Supporting Information to:

Diversity at the water-metal interface: metal, water thickness, and confinement effects

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1. Definitions

1.1 Density

The density values reported in the manuscript have been computed according to the following formula:

\[
\rho = \frac{N \cdot m_{\text{H}_2\text{O}}}{|\mathbf{a} \times \mathbf{b} \cdot \Delta \mathbf{z}|} \quad \text{Eq. S.I. 1}
\]

where \(N\) is the number of water molecules in the system, \(m_{\text{H}_2\text{O}}\) the mass of one of them, \(|\mathbf{a} \times \mathbf{b} \cdot \Delta \mathbf{z}|\) is the volume defined by the two lattice vectors with no \(z\) component, \(\mathbf{a}\) and \(\mathbf{b}\), and \(\Delta \mathbf{z}\), which is computed as:

\[
\Delta \mathbf{z} = \left( \bar{z}_{\text{max}} - z_{\text{min}} + 2 \times 0.60 \right) \hat{z} \quad \text{Eq. S.I. 2}
\]

Where \(\bar{z}_{\text{max}}\) is the \(z\)-coordinate average over all the oxygens belonging to the upper layer, \(z_{\text{min}}\) is the lowest \(z\) coordinate for an oxygen in the system, and 0.60 Å is the ionic radius of the oxygen atom.

1.2 Tetrahedrality

To inspect the phase transition between ice and liquid water, we mapped the tetrahedrality of each oxygen with respect with its four nearest vicinal hydrogen atoms, following the equation.\(^1\)

\[
q = 1 - \frac{3}{32} \sum_{j=1}^{3} \sum_{k=j+1}^{4} \left( \mathbf{r}_j \cdot \mathbf{r}_k + \frac{1}{3} \right)^2 \quad \text{Eq. S.I. 3}
\]

Where \(q\) is defined between 0.00 and 1.00. Values close to 1.00 correspond to a tetrahedral configuration. Values lower than 0.88 corresponds to tri-coordinated oxygen atoms, i.e. acceptors of one hydrogen bond. Values lower than 0.72 were seldom detected during the dynamics and correspond to oxygens that are not acceptors of any hydrogen bond, or other short-lived fragments (or topmost layer in contact with the vacuum). \(\mathbf{r}_j\) is the unitary vector whose direction is defined by the central oxygen and the hydrogen “\(j\)”, in Cartesian coordinates. “\(\cdot\)” is the usual inner product defined in \(\mathbb{R}^3\).

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\(^1\) Chau, P-L., and A. J. Hardwick. A new order parameter for tetrahedral configurations. Molec. Phys. 93 (1998) 511-518.
To generate the cumulative normalized histogram:

- We split the possible values of tetrahedrality in 50 segments of 0.01 units of width each one, from 0.50 to 1.00. We did not observe any molecule whose tetrahedrality were lower or equal than 0.50.
- We counted the number of water molecules whose tetrahedrality belongs to each segment.
- We divided the number obtained in step 2 by the total number of molecules presented in all the steps of the BOMD, which is 360000 for 2 unconfined bilayers, 720000 for 4 confined bilayers, and 1440000 for 4 unconfined and 8 confined bilayers.

1.3 Water-Metal interface tessellation

Structures reported in Figure 4 of the main text show the interfacial water structure in terms of the N-membered rings formed for Pd4, Pt4, and Ru4. To compute the tessellation, we removed all the atoms above 3.3 Å for Pd4 and Pt4; in the case of Ru4, water fragments are closer to the surface, and we employed a cutoff of 2.6 Å. We then proceeded to connect the oxygen centers through their hydrogen bonds, creating the geometric structures as in Figure 4 of the main text. Finally, we computed the geometric center of the oxygens of each geometric structure, and from there we proceeded to color the surface according to its number of edges: silver (4), dark yellow (5), orange (6), wine (7), wine (8), and dark purple (9). This procedure is analogous to Voronoi tessellations.
2. Tests

2.1 k-point sampling

We tested the k-point sampling to search for deviations on the measured properties, i.e. RDF and tetrahedrality. To do so, we chose the most variable system under study, the Pd/Pt/Ru4 and added 500 fs of simulation. We increase the k-point sampling to $2\times2\times1$, and preserve all the other settings. We show in Figures S.I. 1–3 the excellent match between the resulting RDF, which are almost indistinguishable from each other. Figure S.I. 4 compares the cumulative tetrahedrality, also showing an excellent match. Therefore, we can safely use $\Gamma$-point calculations to describe all the structural features of the systems under study, without any significant mismatch.

