIMD simulations and experiment. It is immediately apparent when treating the experimental RDFs as ground truth that ReaxFF does a better job describing water structure than PBE-D3. It is well known that PBE-D3 predicts overly structured and under-dense water at 300 K, so it is not surprising that this commonly used functional performs poorly here. ReaxFF does about as well as BLYP-D3 at modeling the experimental RDFs at this temperature. Like BLYP-D3, the ReaxFF errors in the water partial RDFs are most prominent at small separation distances. Both BLYP-D3 and ReaxFF accurately reproduce long-range structure, with ReaxFF performing better in some instances (e.g., the O-O interaction). The self diffusion coefficient of water calculated for ReaxFF is similarly in good agreement with experiment.
at this temperature \((2.384 \times 10^{-5} \text{ cm}^2\text{ s}^{-1} \text{ and } 2.299 \times 10^{-5} \text{ cm}^2\text{ s}^{-1}\) respectively).

Figure 5: Partial radial distribution functions for \(\text{Al(H}_2\text{O)}_6\) species in bulk liquid water using ReaxFF with comparison to AIMD at \(T=300\text{ K}\). ReaxFF and AIMD simulations performed at \([\text{Al}]=0.5\text{ M} \text{ and } 0.55\text{ M}, \text{ respectively}. \) (i) Representative solvated \(\text{Al(H}_2\text{O)}_6\) species. Asymmetry in axial and equatorial coordination accounts for the splitting in the ReaxFF Al-O and Al-H partial RDFs. (ii) Representative “correlated water dimer.” Existence of these dimers accounts for the small signal in the ReaxFF O-O partial RDF at around 2.5 Å.

Analogous partial RDFs are shown in Figure 5 for bulk liquid water containing solvated \(\text{Al}_{\text{aq}}\) ions as predicted with ReaxFF and the PBE-D3 and BLYP-D3 DFT functionals. Water-water related interaction pairs are shown in the top row and aluminum-water interaction pairs are in the bottom row. Note that a meaningful RDF for Al-Al interactions cannot be computed with DFT-sized cells despite the high \(\text{Al}_{\text{aq}}\) concentration, as the DFT simulation cell only contains a single Al atom.

ReaxFF predicts that water-water interactions become considerably less structured in the presence of \(\text{Al}_{\text{aq}}\) ions, whereas both DFT functionals predict O-O, O-H, and H-H RDFs that are much closer to their pure-water baselines. The small signal in the ReaxFF O-O partial RDF at around 2.5 Å results from the existence of a small number of correlated water dimers. These water dimers, which have the corresponding 2.5 Å average separation...
distance shown in panel (ii), account for 3.8% of all the water in the system after the initial 100 ps thermalization. This amount decays to 1.5% after an additional 1000 ps of simulation time. Comparison against BLYP-D3 indicates that errors in the water-water interactions described by ReaxFF are modest overall, with the locations and values of most minima and maxima in the distributions being largely consistent.

Larger discrepancies are found in the aluminum-water interactions predicted by ReaxFF. The most notable is an asymmetry in the six water molecules that coordinate to the Al_{aq} ions. Experimentally, the Al-O bond distance in the [Al(H$_2$O)$_6$]$^{3+}$ ion have been found to be between 1.87 and 1.90 Å.\textsuperscript{82,83} ReaxFF predicts two distinct coordination distances of 1.85 Å and 2.23 Å that respectively correspond to equatorially and axially coordinated water molecules. This can be clearly seen in the unexpected splitting in the ReaxFF Al-O and Al-H partial RDFs for r < 3 Å. In contrast, both DFT functionals predict a single coordination distance. We note that both ReaxFF and DFT predict six-fold coordinated Al_{aq} ions under these conditions, which is consistent with experiments.\textsuperscript{82,84,85} The onset of the second solvation shell occurs at the same location with ReaxFF and both DFT functionals. The structure of the ReaxFF second solvation shell is less well described compared to DFT, but does conform well with the structure of experimentally-derived RDFs based on x-ray diffraction measurements of concentrated AlCl$_3$ solutions performed by Caminiti and coworkers\textsuperscript{82} (not shown).

