Ewald methods for polarizable surfaces with application to hydroxylation and hydrogen bonding on the (012) and (001) surfaces of α-Fe$_2$O$_3$

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We present a clear and rigorous derivation of the Ewald-like method for calculation of the electrostatic energy of the systems infinitely periodic in two-dimensions and of finite size in the third dimension (slabs). We have generalized this method originally developed by Rhee et al. [Phys. Rev. B 40, 36(1989)] to account for charge-dipole and dipole-dipole interactions and therefore made it suitable for treatment of polarizable systems. This method has the advantage over exact methods of being significantly faster and therefore appropriate for large-scale molecular dynamics simulations. It however involves a Taylor expansion which has to be demonstrated to be of sufficient order. The method was extensively benchmarked against the exact methods by Leckner and Parry. We found it necessary to increase the order of the multipole expansion from 4 (as in original work by Rhee et al.) to 6. In this case the method is adequate for aspect ratios (thickness/shortest side length of the unit cell) ≤ 0.5.

Molecular dynamics simulations using the transferable/polarizable model by Rustad et al. were applied to study the surface relaxation of the nonhydroxylated, hydroxylated, and solvated surfaces of α-Fe$_2$O$_3$ (hematite). We find that our nonhydroxylated structures and energies are in good agreement with previous LDA calculations on α-alumina by Manassidis et al. [Surf. Sci. Lett. 285, L517, 1993]. Using the results of molecular dynamics simulations of solvated interfaces, we define end-member hydroxylated-hydrated states for the surfaces which are used in energy minimization calculations. We find that hydration has a small effect on the surface structure, but that hydroxylation has a significant effect. Our calculations, both for gas-phase and solution-phase adsorption, predict a greater amount of hydroxylation for the α-Fe$_2$O$_3$ (012) surface than for the (001) surface. Our simulations also indicate the presence of four-fold coordinated iron ions on the (001) surface.

I. INTRODUCTION

In a wide variety of scientific and engineering problems, simulation techniques connecting models at Ångstrom scales to ‘microstructural’ scales $10^3$-$10^5$ times larger are required. Classical simulation of atomic and molecular systems works between these two extremes and is useful for moving atomic scale predictions into the microstructural or thermodynamic regime.

Here, we consider simulations using models with analytical interaction potentials involving charges and dipoles in interfacial environments. The long-range coulomb interactions in such systems must typically be taken into account over distances much larger than the sizes of samples which can be directly simulated. Historically this problem has been approached by infinitely and periodically repeating the simulation sample in all three dimensions. The long-ranged contributions to forces can be determined by a variety of methods. They include transformation to rapidly convergent sums in real space, the fast multipole method and various Ewald-type methods. The latter involve summations over the reciprocal lattice of the 2-D lattice. The relative merits of different methods are reviewed by Tildesley. The original 2-D Ewald method due to Parry is commonly used in quantum mechanical calculations where the Ewald summation comprises a small fraction of the computation time. For simulations with parameterized analytical potentials, using Parry’s method makes the Ewald summation procedure rate-limiting and it becomes worthwhile to explore alternatives to Parry’s method.

In the present paper we extend the 2-D periodic Ewald method of reference to include polarizable atomic centers. Effective pairwise potential energy functions parameterized for bulk systems do not work well at surfaces because the surface intermolecular environment is entirely different from that of the bulk. The first step in enhancing
the transferability of empirical potentials is to consider explicitly the effects of electronic polarization \[11\]. Therefore, the extension to polarizable systems is quite important in a method designed to be used at interfaces. In addition, we have fixed some omitted fourth order terms in reference \[8\] and we have carried out the Taylor expansion to sixth order in the aspect ratio, significantly improving the accuracy of the method. We have also clarified the extension to charged systems.

The generalized method is tested against previously-published benchmarks, and then applied to investigate the structure and hydroxylation of $\alpha$-Fe$_2$O$_3$ (hematite) surfaces. Hematite is chosen because it (as well as its aluminum analog, corundum) is a good example of a material which is well-studied using high-vacuum techniques and state of the art theoretical methods, and is also important in natural weathering and adsorption processes of interest in soil chemistry \[12\].

II. METHODS

Our polarizable system is most conveniently treated by generalizing the expressions for charge-charge interactions from Ref. \[8\] to include charge-dipole and dipole-dipole energies and forces.

We start by deriving the Ewald-type expression for the energy of a system of point charges periodic in two dimensions and finite along the third dimension. If the monopole-monopole potential energy expression is given by $\Phi_{mm}(r, s, z)$, then one can work out the expressions for the charge-dipole, and dipole-dipole interactions using:

$$\Phi_{md}(r, s, z) = -q_j \hat{\mu}_i \cdot \nabla \Phi_{mm}(r, s, z)$$

for the charge-dipole interaction, and

$$\Phi_{dd}(r, s, z) = -(\hat{\mu}_j \cdot \nabla)(\hat{\mu}_i \cdot \nabla)\Phi_{mm}(r, s, z)$$

for the dipole-dipole interaction, as well as gradients involving these terms arising in the expressions for the forces \[13\].

The derivation of the Ewald summation for the case of two-dimensional slabs of finite thickness is given in previous publications \[8\] and \[9\]. We present another method of derivation that we believe is easier to follow and rigorous. It is essentially a special case of the derivation presented in \[9\].

The electrostatic energy of the system of point charges with 2-D periodicity is given by

$$\Phi_{mm} = \frac{1}{2} \sum \sum' q_i q_j \frac{1}{|\vec{r}_{ij} + \vec{\nu}|} - \frac{1}{2} \sum_{i=1}^{N} q_i^2 \frac{1}{A} \int \frac{d\vec{s}}{s}$$

(3)

Here $\vec{r}_{ij}$ is the separation between particles $i$ and $j$, $\vec{s}_{ij}$ is the projection of this vector on the plane, $\vec{\nu}$ is the translation vector in the plane. $N$ is the total number of particles, and $A$ is the surface of the 2-D unit cell. The last term is the energy of the interaction of the slab (if non-neutral) with the uniform neutralizing background. The prime on the summation sign means that the term $i = j$ is skipped when $\vec{\nu} = 0$. A vector quantity without an arrow denotes the magnitude of the vector.

As in the 3-D Ewald method, we split the infinite sum \[3\] into short-ranged ($V_S$) and long-ranged ($V_L$) parts. $V_L$ will be replaced by its Fourier series expansion. To perform this separation, we write the identity

$$\frac{1}{r} = \frac{h_0(s, \gamma)}{s} + \frac{h_0(s, \gamma)}{s},$$

(4)

where $h_0(s, \gamma)$ is the convergence function with a parameter $\gamma$ (to be defined below). One then obtains:

$$\Phi_{mm} = V_S + V_L,$$

(5)

$$V_S = \frac{1}{2} \sum \sum' q_i q_j \left(1/r_{ij\nu} - h_0(s_{ij\nu}, \gamma)/s_{ij\nu}\right)$$

(6)

$$V_L = \frac{1}{2} \sum \sum' q_i q_j h_0(s_{ij\nu}, \gamma)/s_{ij\nu} - \frac{1}{2} \left(\sum q_i\right)^2 \frac{1}{A} \int \frac{d\vec{s}}{s}$$

(7)
The cutoff function $h(s)/s$ is defined by specifying its Fourier image. Consider the function 
\[ w(s) \equiv \sum_{\nu} h_0(s_\nu)/s_\nu = \sum_{\vec{G}} C_{\vec{G}} \exp(i\vec{G} \cdot \vec{s}) \]  
(8)
The sum is over all reciprocal lattice vectors, including $\vec{G} = 0$. Following the same notation as in Ref. |9|, we define the function $f(G)$ from
\[ C_{\vec{G}} = \frac{2\pi}{A} \frac{f(G)}{G}, \]  
(9)
where $A$ is the area of the 2-D unit cell. The Fourier coefficients $C_{\vec{G}}$ of the function $\sum_{\nu} h_0(s_\nu)/s_\nu$ are
\[ C_{\vec{G}} = \frac{1}{A} \int_{\text{all } s\text{-space}} \frac{h_0(s_\nu)}{s_\nu} \exp(-i\vec{G} \cdot \vec{s}) d\vec{s}. \]  
(10)
Changing the order of summation and integration and using the additivity of integration, one can write
\[ C_{\vec{G}} = \frac{1}{A} \int_{\text{all } \vec{G}\text{-space}} \frac{h_0(s)}{s} \exp(-i\vec{G} \cdot \vec{s}) d\vec{s} \]  
(11)
Comparing the expression above to the definition of the 2-D Fourier transformation of the function $h_0(s)/s$,
\[ \frac{1}{2\pi} \int_{\text{all } s\text{-space}} \frac{h_0(s)}{s} \exp(-i\vec{G} \cdot \vec{s}) d\vec{s}, \]  
one obtains
\[ \frac{f(G)}{G} = \frac{1}{2\pi} \int_{\text{all } s\text{-space}} \frac{h_0(s)}{s} \exp(-i\vec{G} \cdot \vec{s}) d\vec{s}. \]  
(12)
This means that $f(G)/G$ is the 2-D Fourier image of $h_0(s)/s$. Following Ref. |8|, we choose
\[ f(G) = \exp[-(\gamma G)^3]. \]  
(13)
The direct space cutoff function $h_0(s)/s$ is obtained by transforming back from $\vec{G}$-space to $\vec{s}$-space
\[ \frac{h_0(s)}{s} = \frac{1}{2\pi} \int_{\text{all } \vec{G}\text{-space}} \exp(i\vec{G} \cdot \vec{s}) \frac{\exp[-(\gamma G)^3]}{G} d\vec{G}. \]  
(14)
This integration is conveniently done using polar coordinates in the $\vec{G}$-plane:
\[ \frac{h_0(s)}{s} = \int_0^\infty GdG \left[ \frac{1}{2\pi} \int_0^{2\pi} \exp(iGs \cos \theta) d\theta \right] \frac{\exp[-(\gamma G)^3]}{G} = \int_0^\infty J_0(Gs) \exp(-\gamma^3 G^3) dG. \]  
(15)
Here we used the well-known integral
\[ \frac{1}{\pi} \int_0^\pi \exp(ix \cos \theta) d\theta = J_0(x), \]  
(16)
where $J_0(x)$ is the Bessel function. $V_L$ will be calculated as the sum of Fourier series. To do so, rewrite it using the periodic function $w(s)$ defined above. This is done by adding and subtracting $i = j$ term.
\[ V_L = \frac{1}{2} \sum_i \sum_j q_i q_j w(s_{ij}) - \frac{1}{2} \left( \lim_{s \to 0} \frac{h_0(s)}{s} \right) \sum_{i=1}^N q_i^2 - \frac{1}{2A} \left( \sum_{i=1}^N q_i \right)^2 \int_{\text{all } s\text{-space}} \frac{d\vec{s}}{s}. \]  
(17)
The limit in the expression above exists, and the direct calculation yields

\[ \lim_{s \to 0} \frac{h_0(s)}{s} = \frac{1}{3\gamma} \Gamma \left( \frac{1}{3} \right). \]  