![Graph showing RDF for Pd, Pt, and Ru](image)

**Figure S.I. 1.** Radial distribution function ($g_{O-O}$) for the oxygen-oxygen distance in Pd4 (orange), Pt4 (dark yellow), and Ru4 (wine) averaged for the last 0.5 ps. Dotted lines represent the RDF obtained on $\Gamma$–point, whereas solid lines are retrieve from $2\times2\times1$ $\Gamma$–centered k–points.
Figure S.I. 2. Radial distribution function ($g_{O-H}$) for the oxygen-hydrogen distance in Pd4 (orange), Pt4 (dark yellow), and Ru4 (wine) averaged for the last 0.5 ps. Dotted lines represent the RDF obtained on Γ–point, whereas solid lines are retrieve from 2×2×1 Γ–centered k–points.

Figure S.I. 3. Radial distribution function ($g_{H-H}$) for the hydrogen-hydrogen distance in Pd4 (orange), Pt4 (dark yellow), and Ru4 (wine) averaged for the last 0.5 ps. Dotted lines represent the RDF obtained on Γ–point, whereas solid lines are retrieve from 2×2×1 Γ–centered k–points.
Figure S.I. 4. Tetrahedrality distribution for Pd4 (a), Pt4 (b), and Ru4 (c). Solid lines represent the ab-initio molecular dynamics done on gamma-point, while dotted lines represent the ones done on 2×2×1.
2.2 Time step

Figure S.I. 5. RDF O-O (a), O-H (b), and H-H (c) for at 0.5 fs and 1.0 fs of time-step.
Figure S.I. 6. Tetrahedrality distribution for Ru4v at (a) 0.5 fs and (b) 1.0 fs of time-step. (c) Probability Distribution Function, $P(q)$ of the tetrahedrality, $q$, for both systems.

As can be seen from the figures above no significant change is observed when changing from time steps of 1fs to 0.5fs.
2.3 Tetrahedrality overlap

The tetrahedrality $P(q)$ follows a bimodal distribution, where the first mode corresponds to tricoordinated molecules, $P_3(q)$, and the second mode to tetracoordinated ones, $P_4(q)$, Eq. S.I. 4. Because the tetrahedrality is defined between 0 and 1, the addition of both Probability Density Functions (PDF) should be equal to one, Eq. S.I. 5:

$$P(q) = P_3(q) + P_4(q)$$  \hspace{1cm} \text{Eq. S.I. 4}

$$\int_0^1 P(q) \, dq = 1$$  \hspace{1cm} \text{Eq. S.I. 5}

The tri-coordinated water molecules follow a Gaussian distribution, Eq. S.I. 6, which define effectively the peak around $q=0.84$. The limit $q=1.00$ lies ~8 standard deviations from the mean value, therefore the percent of molecules outside the range $[0.00, 1.00]$ for that distribution will be negligible, in the order of $10^{-15}$. The distribution of the trihedral molecules is defined by the mean, $\mu$, the standard deviation, $\sigma$, and the ratio of molecules that are trihedral, $1-\rho$. All parameters were dimensionless.

$$P_3(q) = (1-\rho) \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(q-\mu)^2}{2\sigma^2}}$$  \hspace{1cm} \text{Eq. S.I. 6}

On the other hand, it would be inconvenient to define the tetra-coordinated molecules by a Gaussian function, provided that the mean values (around 0.98) would be very close to the limiting value 1.00, in the order of one standard deviation. Therefore, we chose to model the tetra-coordinated molecules as a Beta distribution, Eq. S.I. 7, which is suitable for variables defined for the range $[0.00; 1.00]$. The Beta distribution is defined by the shape parameters $\alpha$ and $\beta$, dimensionless, and the ratio of molecules that are trihedral, $\rho$. $\Gamma(x)$ is the Gamma function of $x$, $x \in \{\alpha, \beta\}$.