These predictions for the aluminum-water interactions are different from those reported by Soleymanibrojeni and coworkers,\textsuperscript{45} who also used this ReaxFF potential to study aluminum ion solvation in water. Their work considered a single solvated Al ion with its electric charge held fixed at +3e along with three OH$^{-}$ counter-ions with net charges fixed at -1e. When we attempted a similar approach, we observed dynamic bond-breaking and formation events, so in the present work we allowed the $Q_{eq}$ charge equilibration procedure to determine the charge of all atoms at each time step. It is possible that the observed differences in aluminum ion-water interaction can be accounted for by this different charge
scheme. While the accuracy of ReaxFF relative to DFT is non-optimal, the simulations
described in this work required ns-long trajectories with many thousands of atoms, so the
advantages in computational cost and scaling that ReaxFF provides over DFT cannot be
overlooked.

Table 1: Cell parameters and densities for bulk materials calculated with ReaxFF from NPT-
MD at 300 K and via 0 K cell optimization for PBE-D3. ReaxFF percent differences (%Δ)
were computed with respect to PBE-D3 values. Experimental room temperature densities,
α-alumina cell parameters, and aluminum cell parameters provided for comparison.

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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>%Δ</td>
<td>-0.100</td>
<td>2.749</td>
<td>0.013</td>
<td>3.186</td>
</tr>
</tbody>
</table>

Equilibrium structural properties for condensed phases are collected in Table 1 and in-
clude liquid water, γ-alumina, and face-centered cubic (FCC) aluminum. These materials
were chosen as they comprise the principal components of an aluminum corrosion pit: the
corroding metal, the protective oxide layer, and the aqueous medium which metal ions diffuse
through. While aluminum metal is not explicitly present in the MD diffusion simulations,
it may be explicitly incorporated in future work as it implicitly exists in our simplified 1D
diffusion-reaction model.

Simulation predictions for water were obtained at 300 K and 1 atm using NPT-MD.
The PBE-D3 predictions for both Al and γ-alumina crystals were obtained through cell
optimization at 1 atm whereas the ReaxFF results were obtained via NPT-MD at 300 K.
The a, b, and c cell parameters for γ-alumina correspond to an orthorhombic conventional
cell used to describe the monoclinic crystal. 52

The ReaxFF parameters for Al-Al and Al-O bonding, non-bonding, and coordination
energies were originally fit to reproduce equations of state for FCC Al and α-alumina. 47 It is
perhaps not surprising that ReaxFF does well at reproducing the 0 K lattice parameters for
Al and α-alumina calculated with PBE-D3, which the model was trained against. Similarly,
Figure 6: Two-mode (Langmuir + pooling) water sorption model on alumina single-crystal surfaces. Sorption model is fitted to XPS results collected by Deng et. al. for water sorption on alumina single-crystal thin films at 295 K.

the water-specific parameters of this ReaxFF model were trained to fit water density and structure, which we confirm in the present work has good agreement. However, we find that ReaxFF yields modest errors in the density of $\gamma$-alumina, which was not included in the original training set. This may be because the time-averaged room-temperature Al-O bond distances in $\gamma$-alumina are slightly larger with ReaxFF than with PBE-D3 at 0 K (1.845 Å and 1.832 Å respectively). The source of this difference may be partly a thermal effect and could also indicate a modest error in the strength of Al-O bonds. We do not anticipate that these differences will have a strong bearing on our results, as the focus of this study is on mass transport through the adsorbed water films on the $\gamma$-alumina surface.
Structure and transport properties of water on alumina surfaces

The primary adjustable parameter in our simulation cell construction is the number of water molecules on the alumina surface, which upon thermalization yields a water film thickness. In order to relate this to a typical environmental descriptor such as RH, we required a description of water film thickness as a function of RH on alumina surfaces. Experimental XPS data for water on γ-alumina single-crystal surfaces at 295 K collected by Deng and coworkers\textsuperscript{17} reveals a sigmoidal shape of the adsorption isotherm, which is indicative of strong monolayer bonding at low RH followed by the formation of a liquid-like layer at higher RH. Therefore, we chose a two component Langmuir plus pooling model to fit the data using Park’s clustering model\textsuperscript{88} for the “pooling” portion. The experimental water layer thicknesses and fitted two-mode adsorption model are shown in Figure 6.