(18)

Substituting (18) and (15) in (17), one obtains

\[ V_L = \pi A \sum_{\bar{G} \neq 0} \frac{\exp(-\gamma^3 G^3)}{G} \left| \sum_{i=1}^{N} q_i \exp(i\bar{G} \cdot \bar{s}_i) \right|^2 - \frac{1}{6\gamma} \Gamma \left( \frac{1}{3} \right) \sum_{i=1}^{N} q_i^2 - \frac{1}{2A} \left( \sum_{i=1}^{N} q_i \right)^2 \int_{s \text{-space}} \frac{d\bar{s}}{s} \]  

(19)

This expression contains two infinite terms, the \( \bar{G} = 0 \) term in the Fourier sum and the last term. The sum of these terms, \( I = \int_{s \text{-space}} \frac{h_0(s)-1}{s} d\bar{s}, \) can be written as

\[ I = \lim_{G \to 0} \frac{1}{A} \int_{s \text{-space}} \frac{h_0(s)}{s} \exp(-i\bar{G} \cdot \bar{s}) d\bar{s} - \frac{1}{A} \int_{s \text{-space}} \exp(-i\bar{G} \cdot \bar{s}) d\bar{s} \]  

(20)

As one can see from the Eqs. (8) and (9), the first integral in (20) is \( \frac{2\pi f(G)}{G} \). The second integral is calculated by transforming to polar coordinates and using the formula

\[ \int_{0}^{\infty} J_0(bx) dx = 1/b. \]

Its value is \( \frac{2\pi}{\bar{G}} \). Combining these expressions, one obtains:

\[ I = \lim_{G \to 0} \frac{2\pi (f(G) - 1)}{A} = \lim_{G \to 0} \frac{2\pi (\exp(-\gamma^3 G^3) - 1)}{G} = 0. \]  

(21)

Thus for our choice of \( f(G) = \exp(-\gamma^3 G^3) \), as well as other functions \( f(G) \) satisfying the above condition, the term due to the background charge cancels exactly the \( \bar{G} = 0 \) term of the reciprocal space sum. Therefore the long-ranged part of the interactions can be written as

\[ V_L = \pi A \sum_{\bar{G} \neq 0} \frac{\exp(-\gamma^3 G^3)}{G} \left| \sum_{i=1}^{N} q_i \exp(i\bar{G} \cdot \bar{s}_i) \right|^2 - \frac{1}{6\gamma} \Gamma \left( \frac{1}{3} \right) \sum_{i=1}^{N} q_i^2 \]  

(22)

Here we used the identity

\[ \sum_{i,j} q_i q_j \exp(i\bar{G} \cdot \bar{s}_{ij}) = \left( \sum_{i=1}^{N} q_i \exp(i\bar{G} \cdot \bar{s}_i) \right)^2 \]  

(23)

In practical calculations, the summations in real space are truncated at \( |\bar{v}| = \bar{v}_{\text{max}} \). The cutoff function \( h(s)/s \) does not dissipate at large distances fast enough like it does for the 3-D Ewald method. Instead it has the asymptotic behavior \( h(s)/s \approx 1/s \) at large distances. It is also convenient to separate the \( i = j \) term in real space. We therefore write

\[ \Phi_{mm}(r, s, z) = V_s' + V_L + V_m \]  

(24)

\[ V_s' = \frac{1}{2} \sum_{i,j,j \neq i} q_i q_j \sum_{\bar{v} \leq \bar{v}_{\text{max}}} \left( \frac{1}{|\bar{r}_{ij} + \bar{v}|} - h(s_{ij})/s_{ij} \right) + \frac{1}{2} \sum_{i} q_i^2 \sum_{\bar{v} > 0} \left( \frac{1}{\bar{v}} - \frac{h_0(\bar{v})}{\bar{v}} \right) \]  

(25)

\[ V_m = \frac{1}{2} \sum_{i,j,j \neq i} q_i q_j \sum_{\bar{v} > \bar{v}_{\text{max}}} \left( \frac{1}{|\bar{r}_{ij} + \bar{v}|} - \frac{1}{|\bar{r}_{ij} + \bar{v}|} \right) \]  

(26)

\[ 1 \Gamma \left( \frac{1}{3} \right) = 2.67893853471 \]
The expression for $V_L$ is given by Eq. (22).

The series for $V_m$ (Eq. 26) converges slowly, and direct calculation is extremely inefficient. Therefore it is advantageous to be able to precompute certain terms. Defining the function $v'_m$

$$v'_m(r, s) = \sum_{\nu > \nu_{\text{max}}} \left( \frac{1}{|r + \nu|} - \frac{1}{|s + \nu|} \right),$$

one can write

$$V_m = \frac{1}{2} \sum_{i,j,i \neq j} v'_m(r_{ij}, s_{ij}) \quad (28)$$

The key to the method of reference [8] is the use of a multipole expansion to compute $V_m$. The Taylor expansion of $\frac{1}{(1+x)^{1/2}}$ is

$$\frac{1}{(1+x)^{1/2}} = 1 - \frac{x}{2} + \frac{3}{8} x^2 - \frac{15}{48} x^3 + \frac{105}{384} x^4 + \ldots \quad (29)$$

This, in conjunction with the elementary definitions of $r$ and $s$:

$$r = \left( |s + \nu|^2 + z^2 \right)^{1/2} = \nu \left( \frac{s^2}{\nu^2} + \frac{z^2}{\nu^2} + 2 \frac{\vec{s} \cdot \vec{\nu}}{\nu^2} + 1 \right)^{1/2} \quad (30)$$

$$s = \left( |s + \nu|^2 \right)^{1/2} = \nu \left( \frac{s^2}{\nu^2} + 2 \frac{\vec{s} \cdot \vec{\nu}}{\nu^2} + 1 \right)^{1/2} \quad (31)$$

and noting that any odd powers of $\vec{s} \cdot \vec{\nu}$ will vanish in the sum on $\nu$, yields the following expression for the multipole expansion in powers of $(s, z)/\nu$:

$$v'_m = -\frac{1}{2} z^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + \frac{3}{4} z^2 s^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + \frac{3}{8} z^4 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^5} - \frac{15}{4} z^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{(\vec{s} \cdot \vec{\nu})^2}{\nu^3}$$

$$-\frac{15}{16} z^4 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^4} - \frac{15}{48} z^6 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^5} + \frac{105}{8} z^2 s^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{(\vec{s} \cdot \vec{\nu})^2}{\nu^3}$$

$$+ \frac{105}{16} z^4 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{(\vec{s} \cdot \vec{\nu})^2}{\nu^3} \quad (32)$$

where we retain only the terms $s^n z^m$ for which $n+m \leq 6$.

Application of equations 1 and 2 to obtain $\Phi_{md}$ and $\Phi_{dd}$ is straightforward for $V_s$ (equation 25) and $V_L$ (equation 22), following closely the 3-D periodic methods [13]. Reference [14] gives a generalization of the method to polarizable systems.

To implement these equations we split the interval of interest in 3 parts and approximated $h_0(s)/s$ using the ratio of two polynomials. The 3 derivatives of $h_0(s)/s$ were approximated separately, also using rational approximation. The optimal rational approximation can be easily constructed using the code given in Numerical Recipes [15].

We report here the derivatives of $V_m$ (equation 22) in the Appendix, as these terms, while straightforward, are somewhat tedious to compute. We also note, as pointed out in reference [8], that the expressions given in [8] do not contain all the terms to the fourth order. The expressions in the Appendix include multipole contributions up to the sixth order. Also, the numerical value of $\sum_{all \vec{g} \sqrt{1/\nu^3}}$ for the square lattice with parameter $L$ as given in reference [8] has only 3 correct digits and should be replaced with 9.0333388/L^3. This result was calculated with quadruple precision.
III. BENCHMARKS AND CONVERGENCE TEST

As one can see from the previous section, the Ewald-type method for 2-D slabs has 4 computational parameters: the convergence parameter \( \gamma \), cut-off parameters for summations in real and reciprocal space and the order of Taylor expansion used to calculate \( V_m \). In this study we used \( \gamma = 0.1L_{\text{short}} \), where \( L_{\text{short}} \) is the shortest side of the rectangular unit cell. The summations in real space included the first shell of neighboring cells, the total number of cells included being 9. We increased the order of expansion from 4 (as was originally used by Rhee et al \cite{6} and also used in Ref. \cite{6}) to 6, and this improved the accuracy of the calculations.