$$P_4(q) = \rho \frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha) \Gamma(\beta)} q^{\alpha-1} (1-q)^{\beta-1}$$  \hspace{1cm} \text{Eq. S.I. 7}

Because the functions $P_3(q)$ and $P_4(q)$ overlap around $q=0.88$, it is unclear what is the true coordination of such molecules. To determine the magnitude of this error, we calculated parameters that define Eq. S.I. 6–7, taking as reference the system Pd4. The regression was performed minimizing the absolute error between the observed $P(q)$, orange line in Fig. S.I. 6 (a), and the one obtained from Eq. S.I. 4–7, obtained the dotted line in Fig S.I. 6 (a), using a precision of three decimals (five for $\sigma$). In Fig S.I. 6 (b) we separate the equations $P_3(q)$ and $P_4(q)$, highlighting in red the overlap between them. For the values reported in Table S.I. 1, this overlap is lower than 0.525%, calculating them by Eq. S.I. 8. To assure that the denominator in Eq. S.I. 8 were 1, we increased the accuracy by increasing the discretization of $q$ to step sizes of 0.002. Therefore, the tetrahedrality is demonstrated to be a sufficiently robust descriptor for the coordination environment.
\[ \text{overlap} = \frac{\int_0^1 \min(P_3(q), P_4(q)) \, dq}{\int_0^1 P_3(q) \, dq + \int_0^1 P_4(q) \, dq} \]  

Eq. S.I. 8

**Table S.I. 1.** Parameters that describe the Probability Density Functions for Pd4. All values are dimensionless.

| Parameter | Value   |
|-----------|---------|
| \( \alpha \) | 59.051  |
| \( \beta \)  | 1.925   |
| \( \sigma \) | 0.02004 |
| \( \mu \)   | 0.836   |
| \( \rho \)  | 0.842   |

**Figure S.I. 7.** (a) Observed Probability Distribution Function for Pd4, in orange, and the Bimodal distribution defined by Eq. S.I. 4–7. (b) The overlap area between both PDF, filled in red, is 0.00525.
2.4 Speciation cutoff radius dependence Ru(0001)

Figure S.I. 8. Test for different cutoff radii: 1.20 Å and 1.30 Å. Results show the difference (Δ) in the number of the computed species with respect to the cutoff used in the article, 1.25 Å. Warm colors for acidic species (H\(^+\), H\(_3\)O\(^+\), and H\(_5\)O\(_2\)\(^+\)), and cold colors for basic ones (OH\(^-\), H\(_3\)O\(_2\)\(^-\), and H\(_5\)O\(_3\)\(^-\)).

All the data reported in the main manuscript assume that hydrogen atoms are not connected to any oxygen more than 1.25 Å apart. To check the robustness of our settings, we monitored the number of species as a function of the cutoff radius (\(r_c\)), being it 1.20 or 1.30 Å, for a system of reference, namely Ru2.

Figure S.I. 8 reports the difference between the number of the species with the cutoff reported in the legend, and the same species with \(r_c = 1.25\) Å, used in the main manuscript. The closer the values are to zero, the more robust is our setting. Acidic species H\(^+\), H\(_3\)O\(^+\), and H\(_5\)O\(_2\)\(^+\) are mildly affected by the different \(r_c\): the average number of H\(^+\) species is increased by 0.24 with \(r_c = 1.20\) Å and decreased by 0.01 for \(r_c = 1.30\) Å. H\(_3\)O\(^+\), and H\(_5\)O\(_2\)\(^+\) are basically not affected by the change in the cutoff. This means that, for the run recorded, the number of H\(^+\) is 9 for any 1.20 ≤ \(r_c\) ≤ 1.30.