\begin{equation}
L = \frac{S_0 \cdot \beta \cdot \text{RH}}{1 + \beta \cdot \text{RH}} + \alpha \cdot \text{RH}^n \tag{9}
\end{equation}

Equation 9 shows the form of the model for water film height $L$ as a function of RH. In this model $S_0$ is the effective thickness of the Langmuir layer at capacity, $\beta$ is the Langmuir affinity, and $\alpha$ and $n$ are pooling parameters. The first term on the right-hand side corresponds to the Langmuir sorption mode and the second term corresponds to the pooling mode. Optimized values for the model parameters were obtained by a least-squares fit and are collected in Table 2. These data provide an additional validation test for the ReaxFF potential: the effective capacity of the Langmuir layer of the XPS-based model is approximately 3.9 Å, while the observed thickness of the first monolayer obtained from our ReaxFF simulations is quite similar at $\approx$5 Å. The first monolayer thickness was determined from MD based on when the water density profile converges to a bulk-like density, and is discussed in more detail immediately below.

Figure 7 shows how various structure and transport properties vary as a function of
Table 2: Langmuir + pooling sorption model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>4.04 Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.271 (unitless)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$2.46 \times 10^{-4}$ Å</td>
</tr>
<tr>
<td>$n$</td>
<td>2.46 (unitless)</td>
</tr>
</tbody>
</table>

Figure 7: (a) Water oxygen mass population, (b) Al ion mass population, (c) mean cross-sectional charge, and (d) water self-diffusion as a function of height within the adsorbed water film. Horizontal dashed lines indicate values for bulk liquid water. Results shown for a 2 nm thick water film with $[\text{Al}] = 1.0$ M and $T=300$ K.

height inside the adsorbed water film at 90% RH, $T = 300 \, K$, and $[\text{Al}] = 1.0$ M. From the 1.5 ns of trajectory collected, the last 500 ps was used for analyzing the time-averaged properties of interest. These height-dependent properties from Figure 7 span the thickness of
the adsorbed water film, and include (a) the population of water oxygen, (b) the population of aqueous Al ions, (c) the mean cross-sectional charge through the water film, and (d) the self-diffusion coefficient of water. Temporal convergence of these properties was tested by comparing separate time averages computed for \( t \in [1000, 1200] \) ps and \( t \in [1300, 1500] \) ps.

From \( z = 10 \) Å to \( z = 15 \) Å, which is near the alumina-water interface, the water molecules are highly structured. This can be seen most clearly from the relative water density in panel (a). In this region there is a distinct chemisorbed water film containing -OH groups bonded to the alumina surface, and above that there is a layer of highly structured water that is hydrogen-bonded to the surface hydroxyls. Panel (d) shows that the average water self-diffusion coefficient in this region is several orders of magnitude smaller than bulk-liquid water diffusion at this temperature.\(^8\) No Al\(_{aq}\) ions are present in this region of the water film, and the mean cross-sectional charge oscillates strongly near the alumina-water interface due to the surface potential between water and the oxide. These results indicate it is highly unfavorable for Al\(_{aq}\) ions to penetrate this highly structured, ice-like layer of the water film. The implication for aluminum corrosion is clear: in systems where an adsorbed water film thickness is 5 Å or less (around 30% RH), the entire water film will assume an ice-like structure, and dissolved Al\(_{aq}\) ions will be highly immobile. It is likely that this phenomena is closely related to the fact that atmospheric corrosion of pristine aluminum is observed to begin only at RH greater than about 70%.\(^{3,89,90}\)

Réocreux and coworkers\(^{34}\) predicted similar structural and transport features of water near the \( \gamma\)-alumina/water interface with PBE-D3 AIMD simulations. In their study, they found water near the interface to be overstructured, with a severely dampened self-diffusivity with respect to bulk liquid water. Our results are also similar to classical MD simulations performed by Deshmukh et al.\(^9\) of SPC/E water on MgO surfaces. Their simulations showed that water in the adsorbed film was highly ordered in the two monolayers closest to the oxide surface. The ability of water to form a hydrogen-bonding network at an oxide surface has been shown to depend heavily how the oxide is hydroxylated. Surface hydroxylation can
either facilitate or disrupt water’s ability to hydrogen bond. The extent of hydroxylation will depend on various factors, such as the exposed crystal facet, the pH of the aqueous environment, and surface roughness.