A valid test of convergence with respect to all computational parameters is a benchmark against another method. A test example for the monopole-monopole interaction was provided in Ref. \cite{10}. As discussed in that review, the method of Leckner \cite{4} has only one computational parameter, the cutoff of the summation in real space. It has exponential convergence and can be made as exact as required by choosing this cutoff appropriately. Therefore it is ideal as a benchmark \cite{4}. The comparison of the forces and potential energies calculated in this study with those from Ref. \cite{10} and calculated using the implementation of Parry’s method \cite{6} is given in Tables \ref{tab:1} through \ref{tab:4}. As one can see from Tables \ref{tab:1} and \ref{tab:4}, the two benchmark methods (Leckner’s and Parry’s) yield exactly the same results. One can therefore be confident in the benchmark itself. The results of our method are in excellent agreement with the benchmark for small interparticle separations in \( z \) direction. Once the ratio of the maximum separation in \( z \) direction to the magnitude of the translation vector (aspect ratio of the slab) increases, the agreement degrades slightly, the maximum error being 2.5 % for the aspect ratio 0.5. The Taylor expansion used here to efficiently evaluate \( V_m \) is in powers of \((z_{ij}/\nu)^2\). Therefore the quality of representation of \( V_m \) degrades as the expansion parameter increases. This explains the results of the benchmark. The error of 2.5 % in \( F_z \) can be considered acceptable. Real molecular dynamics simulations are done with \( \sim1000 \) atoms, not with 2 atoms. As noted by Tildesley \cite{10}, the convergence of 2-D Ewald-type methods improves when the cell is filled with charges, so that ions on opposite faces of the slab are shielded from each other.

We performed a test on the slab of 216 formula units of \( \text{Fe}_2\text{O}_3 \) (1080 atoms) that corresponds to the neutral termination of the (012) face. The electrostatic part of the total energy and forces in this system were calculated using Parry’s method and the method described in this study. The calculations yielded the total energy of -2584.148 \( \text{eV/Å} \) and -2583.626 \( \text{eV/Å} \) respectively. The maximum deviation in the magnitude of any force on any atom was 1.17 % of the exact value.

To the best of our knowledge, the benchmarks for charge-dipole and dipole-dipole interactions in 2-D periodic boundary conditions have not been published. We therefore present them in Tables \ref{tab:5} and \ref{tab:6}, respectively. Once dipoles are present, the energies calculated using the Parry’s method \cite{6} and our method differ by an additive constant. This stems from the fact that the surface terms are treated differently. The agreement of forces is good. Since evaluation of charge-dipole and dipole-dipole interactions involves successive differentiation of \( V_m \), the order of expansion decreases. Therefore it is not surprising that the quality of calculated charge-dipole and dipole-dipole forces degrades faster with the aspect ratio of the slab than does the force for the case of charge-charge interactions. Overall, the agreement is still totally satisfactory. Since the agreement with an independent method was good, we conclude that the choice of the computational parameters is adequate.

IV. APPLICATION TO HEMATITE SURFACES: BACKGROUND AND PREVIOUS WORK

The morphology of hematite (\( \alpha\text{-Fe}_2\text{O}_3 \)) crystals is complex \cite{23,24}, both in natural and synthetic samples. The wide variety of crystal faces present has tended to discourage atomistic interpretation of binding at hematite surfaces, with some notable exceptions \cite{6,17}. This contrasts with goethite (\( \alpha\text{-FeOOH} \)), where there have been several experiments and much discussion concerning the role of contiguous surface (monocoordinated) hydroxo groups in bidentate binding of oxyanions \cite{15,18}.

The properties of both hematite (\( \alpha\text{-Fe}_2\text{O}_3 \)) and corundum (\( \alpha\text{-Al}_2\text{O}_3 \)) surfaces in \textit{vacuo} have been studied experimentally \cite{25,26,33,34,35} and by computer simulations \cite{27,28,36,37,38}. In this section we consider both ideal vacuum-terminated and hydroxylated (001) and (012) surfaces of hematite. These are by far the best studied, and among the most prevalent surfaces for both hematite and corundum \cite{24,34}.

As is the case for any oxide surface, neither the extent of hydroxylation of hematite, nor its hydroxylated structure is well-understood \cite{39}. Surface hydroxylation has been demonstrated to occur on hematite by vibrational spectroscopy \cite{18,38}, but the spectra are very complicated and not easily interpreted. Here, we offer an application of our 2-D periodic Ewald summation method for polarizable systems to investigate the surface structures using our previously-developed methods for treating Fe-OH and Fe-OH\(_2\) interactions \cite{5,6}. 

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V. APPLICATION TO HEMATITE SURFACES: SIMULATION PROCEDURE

The atomic interactions were described using parameterized potential functions developed previously [38]. Briefly, this model includes formal charges on all ionic species, polarizable oxygen anions with a cut-off function to reduce induced polarization at short interionic separations, and various two- and three-body short-ranged terms. The functional form of all interactions and the list of parameters is given in Ref. [38]. The lattice parameters of hematite at zero pressure were determined in Ref. [38] by minimizing the total energy of the system with respect to the magnitudes of lattice vectors and internal structural parameters. They are listed in Table 3 of Ref. [38] along with experimental values. It is worth pointing out that the O-O and H-O interaction parameters used here were exactly the same as in the model for liquid water and gas phase clusters of water molecules. Considering this stringent transferability requirement the agreement of the calculated lattice constants with experimental values can be considered good. However, the Fe-O bonds predicted by the model are systematically about 3%-4% too long.

The simulations were done in two different geometries: in “sandwich” geometry with 3-D periodic boundary conditions (PBC) and in slab geometry. In simulations with 3-D PBC the length of the translational vector along \( z \) direction was 3 nm for all faces. Therefore the slabs were separated from each other by empty space in \( z \)-direction (~1.5 nm thick).

The atomic positions were relaxed by the following procedure: The sample was heated to 400 K and cooled to 0 K in 3-D molecular dynamics (MD) simulations 2 ps long. Then the energy of the system was minimized with respect to atom positions using the individual damping method by Bennett [39]. In this method, the equations of motion are solved as in standard MD but the velocity \( \vec{v}_i \) of an atom is set to zero if \( \vec{F}_i \cdot \vec{v}_i < 0 \), \( \vec{F}_i \) being the force acting on the atom. This procedure is carried out until convergence of the potential energy is reached. The 3-D minimal structure was used for the initial configuration for 2-D energy minimization (with no periodicity along \( z \)-direction).

Our surface energies are calculated using

\[
\gamma = \frac{1}{2} \left( E_{\text{slab}} - E_{\text{bulk}} \right) / A \tag{33}
\]

where \( E_{\text{slab}} \) is the potential energy of the slab system, \( E_{\text{bulk}} \) is the potential energy of an equivalent number of \( \text{Fe}_2\text{O}_3 \) molecules in the bulk, and \( A \) is the surface area.

VI. RESULTS

A. Nonhydroxylated Surfaces

The main utility of our potential set is our ability to treat surface hydroxylation. However, because there is little basis for comparison with other theoretical or experimental results on hydroxylated surfaces, we are compelled to test the performance of our potential set on non-hydroxylated surfaces. Even for these, there is little information available on hematite specifically. However, as mentioned above, there has been a substantial amount of work on corundum surfaces to which we can qualitatively compare our results [29–31,33,32]. We limit the investigation to the structure and energetics of the (001) and (012) surfaces, as these are the surfaces receive the most attention both theoretically and experimentally.

1. (012) Surface

The (012) surface has been previously studied in references [24,40,23,30]. The (012) surface is often indexed using the symmetrically equivalent (1102) surface in hexagonal notation; also note that in reference [24] this surface is indexed as (1012). A cross section of the (012) slab, as viewed down [100] is shown in Figure 1(a). This surface can be built up from neutral O-Fe-O-Fe-O units as described in reference [30]. The slab in Figure 1(a) is comprised of three such stacking units. The unit cell predicted by the model is 0.556 nm \( \times \) 0.518 nm. For the calculations here, we use a supercell consisting of 6 \( \times \) 6 unit cells; the supercell is periodic in X and Y directions.

The atomic coordinates for the unit cell of the slab are given in Table VI. In Figure 1 we show the two side views and the map view of the relaxed (012) top stacking unit (including the top O layer from the middle stacking unit). The noteworthy zig-zag oxygen ridges characterizing the (012) surface are clearly seen in Figure 1(a). The “slopes” of the oxygen ridges are occupied by five-fold coordinated iron ions. These are the darkly shaded iron ions in Figure 1.
two, three, and four O-Fe-O-Fe-O layers. From Tables VII and VIII, one concludes that 3 layers is sufficient for convergence for both energy and structure. The thickness of the nonhydroxylated 3 layer slab, shown in Figure 1, is 0.964 nm, and, for the size of the computational supercell considered here, the system consists of 216 Fe$_2$O$_3$ molecules (1,080 total atoms). The relaxation of each layer in the direction normal to the surface is shown in Table VII. Upon relaxation, the top three layers are brought closer together, compensated by separation of the bottom O-Fe layer. The Fe-O distance across this layer increases from 216 pm to 228 pm.

There is, to our knowledge, only one theoretical study of α alumina (012) [30]. That work employed embedded-cluster LDA methods to calculate energies of unrelaxed surfaces. Our size-converged unrelaxed surface energy of 2.8 J/m$^2$ (see Table VIII) compares well with the value of 2.95 J/m$^2$ obtained there. We find that allowing for relaxation decreases the surface energy to 2.0 J/m$^2$.

2. (001) Surface

The (001) surfaces of both hematite and corundum have been studied extensively [24,41]. We consider here the standard neutral, nonpolar, nonhydroxylated termination based on the stacking of Fe-O-Fe building blocks, as described in [30]. A cross section of the four Fe-O-Fe layer (001) slab, viewed down [100], is shown in Figure 2(a). The primitive hexagonal unit cell has a=0.518 nm; here we work with a nonprimitive orthorhombic cell with dimension a=0.898 nm and b=0.518 nm. The computational supercell is 4×6 orthorhombic unit cells. An orthorhombic cell was chosen for computational efficiency.