In the region of \( z = 15 \, \text{Å} \) to \( z = 27 \, \text{Å} \), the water assumes a much more bulk-like character. The water density is mostly uniform and close to that of bulk liquid water. This bulk-like character is further evidenced by the mean cross-sectional charge, which is approximately zero. Classical MD simulations performed by Argyris et al. of SPC/E water adsorbed on an \( \alpha \)-alumina surface similarly found that water assumed bulk-like character around 10 Å from the oxide interface. The population of \( \text{Al}_{\text{aq}} \) ions is entirely localized in this region, despite having initial positions with a uniform random distribution over the entire water film. The ion density is largest near the water-vacuum interface and exhibits structure that we attribute to the surface polarization of the water film. In this region of the film, water diffuses nearly as fast as in bulk liquid (panel (d), horizontal dashed line), but cross-inspection with panel (b) shows that the diffusivity of water decreases where \( \text{Al}_{\text{aq}} \) ions are most concentrated.

From \( z = 27 \, \text{Å} \) to \( z = 32 \, \text{Å} \), the water density drops off rapidly at the water-vacuum interface, eventually assuming a vapor-like phase. This results in the much faster water self-diffusion seen beyond 30 Å. As with the region near the alumina-water interface, there are no \( \text{Al}_{\text{aq}} \) ions in this region. It can be seen from panel (c) that an average negative charge develops at the water film surface as a manifestation of the water surface polarization. A negatively signed surface potential has also been calculated from AIMD and classical MD, though the actual magnitude of the surface potential as computed from molecular simulation has been shown to be highly sensitive to simulation details and finite size effects. This polarization is induced by anisotropy in the population of water dipole moments near the surface, which originates from the reorientation of water to maximize hydrogen bonding in an under-coordinated environment. The localization of ions in these simulations is sensible, as all \( \text{Al}_{\text{aq}} \) is in the form of the hexaaqua ion, and will therefore have a tendency to strongly
interact with the more-ordered hydrogen bonding network at the surface, as is the case with hydronium ions.\textsuperscript{101}

**Effect of Al\textsubscript{aq} ion concentration on surface water properties**

Within a corrosion pit, local metal ion concentration may transiently exceed equilibrium saturation limits. Therefore, it is important to understand the role that high Al\textsubscript{aq} ion concentration plays on the height-dependent properties observed in Figure 7. To this end, additional Al\textsubscript{aq} diffusion simulations were performed using adsorbed water films with a range of increasing ion concentrations, spanning from a pure water film to a highly concentrated layer of 1.0 M. In doing so, we aimed to determine which of the observed properties are intrinsic to the water film itself, and which, if any, are induced or altered by the ion concentration.

Figure 8 shows how the water density, mean cross-sectional charge, and Al\textsubscript{aq} ion density
profiles vary as a function of Al\textsubscript{aq} ion concentration inside the water film at 90\% RH and $T = 300$ K. Note that the concentration of Al\textsubscript{aq} ions increases from 0.0 M to 1.0 M going from top to bottom and that the alumina/water interface is located at $z = 10$ Å. The principle features of both the oxygen density and mean cross-sectional charge first observed for the 1.0 M case in Figure 7 are also present here in the pure water case (compare top and bottom rows in Figure 8). This indicates that the Al\textsubscript{aq} ions do not appreciably perturb the water structure beyond the subtle coordination effects identified in Figure 5. There is a minor shift in where the negative surface charge is centered with increasing Al\textsubscript{aq} concentration. Likewise, the pure water film expands by 1-2 Å with respect to highly concentrated water films.