The atomic coordinates for the unit cell of the slab are given in Table X. In Figure 2, we show the two side views and the map view of the relaxed (001) surface. We include the top two Fe-O-Fe stacking units, but omit the bottom Fe layer for clarity. In other words, we show the top octahedral layer plus the overlying layer of iron ions. The model surface structure is characterized by a top layer three-fold coordinated iron ions (darkly shaded in Figure 2) in hexagonal arrangement. Configurations with two, three, four, five, and six such blocks were used to test for convergence of surface energy and surface structure as a function of the thickness of the slab. Table X shows the percent change in distances between layers parallel to the surface with respect to bulk distances. Relaxation brings both the top Fe and O layers and the two interior Fe layers closer together.

As shown in Table X, our calculations are in good agreement with previous calculations on isostructural α alumina, [40, 31, 33] except that in the tight-binding calculations of reference [33], the distance between the two intra-octahedral layers of Al ions increased by 20%; in contrast to the 40-50% decrease predicted by other empirical models and LDA [31]. The relaxed and unrelaxed surface energies are reported in Table XII. These compare favorably with the energies for α alumina reported in reference [31], as well as the unrelaxed surface energy reported in [31] (see Table XIII). The structure, energy, and relaxation energy of the (001) slab appear to be well-converged by the fourth, (or even third) Fe-O-Fe layer. The thickness of the four-layer slab, shown in Figure 2(a) is 0.773 nm. For the X and Y dimensions of the computational supercell, the four-layer slab consists of 224 molecules (1120 total atoms). The convergence with thickness is again similar to what was found for α alumina in reference [31].

Experimental fracture surface energies, as discussed in reference [30], range between 24 J/m$^2$ and 6 J/m$^2$ for (012) to around 40 J/m$^2$ for (001). The reason for the uniformly low values estimated by all theoretical methods cannot be speculated on at this time, but is a subject for future work.

3. 2-D Periodic vs. 3-D Periodic Calculations

As one can see from Tables VII and XII, the minimal energy for the case of 2-D PBC was always slightly higher than that for 3-D PBC. This difference can however be considered small. We have therefore demonstrated convergence with respect to the thickness of the empty space for 3-D calculations. The difference in atomic positions between 3-D and 2-D minimal energy structures was no more than 0.002 nm for all surfaces considered. The fact the 2-D calculations agree well with the 3-D (which don’t have any Taylor expansion) in case of sufficient separations between slabs in z direction suggests that for the actual system of interest the convergence with respect to computational parameters was reached. This is of further interest because 3-D PBC need to be implemented in electronic structure methods incorporating plane waves [31]. Our calculations support the inherent assumption that repeating the slab in the z direction with sufficient empty space between the layers has only a small effect on surface structures and energies for the systems considered here. This conclusion is of course system-dependent and would need to be demonstrated in any given case.
B. Hydroxylated Surfaces

In the previous section, it was demonstrated that our interaction potential was in good agreement with other theoretical studies for predictions on nonhydroxylated surfaces. Extension to hydroxylated systems is quite difficult for both the Hartee-Fock and LDA methods. It has been demonstrated that treatment of hydrogen bonds requires very large basis sets and correlated wave functions for Hartree-Fock-based methods \[42\] and gradient corrections are required for density-functional methods \[43\]. Our potentials are competitive with these methods. For example, we obtain the same ordering of conformers of \(H_3O(H_2O)_4^{+}\) as \[44\] and the same ordering of the \(OH(H_2O)_3^-\) as \[45\]. Our model will provide a semi-quantitative representation of surface hydrogen bonding.

1. Generation of the Hydroxylated Surface: Molecular Dynamics Calculations

Defining the hydroxylated surface structure is in itself a difficult problem \[35,46\]. The coordination numbers of the iron atoms and extent of hydroxylation are unknown. Because our potential model is as general as possible, we generate the hydroxylated surface structures through molecular simulation. To begin the simulations of the interfacial systems, we take the vacuum terminations of the 216 formula unit (012) system (3 layers of O-Fe-O-Fe-O), and 224 formula unit (001) system (four layers of O-Fe-O-Fe-O) as starting configurations. The vacuum configurations were then placed in contact with a layer of water (about 1.5 nm thick) obtained from a simulation of bulk water at 300 K. Simulations of both the (012) and (001) interfacial systems were run for 50 picoseconds at 300 K. This time was deemed sufficiently long; by about 40 picoseconds, the potential energy had ceased drifting downward and began to fluctuate about its mean value.

The surface structures for the (012) and (001) systems are shown in Figures 3 and 4, respectively. For the (012) surface, as might have been expected, each bare iron ion has indeed adsorbed a water molecule from the solvent. In several cases, “chemisorption” has occurred, and some of the \(Fe_3O\) sites on the surface have protonated. For the (001) surface, however, the assumption of six-fold iron coordination does not appear to be strictly valid; most iron atoms are four-fold coordinated. Here there is a balance among the surface relaxation forces (acting to pull the iron ion inward toward the surface), the forces of solvation (acting to pull the iron ion out towards the solution), and the lateral surface hydrogen bonding forces. Those surface iron ions which are 6-fold coordinated have slightly “popped out” of the relaxed top layer of iron ions. Because the relaxation energy for this surface is quite large, this evidently requires a significant amount of work. Thus the large surface relaxation energy tends to keep the top iron layer in a four-fold coordinated state.

The issue of the coordination state of the top iron layer is important because x-ray adsorption studies of the oxidation of metallic iron have often revealed evidence for the presence of four fold coordinated iron oxides in the passivation layer \[47\]. This has been used to suggest that the passivation layer consists of maghemite (\(\gamma Fe_2O_3\)). While this seems likely due to the additional evidence from x-ray scattering, it is important to note that the presence of four-fold coordination of iron does not appear to be a sufficient condition for the presence of maghemite. Of course, for a hematite crystal growing in the presence of a supersaturated solution of iron ions, this artificially cleaved and hydroxylated surface will adsorb iron ions and grow. This study obviously says nothing about the mechanisms of iron adsorption and crystal growth. For example, it is possible that our artificially-prepared surface has an extremely high affinity for iron and would never be realized for a surface in equilibrium with iron in solution. In other words it may only exist in nature over, say, microsecond time intervals (where no growth occurs) after the solvation of a freshly fractured hematite crystal. At the present time, however, it represents our best, least-biased guess for the structure of a hydroxylated hematite (001) surface.

These molecular dynamics studies are meant to reveal the coarse aspects of the surface structure. Interpretation beyond this is unwarranted because the thermodynamic states of the systems during hydroxylation are not well-defined. In particular, there is no reliable way of defining a solution pH, which is clearly a controlling variable in the extent of surface hydroxylation. However, it is possible to make some fairly precise statements about the predictions of the model concerning the energetics of hydroxylation at 0 K with no solvent present at the interface.

2. Structure and Energetics of Gas-phase Hydroxylation: Molecular Statics Calculations

\(\text{(012) Hydroxylated Surface Structure}\)

For the (012) surface, the first step toward “gas phase” surface hydroxylation is the adsorption of a water molecule to the five-fold coordinated iron ion (see Figure 3). This produces a chain of water molecules sitting over the “valleys”
formed at the middle oxygens in the O-Fe-O-Fe-O sequence, spaced about 300 pm apart. The bond distance to the (formerly) five-fold coordinated iron ions is 212 pm. The coordinates of atoms in the unit cell of the slab for hydrated and hydroxylated surface are given in Table XIV and XV, respectively. As shown in Table XVI, adsorption of water molecules has only a minor effect on the rest of the surface. Hydroxylation of the surface takes place by dissociation of the adsorbed water and protonation of the zig-zag ridge of oxygens (Figure 3). The rows of adsorbed hydroxide ions over the oxygen “valleys” move closer together (280 pm). Hydroxylation has a significant effect on the surface structure, moving the top layer of iron ions much closer to the top of the oxygen “ridges”. The bond between the top-layer iron ion and the bottom-layer oxygen ion in the O-Fe-O-Fe-O sequence is elongated from 210 pm (nonhydrated) to 212 pm (hydrated) to 238 pm (hydroxylated).

Concerning the speciation of surface hydroxyls, per unit cell, there are two $\equiv$Fe$_2$OH and two $\equiv$Fe$_1$OH sites, with a relatively weak 203 pm hydrogen bond forming between the singly and triply coordinated hydroxyls. The O-O distance between $\equiv$Fe$_2$OH and $\equiv$Fe$_1$OH is 290 pm. The singly-coordinated sites are nearly collinear along the X direction, spaced 280 pm apart. Overall, the arrangement of $\equiv$Fe$_1$OH groups is quite similar to the (110) surface of goethite in having a linear array of singly-coordinated sites which accept hydrogen bonds from triply-coordinated surface hydroxyls. The main differences are that the O-O distances are closer, the linear arrays are more closely spaced in the Y direction (0.518 nm vs 1.139 nm) and the hydrogen bonds donated by the triply coordinated hydroxyls are weaker. The hematite (012) surface should therefore prefer oxygen ions with smaller O-O distances and have a higher overall specific adsorptive capacity than goethite (110). Assume for the sake of argument that binding is bidentate (e.g. ($\equiv$FeOH)$_2$(PO$_4$) groups). For hematite (012) there are 2 bidentate sites per unit cell (0.288 nm$^2$) or 6.9 bidentate sites/nm$^2$, whereas for goethite there is one bidentate site per unit cell (0.358 nm$^2$), or 2.8 bidentate sites/nm$^2$. Also, because of the close spacing of the hydroxide rows, hematite might be less effective in binding elongated adsorbates.

(001) Hydroxylated Surface Structure

For the (001) surface, the first step toward hydroxylation is the adsorption of a water molecule directly over the three-fold coordinated iron ion (Figure 3). For the minimized configuration, this breaks the symmetry and a rectangular unit mesh results. The adsorbed water molecule sits 207 pm above the (formerly) three-fold coordinated iron ion. The coordinates of atoms in the unit cell of the slab for hydrated and hydroxylated surface are given in Table XVIII and XIX, respectively. As shown in Table XVI, hydration of the (001) surface has almost no effect on surface relaxation. Surface hydroxylation (Figure 8) takes place by dissociating the adsorbed water molecule and protonating 1/3 of the three-fold coordinated surface oxygens. As for the (012) surface, hydroxylation has a significant effect on the surface relaxation. The top iron ion moves upward relative to the first oxygen layer increasing the distance between the top Fe and O planes to approximately the bulk value value. The hydroxide layer is not indicated in Table XVII moves about 22 pm above the oxygen ions not receiving protons in the first structural oxygen layer. There are no significant hydrogen bonding interactions at the surface.

The surface hydroxyl speciation for (001) is two Fe$_3$OH and two FeOH sites per unit cell (0.465 nm$^2$), resulting in a density of 4.3 sites/nm$^2$ of each type (separately). There is no possibility for bidentate binding at the (001) surface, at least for the model arrived at here.

Hydroxylation Energetics

The energy of adsorption of water to the (012) surface in the configuration shown in Figure 3 is -1.6 J/m$^2$ (the adsorbed water molecule is assumed to be removed from bulk ice at 0 K). If, in addition, the water is allowed to dissociatively adsorb (as shown in Figure 3), the adsorption energy is -2.7 J/m$^2$. Therefore, one obtains more energy for adsorption of the water layer than the 2 J/m$^2$ required to fracture the crystal. This is clearly not correct, since hematite crystals are stable in the presence of water.

The same considerations apply to the “gas phase” hydroxylation of the (001) surface. Here the energy of adsorption of undissociated water in the configuration shown in Figure 3 is -1.2 J/m$^2$. The energy of dissociative adsorption in the configuration shown in Figure 8 is -1.8 J/m$^2$. Again the energy of dissociative adsorption exceeds the surface fracture energy (1.6 J/m$^2$).

The surface enthalpy of hematite has been estimated in reference [48] by measuring the heat of dissolution of hematite crystals as a function of surface area [$^\circ$C]. Taking this result at face value, and assuming the experimental value is representative of the (012) surface, there is a discrepancy of 1.4 J/m$^2$ between the experimental value and the theoretical estimate. The failure to obtain the correct sign could be due to either overestimating the binding energy of water, hydroxide, and protons to the surface, or underestimating the energy required to fracture the surface. As discussed above, nearly all theoretical estimates of the fracture energy are in fair agreement predicting that the surface energy is 1.6-2.0 J/m$^2$ yet experimental estimates
range from 6-40 J/m\(^2\). The discrepancy of 1.4 J/m\(^2\) is small in relation to this range of experimental values for the fracture energy. The same arguments apply if the predominant surface in the surface enthalpy experiments is (001). Meaningful discussion of the hydroxylation issue must wait until the overall discrepancy between the theoretical and experimental fracture surface energies is better understood. We will, however, point out that our model predicts a greater amount of dissociation on (012) than (001), both in terms of “gas phase” calculations and qualitatively in the MD simulations of the hematite-water interface.

VII. SUMMARY AND CONCLUSIONS

We have presented a simple yet rigorous derivation of the 2-D Ewald summation method of Rhee et al. and its generalization to polarizable systems. This provides a viable means of investigating the surfaces of oxide minerals using thousands of atoms. As one can see from the presented results of benchmarks against exact methods, the method of Rhee and co-workers is adequate for systems with aspect ratios \((z_{\text{max}} - z_{\text{min}})/(\text{min}(L_x, L_y))\) less than approximately 0.5. We increased the order of the Taylor expansion for \(V_m\) from 4 (as in \(\text{(3)}\)) and found this to yield significantly better accuracy. These expressions are given in the Appendix.

We have applied the method to investigate the structures of hydroxylated and non-hydroxylated (012) and (001) surfaces of hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) in slab geometry, and solidly document the convergence of our results with respect to slab thickness. Our nonhydroxylated structures and energies are in good agreement with previous calculations on isostructural \(\alpha\)-Al\(_2\)O\(_3\). We used the flexibility and economy of our parameterized analytical potential approach to run simulations of solvated interfaces. These simulations revealed nonuniform hydroxylation as suggested in \(\text{(35)}\), but revealed end-member structures which were used in more precise “gas-phase” calculations. These calculations revealed that the effect of hydration on surface structure is small, but that hydroxylation has a significant effect. Hydroxylation appears to be energetically favored both in the gas-phase calculations and the solution phase simulations, with the (012) surface exhibiting a greater degree of dissociation of adsorbed water. The (001) surface has a complex solvated structure. Our simulations reveal the presence of both four-fold coordinated and six-fold coordinated iron ions at the solvated surface, with four-fold coordination predominant. Conversion of four-fold to six-fold coordination requires significant movement of top-layer iron atoms out into the aqueous solvent. This movement should be detected in x-ray reflectivity experiments designed to measure the location of the top layer of iron ions and their bound hydroxyl/aquo ligands in the direction normal to the surface plane \(\text{(50,51)}\). It is hoped that the present study will encourage experimental studies of hydroxylated hematite surfaces.

Quantum mechanical simulations are potentially superior to those with parameterized analytical potentials because electronic structure is accounted for explicitly. However, these methods must always compromise some accuracy for the sake of feasibility. This means that even demonstrating convergence with respect to basis set size, density of \(k\)-points mesh for Brillouin zone integration, system size requires tremendous effort. As shown in Tables \(\text{XI}\) and \(\text{XIII}\), results of electronic structure based methods are not always in agreement. We therefore wish to emphasize the usefulness of parameterized analytical potential methods in extending the scope of theoretical calculations on mineral surfaces.

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APPENDIX: MULTipoLE EXPANSIONS

The first, second, and third derivatives of \( V_m \) in equation 26 are required for computation of energies and forces for charge-dipole and dipole-dipole interactions in equations 1 and 2.

\[
\frac{\partial v'_m}{\partial x} = \frac{3}{2} z^2 x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - \frac{15}{2} z^2 x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} - \frac{15}{4} s^2 z^2 x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} - \frac{15}{8} z^4 x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} \\
- \frac{105}{4} z^2 s^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} + \sum_{\nu=\nu_{\text{max}}}^{\infty} \left( \frac{\hat{s} \cdot \hat{v}}{\nu^3} \right) + \frac{105}{8} z^4 x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} \tag{A1}
\]

\[
\frac{\partial v'_m}{\partial z} = -z \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + \frac{3}{2} s^2 z \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^5} + \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} - \frac{15}{8} z^4 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} - \frac{15}{4} s^2 z^3 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} - \frac{15}{8} s^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} + \frac{105}{4} \frac{s^2}{\nu^9} + \frac{105}{4} z^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \left( \frac{\hat{s} \cdot \hat{v}}{\nu^3} \right) \tag{A2}
\]

\[
\frac{\partial^2 v'_m}{\partial x^2} = \frac{3}{2} z^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - \frac{15}{2} z^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} - \frac{15}{4} z^2 (s^2 + 2x^2) \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} - \frac{15}{8} z^4 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} + \frac{105}{4} \frac{s^2}{\nu^9} + \frac{105}{4} z^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \left( \frac{\hat{s} \cdot \hat{v}}{\nu^3} \right) \tag{A3}
\]

\[
\frac{\partial^2 v'_m}{\partial x \partial y} = -\frac{15}{2} z^2 y x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + \frac{105}{2} z^2 y x \left( \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} + \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} \right) \tag{A4}
\]

\[
\frac{\partial^2 v'_m}{\partial x \partial z} = 3xz \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - \frac{15}{2} s^2 z x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^5} - \frac{15}{2} z^3 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} - 15zx \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} + \frac{105}{4} \frac{s^2}{\nu^9} + \frac{105}{4} z \sum_{\nu=\nu_{\text{max}}}^{\infty} \left( \frac{\hat{s} \cdot \hat{v}}{\nu^3} \right) \tag{A5}
\]

\[
\frac{\partial^2 v'_m}{\partial z^2} = -\sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + \frac{3}{2} (s^2 + 3z^2) \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^5} - \frac{15}{2} \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} + \frac{105}{4} s^2 z \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} - \frac{15}{8} \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} \tag{A6}
\]

\[
\frac{\partial^3 v'_m}{\partial x^3} = 6x \left( -\frac{15}{4} z^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + \frac{105}{2} z^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} \right) \tag{A7}
\]

\[
\frac{\partial^3 v'_m}{\partial x^2 \partial y} = -\frac{15}{2} z^2 y \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + \frac{105}{2} z^2 y \left( \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} + \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} \right) \tag{A8}
\]

\[
\frac{\partial^3 v'_m}{\partial x \partial y \partial z} = -15xyz \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + 105xyz \left( \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} + \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} \right) \tag{A9}
\]

\[
\frac{\partial^3 v'_m}{\partial x^3 \partial z} = 3z \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - 15z \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} - \frac{15}{2} (s^2 + 2x^2) \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} - \frac{15}{2} z^3 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^7} + \frac{105}{2} z^3 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^9} + \frac{105}{2} z^3 \sum_{\nu=\nu_{\text{max}}}^{\infty} \left( \frac{\hat{s} \cdot \hat{v}}{\nu^3} \right) \tag{A10}
\]
\[
\frac{\partial^3 v'_m}{\partial x \partial z^2} = 3x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - \frac{15}{2} s^2 x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - \frac{45}{2} z^2 x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - 15x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^3} \\
\quad + \frac{105}{2} x (s^2 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^3} + \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{(\vec{s} \cdot \vec{\nu})^2}{\nu^3}) + \frac{315}{2} z^2 x \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{\nu^2}{\nu^3} \\
\frac{\partial^3 v'_m}{\partial z^3} = +9z \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - \frac{45}{2} s^2 z \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} - \frac{75}{2} z^3 \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{1}{\nu^3} + \frac{315}{2} z \sum_{\nu=\nu_{\text{max}}}^{\infty} \frac{(\vec{s} \cdot \vec{\nu})^2}{\nu^3} 
\] (A11)

FIG. 1. Nonhydrated (012) surface. (a) slab cross section of the system consisting of 3 layers of neutral O-Fe-O-Fe-O sequences. Large red atoms are oxygen, small orange atoms are iron. (b-d) closeup views of top O-Fe-O-Fe-O layer plus the top O layer from the middle neutral stacking sequence. Atoms are color coded according to depth. The top O layer is red, the middle O layer is magenta, and the bottom O layer is pink. The top O layer of the middle stacking sequence is grey. The top five-fold coordinated iron ions are brown, and the lower six-fold coordinated iron ions are orange. In the map view (d) the zig-zag oxygen ridges are emphasized with black vectors.