As Al\textsubscript{aq} ion concentration increases, the structure of the water film and the average charge distribution across it remains very similar. Even very high ion concentrations do not appear to disrupt these features that are present in the pure water film. There are however systematic trends in the Al\textsubscript{aq} ion distributions with increasing concentration. As can be seen in the right-most column of Figure 8, all of the Al\textsubscript{aq} ions localize within the middle portion of the water film regardless of Al ion concentration. Comparison of the 0.1 M case against those at higher concentrations indicates that it is unfavorable for the ions to approach within 10 Å of the alumina surface. There is no population of Al\textsubscript{aq} below 20 Å at 0.1 M and the non-zero population below 20 Å is lower than average for the higher concentrations. A fair degree of structure is apparent, especially for the higher concentration cases.

Figure 9 shows how the water self-diffusion coefficient of a 90\% RH water film changes as a function of height within the water film for different concentrations of Al\textsubscript{aq}. As with the properties shown in Figure 8, increased concentration of Al\textsubscript{aq} ions does not appear to have a significant impact on water diffusivity. Most of the spatially binned diffusion coefficients at a given $z$ value overlap within their computed 95\% confidence intervals. An implication of these findings is that models of water film features (e.g., physical dimensions) can neglect ion concentration absent the potential for phenomena that may be correlated with other
Effect of relative humidity on surface water properties

Determining how environmental humidity effects ion transport is important for developing more sophisticated metal corrosion models. As shown in Figure 6, the thickness of water films adsorbed to oxide surfaces will depend on the RH of the environment and this thickness approaches 25 Å at 100% RH for γ-alumina. A study of water adsorption on aluminum oxide surfaces using Fourier-transform infrared spectroscopy (FTIR) was conducted by Al-Abadleh et al.\textsuperscript{24} showed that at RH>70%, additional water adsorbs to α-alumina in a disordered fashion, consistent with formation of a bulk-like liquid layer. We performed two additional simulations to identify where a bulk-like limit is reached for water adsorption on γ-alumina. These simulations had an Al\textsubscript{aq} ion concentration of 1.0 M with water film thicknesses of approximately 5 Å and 30 Å, which correspond to conditions of 30% RH and excess pooled water respectively.

Figure 9: Water self-diffusion coefficients as a function of height within the adsorbed water film at increasing Al\textsubscript{aq} ion concentrations. Results shown for a 90% RH water film at $T = 300$ K for $0.0 \leq [\text{Al}] \leq 1.0$ M. Error bars correspond to 95% confidence intervals. Horizontal dashed line corresponds to bulk water self-diffusion at 300 K.
Figure 10 shows the effect of RH on Al\textsubscript{aq} ion localization and Al\textsubscript{aq} ion diffusivity. As the amount of water adsorbed on the $\gamma$-alumina surface increases, the spread of distribution of Al\textsubscript{aq} ions increases and the structure of the distribution decreases. At 30\% RH, the ions are extremely localized to either the alumina-water or water-vacuum interface. At 90\% RH, the distribution broadens slightly and shifts away from the alumina interface, such that there are no Al\textsubscript{aq} ions present in the Langmuir region. With excess pooled water, the Al\textsubscript{aq} ion distribution is still localized near the water-vacuum interface, but most of the fine structure of the distribution dissipates.

The diffusivity of the Al\textsubscript{aq} ions increases by almost two orders of magnitude from 30\% RH to excess pooled water. Even at 90\% RH, Al\textsubscript{aq} ion diffusivity is significantly dampened with respect to ion transport through bulk-liquid water (the horizontal dashed line). Al\textsubscript{aq} ion diffusion rates do not begin to reach bulk-like limits until the water film is over 20 Å thick. The
Table 3: Diffusion coefficients averaged over all water and Al\textsubscript{aq} species for various systems, relative to the diffusion coefficient of pure bulk liquid water at 300 K.