FIG. 2. Nonhydrated (001) surface. (a) slab cross section of the system consisting of four layers of neutral Fe-O-Fe sequences. Large red atoms are oxygen, small orange atoms are iron. (b-d) closeup views of top two Fe-O-Fe layers but minus the bottom Fe layer from the 2nd neutral Fe-O-Fe stacking sequence. Atoms are color coded according to depth. The top O layer is red, and the bottom O layer is deep pink. The top three-fold coordinated ion ions are brown, the second iron layer is orange and the third iron layer is grey.

FIG. 3. A snapshot (after 50 picoseconds) of the solvated (012) surface. The initial conditions of the simulation consisted were obtained by placing a 1.5 nm layer of water from a bulk water simulation over the surface shown in Figure 1(a). Atom types are the same as in Figure 1 except that both surface water molecules and solvent hydroxide ions are indicated by large yellow oxygen atoms. A water molecule is considered a surface water molecule if it is bound to at least 1 iron atom, and a hydroxide ion is considered solvated if it is not bound to any iron atoms.

FIG. 4. A snapshot (after 50 picoseconds) of the solvated (001) surface. The initial conditions of the simulation consisted were obtained by placing a 1.5 nm layer of water from a bulk water simulation over the surface shown in Figure 2(a). Atom types are the same as in Figure 2 except that both surface water molecules and solvent hydroxide ions are indicated by large yellow oxygen atoms. A water molecule is considered a surface water molecule if it is bound to at least 1 iron atom, and a hydroxide ion is considered solvated if it is not bound to any iron atoms.

FIG. 5. Three orthogonal views of the hydrated (012) surface. Atom types are the same as in Figure 1 except that adsorbed water molecules are indicated by the yellow oxygen atoms and protons are the small white atoms. Idealized periodic surface structures are those suggested from the MD simulations shown in Figure 3.

FIG. 6. Three orthogonal views of the hydroxylated (012) surface. Atom types are the same as in Figure 1 except that adsorbed hydroxide ions are indicated by the yellow oxygen atoms and protons are the small white atoms. Idealized periodic surface structures are those suggested from the MD simulations shown in Figure 3.

FIG. 7. Three orthogonal views of the hydrated (001) surface. Atom types are the same as in Figure 2 except that adsorbed water molecules are indicated by the yellow oxygen atoms and protons are the small white atoms. Idealized periodic surface structures are those suggested from the MD simulations shown in Figure 4.

FIG. 8. Three orthogonal views of the hydroxylated (001) surface. Atom types are the same as in Figure 2 except that adsorbed hydroxide ions are indicated by the yellow oxygen atoms and protons are the small white atoms. Idealized periodic surface structures are those suggested from the MD simulations shown in Figure 4.
TABLE I. The energy (in units of $e^2/L$) and forces (in units of $e^2/L^2$), between a charge $+e$ at (0, 0, 0) and $-e$ at (0.1, 0.1, 0.1) L in an infinitely periodic 2-D array of square unit cells

| Method          | U     | $F_x$ | $F_y$ | $F_z$ |
|-----------------|-------|-------|-------|-------|
| Leckner ($l_{max} = 10$) | -5.77211 | -     | -     | -     |
| Parry ($\kappa = 5$)     | -5.77212 | 18.8136 | 18.8136 | 20.1628 |
| This study        | -5.77184 | 18.8136 | 18.8136 | 20.1627 |

TABLE II. The energy (in units of $e^2/L$) and forces (in units of $e^2/L^2$), between a charge $+e$ at (0, 0, 0) and $-e$ at (-0.25, -0.15, -0.2) L in an infinitely periodic 2-D array of square unit cells

| Method          | U     | $F_x$ | $F_y$ | $F_z$ |
|-----------------|-------|-------|-------|-------|
| Leckner ($l_{max} = 10$) | -2.82156 | -4.60495 | -2.91052 | -6.44748 |
| Parry ($\kappa = 5$)     | -2.82157 | -4.60495 | -2.91052 | -6.447478 |
| This study ($\gamma = 0.1L_{short}$) | -2.8214336 | -4.60323 | -2.909703 | -6.446037 |

TABLE III. The energy (in units of $e^2/L$) and forces (in units of $e^2/L^2$), between a charge $+e$ at (0, 0, 0) and $-e$ at (-0.25, -0.15, -0.5) L in an infinitely periodic 2-D array of square unit cells

| Method          | U     | $F_x$ | $F_y$ | $F_z$ |
|-----------------|-------|-------|-------|-------|
| Parry’s         | -0.8061173 | -0.6608550 | -0.4514618 | -6.723419 |
| This study      | -0.8067679 | -0.650034 | -0.4461202 | -6.5550016 |
| Error, %        | 0.08  | 1.64  | 1.18  | 2.50  |

TABLE IV. The energy (in units of $e^2/\text{Å}$) and forces (in units of $e^2/\text{Å}^2$), between a charge $+e$ at (0, 0, 0) and $-e$ at (-0.25, -0.15, -0.1) L and also dipole $\vec{\mu} = (-0.33, -0.16, 0.77)$ at the position of $-e$ in an infinitely periodic 2-D array of square unit cells with the side length $L = 10 \text{ Å}$

| Method          | U     | $F_x \times 10^2$ | $F_y \times 10^2$ | $F_z \times 10^2$ |
|-----------------|-------|--------------------|--------------------|--------------------|
| Parry’s         | -0.33385337 | -7.280129828 | -4.56935990 | -8.077974417 |
| This study      | -0.336207073 | -7.2792028 | -4.56935929 | -8.077045 |

TABLE V. The energy (in units of $e^2/\text{Å}$) and force (in units of $e^2/\text{Å}^2$) in a system consisting of a charge $+2e$ at (0,0,0), a charge $-e$ and dipole $\vec{\mu} = (-0.33, -0.16, 0.77)$ at (-0.25, -0.15, -0.1)L and a charge $-e$ and dipole $\vec{\mu}_1 = (0.3, 0.6, 0.7)$ at (0.5, 0.33, -0.05)L in an infinitely periodic 2-D array of square unit cells with the side length $L = 10 \text{ Å}$

| Method          | U     | $F_x$ | $F_y$ | $F_z$ |
|-----------------|-------|-------|-------|-------|
| Parry’s         | -0.8925432834 | -0.13797318 | -0.062559269 | -0.2051223 |
| This study      | -0.89619000 | -0.13788360 | -0.0625851709 | -0.20480698 |

*Only the force acting on charge $+2e$ is given*
TABLE VI. Slab unit cell coordinates for the ideal vacuum-terminated (012) surface. X, Y, and Z coordinates in Å. Orthogonal unit mesh translation vectors are 5.564 Å in X and 5.176 Å in Y.

| atom | x    | y    | z    |
|------|------|------|------|
| O1   | 0.374| 0.254| 1.169|
| O2   | 2.689| 2.746| 4.819|
| O3   | 3.605| 2.856| -2.573|
| O4   | 2.782| 0.000| -3.870|
| O5   | 2.066| 0.000| 3.868 |
| O6   | 5.206| 2.608| -0.001|
| O7   | 2.160| 2.746| -4.820|
| O8   | 1.244| 2.857| 2.572 |
| O9   | 4.474| 0.254| -1.170|
| O10  | 1.692| 4.432| -1.171|
| O11  | 4.942| 1.940| -4.820|
| O12  | 4.026| 1.830| 2.572 |
| O13  | 4.848| 4.687| 3.868 |
| O14  | 2.424| 2.078| -0.001|
| O15  | 0.000| 4.686| -3.870|
| O16  | 0.823| 1.830| -2.573|
| O17  | 5.471| 1.941| 4.819 |
| O18  | 3.156| 4.432| 1.169 |
| Fe1  | 0.901| 1.056| -0.786|
| Fe2  | 3.962| 3.526| -4.531|
| Fe3  | 3.332| 3.656| 3.028 |
| Fe4  | 1.516| 3.655| -3.029|
| Fe5  | 0.887| 3.526| 4.530 |
| Fe6  | 3.947| 1.056| 0.785 |
| Fe7  | 3.669| 1.161| 4.530 |
| Fe8  | 1.165| 3.630| 0.785 |
| Fe9  | 4.298| 1.030| -3.029|
| Fe10 | 1.180| 1.160| -4.531|
| Fe11 | 0.550| 1.031| 3.028 |
| Fe12 | 3.683| 3.630| -0.786|

TABLE VII. Changes in interplanar spacing due to relaxation of hematite (012) surface as a function of size of the simulation cell

| Change from bulk value |
|-------------------------|
| Number of Fe₂O₃ molecules |
| 144 | 216 | 288 |
| O  | 35 | -24% | -18% | -18% |
| Fe | 80 | -24% | -17% | -18% |
| O  | 80 | 8% | 5% | 5% |
| Fe | 35 | 49% | 32% | 34% |
| O  | 149 | -15% | -6% | -7% |
TABLE VIII. Surface energy $\gamma$ (J/m$^2$) for non-hydroxylated (012) face of hematite calculated using the 3-D and 2-D periodic boundary conditions

| Number of Fe$_2$O$_3$ molecules | $\gamma_{3-D}$ relaxed | $\gamma_{2-D}$ relaxed | $\gamma_{3-D}$ unrelaxed |
|-------------------------------|-------------------------|-------------------------|--------------------------|
| 72                            | 2.335                   | 2.325                   | 2.903                    |
| 144                           | 1.882                   | 1.874                   | 2.757                    |
| 216                           | 1.994                   | 2.022                   | 2.775                    |
| 288                           | 1.999                   | 2.094                   | 2.787                    |

TABLE IX. Slab unit cell coordinates for the ideal vacuum-terminated (001) surface. X, Y, and Z coordinates in Å. Orthogonal unit mesh translation vectors are 8.976 Å in X and 5.176 Å in Y.

| atom | x     | y     | z     |
|------|-------|-------|-------|
| O1   | 0.000 | 4.967 | -1.188|
| O2   | 1.410 | 2.409 | 3.428 |
| O3   | 4.488 | 2.380 | -1.188|
| O4   | 5.898 | 4.997 | 3.428 |
| O5   | 7.360 | 2.497 | 3.428 |
| O6   | 5.847 | 0.000 | -1.188|
| O7   | 1.359 | 2.587 | -1.188|
| O8   | 2.872 | 5.084 | 3.428 |
| O9   | 8.798 | 5.011 | 3.428 |
| O10  | 7.231 | 2.365 | -1.188|
| O11  | 2.743 | 4.952 | -1.188|
| O12  | 4.310 | 2.423 | 3.428 |
| O13  | 4.317 | 0.752 | -3.428|
| O14  | 5.727 | 3.369 | 1.188 |
| O15  | 8.805 | 3.340 | -3.428|
| O16  | 1.239 | 0.782 | 1.188 |
| O17  | 8.856 | 3.162 | 1.188 |
| O18  | 7.343 | 0.665 | -3.428|
| O19  | 2.855 | 3.252 | -3.427|
| O20  | 4.368 | 0.574 | 1.188 |
| O21  | 5.905 | 3.326 | -3.428|
| O22  | 7.472 | 0.796 | 1.188 |
| O23  | 1.418 | 0.738 | -3.428|
| O24  | 2.984 | 3.384 | 1.188 |
| Fe1  | 4.359 | 4.167 | -3.863|
| Fe2  | 5.856 | 1.580 | 0.290 |
| Fe3  | 8.847 | 1.580 | -3.863|
| Fe4  | 1.368 | 4.168 | 0.290 |
| Fe5  | 5.855 | 1.580 | -2.603|
| Fe6  | 7.352 | 4.168 | 2.209 |
| Fe7  | 1.367 | 4.168 | -2.602|
| Fe8  | 2.864 | 1.581 | 2.209 |
| Fe9  | 8.847 | 1.581 | -0.289|
| Fe10 | 5.856 | 1.582 | 3.864 |
| Fe11 | 1.368 | 4.169 | 3.864 |
| Fe12 | 4.359 | 4.169 | -0.289|
| Fe13 | 8.848 | 1.581 | 2.603 |
| Fe14 | 7.351 | 4.168 | -2.209|
| Fe15 | 2.864 | 1.581 | -2.209|
| Fe16 | 4.360 | 4.168 | 2.603 |
TABLE X. Changes in interplanar spacing due to relaxation of hematite (001) surface as a function of size of the simulation cell

|                | Bulk value (pm) | 168 | 224 | 280 | 336 |
|----------------|----------------|-----|-----|-----|-----|
| Fe             | 86             | -53%| -50%| -49%| -49%|
| O              | 86             | -3% | -3% | -2% | -3% |
| Fe             | 63             | -43%| -38%| -43%| -41%|
| Fe             | 86             | 24% | 19% | 21% | 21% |

TABLE XI. Surface Energies of Non-hydroxylated Fe/Al Sesquioxide (J/m$^2$): Comparison with previous electronic structure calculations

|                | α-Fe$_2$O$_3$ | α-Al$_2$O$_3$ | HF $^{32}$ | HF $^{30}$ |
|----------------|---------------|---------------|------------|------------|
| (001)          |               |               |            |            |
| Unrelaxed      | 4.24          | 3.77          | 3.3        | 5.0        |
| Relaxed        | 1.64          | 1.76          | 2.0        | -          |
| (012)          |               |               |            |            |
| Unrelaxed      | 2.79          | 2.95          | -          | -          |
| Relaxed        | 2.00          | -             | -          | -          |

TABLE XII. Surface energy $\gamma$ (J/m$^2$) for non-hydroxylated (001) face of hematite calculated using the 3-D and 2-D periodic boundary conditions

| Number of Fe$_2$O$_3$ molecules | $\gamma_{3-D}$ relaxed | $\gamma_{2-D}$ relaxed | $\gamma_{3-D}$ unrelaxed |
|---------------------------------|------------------------|------------------------|--------------------------|
| 112                             | 1.63                   | 1.62                   | 4.32                     |
| 168                             | 1.54                   | 1.46                   | 4.22                     |
| 224                             | 1.64                   | 1.63                   | 4.22                     |
| 280                             | 1.64                   | 1.64                   | 4.23                     |
| 336                             | 1.65                   | 1.60                   | 4.24                     |

TABLE XIII. Nonhydroxylated (001) surface. Percent relaxation in $z$ direction

|                | Ours | LDA $^{31}$ | TBTE $^{33}$ | HF $^{32}$ | HF $^{30}$ |
|----------------|------|-------------|--------------|------------|------------|
| Fe/Al          | -49  | -86         | -87          | -50        | -50        |
| O              | -3   | +3          | -33          | -5         | -          |
| Fe/Al          | -41  | -54         | +20          | -8         | -          |
| O              | 21   | 25          | 0            | -          | -          |
TABLE XIV. Slab unit cell coordinates for the hydrated (012) surface. X, Y, and Z coordinates in Å. Orthogonal unit mesh translation vectors are 5.564 Å in X and 5.176 Å in Y.

| atom | x    | y    | z    |
|------|------|------|------|
| H1   | 1.856| 0.028| -6.877|
| H2   | 1.122| 1.264| -7.312|
| H3   | 3.728| 1.264| 7.314 |
| H4   | 2.987| 0.033| 6.879 |
| H5   | 0.946| 3.942| 7.312 |
| H6   | 0.221| 0.000| 6.883 |
| H7   | 4.628| 0.003| -6.882|
| H8   | 3.906| 3.938| -7.313|
| O1   | 1.135| 0.643| -6.531|
| O2   | 0.377| 0.519| 1.166 |
| O3   | 2.721| 3.024| 4.809 |
| O4   | 3.596| 3.123| -2.575|
| O5   | 2.782| 0.264| -3.846|
| O6   | 2.068| 0.264| 3.846 |
| O7   | 5.207| 2.873| 0.001 |
| O8   | 3.712| 0.644| 6.533 |
| O9   | 2.129| 3.024| -4.809|
| O10  | 1.253| 3.123| 2.576 |
| O11  | 4.472| 0.520| -1.165|
| O12  | 0.931| 4.563| 6.532 |
| O13  | 1.691| 4.690| -1.165|
| O14  | 4.910| 2.185| -4.809|
| O15  | 4.035| 2.086| 2.576 |
| O16  | 4.849| 4.945| 3.847 |
| O17  | 2.425| 2.337| 0.000 |
| O18  | 0.000| 4.945| -3.845|
| O19  | 0.815| 2.086| -2.575|
| O20  | 5.503| 2.186| 4.810 |
| O21  | 3.923| 4.560| -6.533|
| O22  | 3.159| 4.690| 1.166 |
| Fe1  | 0.902| 1.315| -0.786|
| Fe2  | 3.957| 3.813| -4.546|
| Fe3  | 3.332| 3.908| 3.022 |
| Fe4  | 1.518| 3.908| -3.021|
| Fe5  | 0.893| 3.813| 4.547 |
| Fe6  | 3.948| 1.315| 0.787 |
| Fe7  | 3.675| 1.396| 4.548 |
| Fe8  | 1.166| 3.894| 0.787 |
| Fe9  | 4.300| 1.302| -3.021|
| Fe10 | 1.175| 1.396| -4.546|
| Fe11 | 0.550| 1.301| 3.021 |
| Fe12 | 3.684| 3.894| -0.786|
TABLE XV. Slab unit cell coordinates for the hydroxylated (012) surface. X, Y, and Z coordinates in Å. Orthogonal unit mesh translation vectors are 5.564 Å in X and 5.176 Å in Y.