<table>
<thead>
<tr>
<th>Species</th>
<th>$D/D_0$ (30% RH)</th>
<th>$D/D_0$ (90% RH)</th>
<th>$D/D_0$ (Bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O, [Al]=0.0M</td>
<td>0.0438</td>
<td>0.1301</td>
<td>1.0000</td>
</tr>
<tr>
<td>H$_2$O, [Al]=1.0M</td>
<td>0.0150</td>
<td>0.0300</td>
<td>0.2261</td>
</tr>
<tr>
<td>Al\textsubscript{aq}, [Al]=1.0M</td>
<td>0.0044</td>
<td>0.0146</td>
<td>0.0189</td>
</tr>
<tr>
<td>H$_2$O/Al\textsubscript{aq}, [Al]=1.0M</td>
<td>3.41</td>
<td>2.05</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Al\textsubscript{aq} ion diffusion rates are lower still than pure bulk water diffusion at this temperature.\textsuperscript{81} Table 3 shows quantitative measures of this dampening due to confinement. Both the reduction in water film thickness and the presence of Al\textsubscript{aq} ions cause the diffusivity of aqueous species to decrease with respect to pure bulk liquid water ($D_0 = 2.384 \times 10^{-5}$ cm$^2$·s$^{-1}$). The bottom row shows that ion diffusion is more strongly dampened than water self-diffusion. This is relevant for any chemical or physical process involving these species which may be diffusion-limited, such as corrosion.

While Al\textsubscript{aq} ions in the pooled water film approach their bulk diffusion limit for $z > 30$ Å, the 90% RH and pooled water cases give consistent Al\textsubscript{aq} diffusivities over the interval 20 < $z < 30$ Å. In both instances, this is the region of the water film that is adjacent to the Langmuir layer of water over the oxide surface. This region is near the vacuum interface for the 90% RH case but is closer to the center of the pooled water film. Interestingly, the local ion concentration in this region is markedly different for the two cases. While the concentration is at a maximum in the 90% RH water film, it is very dilute in the pooled water film. This may indicate that the Al ion diffusion rate is largely insensitive to the local Al ion concentration. It is possible that the oxide-water surface potential is responsible for this similarity in Al\textsubscript{aq} diffusivities, which otherwise cannot be explained by structural or local concentration effects.
Figure 11: (Left) $\text{Al}^{3+}$ concentration profiles at steady-state conditions for bulk water and 90% RH surface diffusion simulations. (Middle) Effect of $\text{Al}^{3+}$ ion diffusion coefficient on instantaneous reaction rate at the ion source vs. time. (Right) Parametric dependence of steady-state reaction rates at the ion source on $\text{Al}^{3+}$ ion diffusion coefficient value.

**Diffusion-reaction coupling in a 1D model of a corrosion pit**

Corrosion kinetics are extremely complex and depend on reaction rates and diffusivities of participating species. These in turn depend on simultaneous and potentially non-linear couplings with numerous system properties such as temperature, concentration, and RH. In the previous section, we established that diffusion rates of $\text{Al}^{3+}$ ions in water films that develop due to humidity exposure are more than 50% lower than rates in bulk water. However, it is not clear whether these reductions in diffusion rate can have a significant effect on corrosion rates. To better understand whether these changes in diffusion rates can influence corrosion rates, we implemented a reductionist 1D diffusion-reaction model of a corrosion pit following the approach outlined in Section.

Our 1D diffusion-reaction model considers a 1 $\mu$m corrosion pit at the alumina surface, and is described mathematically by Equation 7. In this model, aluminum ions are set to diffuse in 1D either through a bulk-like medium, or along a hydrated alumina surface (see Figure 3). The choice of diffusion medium is made through the choice of Al ion diffusion coefficient for the simulation. At the beginning of the simulation, the concentration of Al ions is zero, and over time, the vertex of the corrosion pit acts as an ion source. Ions are generated according to Equation 8, with faster ion generation occurring when the local
concentration of Al ions at the vertex is lower.

The left-most panel of Figure 11 shows the way that varying aqueous environment, and thereby the diffusivity of the dissolved aluminum, manifests as a change in the steady-state concentration profile across the corrosion pit. In both bulk water and surface water at 90% RH, the ion concentration after 10 ns is highest at the ion source, and decreases over the span of the corrosion pit as ions diffuse from the source. The concentration in both cases at the ion source is approximately equal, due to the inverse dependence of the ion source term on local concentration in the form of \( \frac{C_n}{C_{eq}} \). However, the increased diffusivity of ions in bulk water compared to the surface-adsorbed water results in an overall higher net population of ions within the entire corrosion pit.