| atom | x     | y     | z     |
|------|-------|-------|-------|
| H1   | 1.763 | 0.441 | -7.029|
| H2   | 2.936 | 3.749 | 5.723 |
| H3   | 2.782 | 0.442 | 7.030 |
| H4   | 1.609 | 3.748 | -5.723|
| H5   | 0.000 | 0.068 | 7.030 |
| H6   | 4.391 | 1.937 | -5.723|
| H7   | 0.154 | 1.938 | 5.723 |
| H8   | 4.545 | 0.069 | -7.029|
| O1   | 1.070 | 0.429 | -6.342|
| O2   | 0.218 | 0.764 | 1.144 |
| O3   | 2.587 | 3.251 | 4.895 |
| O4   | 3.364 | 3.334 | -2.612|
| O5   | 2.663 | 0.510 | -3.766|
| O6   | 1.881 | 0.510 | 3.767 |
| O7   | 5.054 | 3.121 | 0.000 |
| O8   | 3.475 | 0.430 | 6.343 |
| O9   | 1.958 | 3.251 | -4.895|
| O10  | 1.181 | 3.334 | 2.612 |
| O11  | 4.327 | 0.764 | -1.143|
| O12  | 0.693 | 0.080 | 6.343 |
| O13  | 1.545 | 4.922 | -1.143|
| O14  | 4.740 | 2.434 | -4.895|
| O15  | 3.963 | 2.352 | 2.612 |
| O16  | 4.663 | 5.176 | 3.767 |
| O17  | 2.272 | 2.564 | 0.000 |
| O18  | 5.445 | 0.000 | -3.767|
| O19  | 0.582 | 2.352 | -2.612|
| O20  | 5.369 | 2.434 | 4.895 |
| O21  | 3.852 | 0.080 | -6.342|
| O22  | 3.000 | 4.922 | 1.143 |
| Fe1  | 0.749 | 1.546 | -0.802|
| Fe2  | 3.912 | 4.265 | -4.733|
| Fe3  | 3.149 | 4.113 | 2.971 |
| Fe4  | 1.396 | 4.113 | -2.970|
| Fe5  | 0.633 | 4.265 | 4.733 |
| Fe6  | 3.796 | 1.546 | 0.802 |
| Fe7  | 3.415 | 1.421 | 4.733 |
| Fe8  | 1.014 | 4.140 | 0.802 |
| Fe9  | 4.178 | 1.573 | -2.970|
| Fe10 | 1.130 | 1.421 | -4.733|
| Fe11 | 0.367 | 1.573 | 2.971 |
| Fe12 | 3.531 | 4.140 | -0.802|
|                  | bulk | relaxed | hydrated | hydroxylated |
|------------------|------|---------|----------|--------------|
| **O**            | 35   | 29 (-18%) | 26 (-26%) | 16 (-54 %)   |
| **Fe**           | 80   | 66 (-17%) | 70 (-12%) | 97 (21 %)    |
| **O**            | 80   | 84 (5%)  | 82 (3%)  | 80 (-1 %)    |
| **Fe**           | 35   | 46 (32%) | 45 (29%) | 36 (4 %)     |
| **O**            | 149  | 140 (-6%) | 141 (-5%) | 147 (-1 %)   |

|                  | bulk | relaxed | hydrated | hydroxylated |
|------------------|------|---------|----------|--------------|
| **Fe**           | 86   | 44 (-49%) | 48 (-44%) | 89 (4%)      |
| **O**            | 86   | 83 (-4%) | 83 (-3%) | 78 (-9%)     |
| **Fe**           | 63   | 39 (-37%) | 38 (-39%) | 42 (-32%)    |
| **Fe**           | 86   | 102 (19%) | 102 (19%) | 98 (14%)     |
TABLE XVIII. Slab unit cell coordinates for the hydrated (001) surface. X, Y, and Z coordinates in Å. Orthogonal unit
mesh translation vectors are 8.976 Å in X and 5.176 Å in Y.

| atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| H1   | 4.989000  | 3.646000  | -6.607000 |
| H2   | 3.927000  | 4.686000  | -6.662000 |
| H3   | 0.400000  | 2.017000  | -6.664000 |
| H4   | 8.314000  | 0.966000  | -6.607000 |
| H5   | 6.296000  | 1.119000  | 6.663000  |
| H6   | 5.210000  | 2.132000  | 6.584000  |
| H7   | 1.875000  | 4.760000  | 6.608000  |
| H8   | 0.795000  | 3.739000  | 6.640000  |
| O1   | 0.000000  | 4.964000  | -1.193000 |
| O2   | 1.410000  | 2.409000  | 3.422000  |
| O3   | 4.490000  | 2.376000  | -1.190000 |
| O4   | 5.904000  | 4.997000  | 3.419000  |
| O5   | 7.366000  | 2.494000  | 3.416000  |
| O6   | 5.851000  | 0.000000  | -1.194000 |
| O7   | 1.364000  | 2.590000  | -1.189000 |
| O8   | 2.877000  | 5.086000  | 3.426000  |
| O9   | 8.800000  | 5.009000  | 3.407000  |
| O10  | 7.231000  | 2.367000  | -1.197000 |
| O11  | 2.743000  | 4.954000  | -1.186000 |
| O12  | 4.314000  | 2.427000  | 3.423000  |
| O13  | 4.316000  | 0.753000  | -3.429000 |
| O14  | 5.731000  | 3.373000  | 1.179000  |
| O15  | 8.810000  | 3.340000  | -3.434000 |
| O16  | 1.245000  | 0.785000  | 1.181000  |
| O17  | 8.857000  | 3.159000  | 1.177000  |
| O18  | 7.344000  | 0.663000  | -3.435000 |
| O19  | 2.855000  | 3.255000  | -3.428000 |
| O20  | 4.369000  | 0.574000  | 1.183000  |
| O21  | 5.906000  | 3.322000  | -3.435000 |
| O22  | 7.477000  | 0.795000  | 1.174000  |
| O23  | 1.420000  | 0.740000  | -3.421000 |
| O24  | 2.990000  | 3.383000  | 1.185000  |
| O25  | 4.447000  | 4.188000  | -5.980000 |
| O26  | 8.867000  | 1.499000  | -5.979000 |
| O27  | 5.779000  | 1.604000  | 5.969000  |
| O28  | 1.324000  | 4.241000  | 5.969000  |
| Fe1  | 4.359000  | 4.168000  | -3.910000 |
| Fe2  | 5.859000  | 1.581000  | 0.293000  |
| Fe3  | 8.851000  | 1.579000  | -3.909000 |
| Fe4  | 1.372000  | 4.168000  | 0.295000  |
| Fe5  | 5.856000  | 1.579000  | -2.601000 |
| Fe6  | 7.356000  | 4.167000  | 2.199000  |
| Fe7  | 1.368000  | 4.169000  | -2.596000 |
| Fe8  | 2.867000  | 1.582000  | 2.205000  |
| Fe9  | 8.848001  | 1.581000  | -0.307000 |
| Fe10 | 5.861000  | 1.582000  | 3.898000  |
| Fe11 | 1.369000  | 4.170000  | 3.898000  |
| Fe12 | 4.362000  | 4.168000  | -0.304000 |
| Fe13 | 8.853000  | 1.581000  | 2.584000  |
| Fe14 | 7.353000  | 4.167000  | -2.217000 |
| Fe15 | 2.865000  | 1.582000  | -2.211000 |
| Fe16 | 4.365000  | 4.171000  | 2.590000  |
TABLE XIX. Slab unit cell coordinates for the hydroxylated (001) surface. X, Y, and Z coordinates in Å. Orthogonal unit
mesh translation vectors are 8.976 Å in X and 5.176 Å in Y.

| atom | x       | y       | z       |
|------|---------|---------|---------|
| H1   | 8.478001| 5.121000| 4.469000|
| H2   | 3.991000| 2.534000| 4.470000|
| H3   | 6.468000| 3.444000| -4.468000|
| H4   | 1.980000| 0.856000| -4.469000|
| H5   | 4.417000| 4.322000| -6.994000|
| H6   | 8.902000| 1.740000| -6.994000|
| H7   | 6.046000| 1.651000| 6.994000|
| H8   | 1.547000| 4.245000| 6.994000|
| O1   | 0.149000| 5.068000| -1.204000|
| O2   | 1.585000| 2.589000| 3.533000|
| O3   | 4.638000| 2.480000| -1.202000|
| O4   | 6.073000| 0.900000| 3.355000|
| O5   | 7.481000| 2.621000| 3.362000|
| O6   | 5.992000| 0.073000| -1.164000|
| O7   | 1.503000| 2.660000| -1.164000|
| O8   | 2.993000| 0.033000| 3.363000|
| O9   | 8.954000| 5.145000| 3.581000|
| O10  | 7.321000| 2.500000| -1.156000|
| O11  | 2.832000| 5.086000| -1.154000|
| O12  | 4.467000| 2.557000| 3.582000|
| O13  | 4.386000| 0.800000| -3.353000|
| O14  | 5.819000| 3.495000| 1.203000|
| O15  | 8.875000| 3.390000| -3.353000|
| O16  | 1.331000| 0.906000| 1.202000|
| O17  | 8.955000| 3.317000| 1.163000|
| O18  | 7.465000| 0.769000| -3.362000|
| O19  | 2.977000| 3.356000| -3.362000|
| O20  | 4.467000| 0.729000| 1.165000|
| O21  | 5.991000| 3.418000| -3.581000|
| O22  | 7.626000| 0.891000| 1.155000|
| O23  | 1.503000| 0.830000| -3.582000|
| O24  | 3.137000| 3.476000| 1.157000|
| O25  | 4.488000| 4.316000| -6.081000|
| O26  | 0.000000| 1.726000| -6.081000|
| O27  | 5.974000| 1.661000| 6.081000|
| O28  | 1.482000| 4.249000| 6.080000|
| Fe1  | 4.317000| 4.316000| -4.252000|
| Fe2  | 5.988000| 1.706000| 0.358000|
| Fe3  | 8.805000| 1.729000| -4.252000|
| Fe4  | 1.500000| 4.292000| 0.357000|
| Fe5  | 5.945000| 1.611000| -2.577000|
| Fe6  | 7.426000| 4.272000| 2.153000|
| Fe7  | 1.457000| 4.197000| -2.577000|
| Fe8  | 2.938000| 1.683000| 2.155000|
| Fe9  | 8.959000| 1.685000| -0.359000|
| Fe10 | 6.142000| 1.661000| 4.252000|
| Fe11 | 1.655000| 4.249000| 4.250000|
| Fe12 | 4.471000| 4.272000| -0.357000|
| Fe13 | 0.024000| 1.779000| 2.579000|
| Fe14 | 7.520000| 4.294000| -2.152000|
| Fe15 | 3.030000| 1.703000| -2.152000|
| Fe16 | 4.512000| 4.365000| 2.579000|