Because the concentration at the corrosion pit vertex converges at steady-state conditions, it is clear that the ion source rate (and therefore the effective metal loss rate) also converges. The middle panel of Figure 11 shows how the corrosion rate at the ion source changes over time for different choices of Al ion diffusion coefficients: the completely non-diffusion-limited case, the bulk liquid water case, and the surface diffusion case at both 30% and 90% RH. Over the course of the simulation, the reaction rate at the ion source stays constant in the non-diffusion limited case, as expected. However, when realistic diffusion coefficients (as constrained by MD) are chosen, the reaction rate decreases over time as ions accumulate at the ion source.

The right-most panel shows the parametric dependence of the steady-state reaction rate on the Al\(_{aq}\) ion diffusion coefficient. It can be seen that the steady-state reaction rate varies by over two orders of magnitude for the range of Al ion diffusion coefficients determined here (approximately \(10^{-12}\) to \(10^{-10}\) cm\(^2\)·s\(^{-1}\)). Furthermore, the reaction rate varies linearly with ion diffusivity within the region constrained by MD. It increases non-linearly with increasing diffusion rate only for diffusion rates that are orders of magnitude larger than those predicted here. We can therefore conclude that the corrosion rates for this model of a corrosion pit are diffusion limited across all water film thicknesses of interest. This demonstrates the
significant impact diffusivity of eroded ions can have on relevant corrosion reaction kinetics.

Increasing the rate constant $k$ in Equation 8 will decrease the time it takes for these curves to reach their steady-state values, but for any diffusion-limited process, those steady-state values will be smaller than the base corrosion rate. Similarly, increasing the equilibrium concentration limit $C_{eq}$ will tend to result in faster corrosion kinetics by way of reducing the amount the base reaction rate is dampened as a function of local metal ion concentration. In this way, our reductionist model can be generalized to other metal loss processes for different metal ions. These simulations are computationally inexpensive and are easily repeatable for different systems given appropriate ion diffusion coefficients, metal loss rates, and saturation concentrations.

Conclusions

We developed here a set of all-atom models of hydrated $\gamma$-alumina surfaces that are parametrically coupled to RH through an experimentally derived water adsorption function. These models were combined with an established reactive force field and classical MD simulations to characterize the structure and transport dynamics of water and aqueous aluminum ions across a range of conditions relevant to aluminum corrosion. Essential features of the modeling framework were validated against experiments and DFT-based AIMD. Our classical MD simulations reproduce many well-understood properties of this system including diffusion coefficients of water and $\text{Al}_{aq}$ ions in bulk water as well as the hydrogen bonding network that forms at the oxide interface.

We found that $\text{Al}_{aq}$ ion diffusion rates are highly dampened in surface water films compared to bulk water, being reduced by up to a factor of $\approx 220$. Damping factors for water self-diffusion rates were considerably different than for solvated ions. Diffusion rates are also found to be a strong function of the adsorbed water film thickness, and therefore the RH of the environment. The nanoscale thickness of surface water films provides sufficient con-
finement to appreciably reduce ion mobility even at RH values as high as 90%. This finding provides a mechanistic explanation for the observation that atmospheric corrosion does not occur on pristine aluminum surfaces below 70% RH.

Analysis of the MD trajectories indicates that the decrease in diffusivity is correlated with several structural features of water films on alumina surfaces. A highly structured phase of water is found near the oxide, which both reduces ion concentrations and transport rates in and near the Langmuir layer. A surface polarization effect is also found which results in an increased effective ion concentration near the water-vacuum interface. While RH is shown to play a significant role in controlling Al_{aq} ion diffusivity, the ion concentration is found to have a very minor effect on either the structure or transport dynamics of the water film.

We used our MD-derived transport coefficients to constrain a reductionist 1D diffusion-reaction equation model of an aluminum corrosion pit. Parametric analysis of this 1D model indicates that the aluminum metal ion dissolution rate is a diffusion-controlled process at ambient atmospheric conditions. Moreover, our results indicate that RH plays a significant role in limiting aluminum corrosion kinetics. Our MD simulations provide direct numerical inputs for more sophisticated continuum-based corrosion models and indicate that RH effects on ion transport rates are an essential physical feature to capture when modeling these processes at higher length scales.

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