Basic species are more sensible to \(r_c\): the number of OH\(^-\) increases by 0.57 when 1.20 is employed as \(r_c\) (some stretched water molecules and the H\(_3\)O\(_2\)\(^-\) species are considered an ionic pair OH/H\(^+\) or H\(_2\)O/OH\(^-\)), whereas decreases by the same extent when 1.30 is
used (opposite reasoning). On the contrary, H₃O₂⁻ species follow an opposite trend: their number decreases by 0.34 at small $r_c$ (some of them convert into the H₂O/OH⁻ pair), whereas they number augments of 0.56 units when the bigger cutoff is employed, and opposite to the trend of OH⁻. This variation in the number of units in each snapshot is only meaningful for the H₃O₂⁻ species, whose average number would oscillate between 0 ($r_c=1.20$ Å) and 1 ($r_c=1.30$ Å). Nevertheless, simulations clearly show the withdrawing of one proton from an adsorbed water molecule to the nearby hydroxyl unit, thus starting a “fast and loose” game where the proton jumps from one species to the other, and many times just hovers in the middle. For this reason, we preferred to use $r_c=1.25$ Å.
3. Results

3.1. Radial distribution functions for O-H and H-H

Figure S.I. 9. RDF $g_{O-H}$ for oxygen and hydrogen in water bilayers on Pd (orange), Pt (green), and Ru (wine) metal surfaces separated by 9 Å with the closest top water layer. Nomenclature is reported in the text. Experimental data have been drawn in solid black (liquid) and dashed line (ice).
Figure S.I. 10. RDF $g_{HH}$ for hydrogen-hydrogen in water bilayers on Pd (orange), Pt (green), and Ru (wine) metal surfaces separated by 9 Å with the closest top water layer. Nomenclature is reported in the text. Experimental data have been drawn in solid black (liquid) and dashed line (ice).

Figure S.I. 9 report the RDF for O–H. Confined systems show wide peaks at 4 and 5 Å, typical of ice. In the case of Figure S.I. 10, the H–H RDF does not give any additional insight into the water structure on these systems: hydrogen, lighter and more mobile than their oxygen partners, quickly lose any long range order. It is important to notice that the computed RDF functions tend to 0, instead of 1. This is due to the finite size of our bilayers, limited in the z direction, compared to the experimental results that deal with almost-infinite systems (bulk).

We also calculated 5.5 ps of an ab-initio molecular dynamics of liquid water at 300 K, using the $4 \times 4 \times 2$ expansion of ice XI, which contains 128 water molecules, as initial guess. The rest of the parameters were the same as specified in the Methods section in
the manuscript. The results of the RDF O–O, O–H, and H–H are summarized in Fig S.I. 11, and compared with the experimental values.²

Figure S.I. 11. RDF $g_{O-O}$, $g_{O-H}$ and $g_{H-H}$ for liquid water experimental (continuous) and calculated (dashed line).

3.2. Tetrahedrality for the systems considered

Figure S.I. 11 shows the tetrahedrality changes over time when only two unconfined bilayers are placed on the metal (panels a-c), and for the confined systems with four (panels d-f) and eight (panels g-i) bilayers. The cumulative values for those systems are shown in figure S.I. 12. For the confined systems, the intermediate bilayers maintain a highly tetrahedral, ice-like structure for both Pd and Pt. The Ru4c is slightly different by

² ISIS Disordered Materials Database. [http://www.isis.stfc.ac.uk/groups/disordered](http://www.isis.stfc.ac.uk/groups/disordered).
the end of the MD run the central layers exhibit HDL-like features probably a consequence of the dissociation at the interface but the time scale for reorientation is still longer than for the vacuum interleaved 4 bilayer.

**Figure S.I. 12.** Tetrahedrality evolution as a function of time for two unconfined water layers on a) Pd(111), b) Pt(111), and c) Ru(0001). Central panel (d-f): four confined layers. Bottom panel (g-i): eight confined layers. Upper bars show the scale for tetrahedrality on panels a-i.
Figure S.I. 13. Distribution of tetrahedrality for two unconfined (a), four confined (b), and eight confined (c) water layers on the metals under study.

Figure S.I. 14. Heights with respect to the metal surface of three water molecules assigned originally to the second bilayer, and diffused to the first bilayer, #19 and #34 for Pd4, and #35 for Pt. Tetrahedrality maps are shows for comparison. The behaviour of these molecules is indistinguishable from the ones of the bulk liquid, Figure 3 in the main text.
Figure S.I. 15. shows the Probability Density Function of the tetrahedrality parameter for each layer in the Pd4, Pt4, and Ru4 systems. The reactivity of Ru4 is the responsible for the peak around q=0.90 that is observed in Figure 3 on the main text. As discussed in the main text, in the second layer, around 35% of the molecules are non tetrahedral, because fewer oxygens are coordinated with the first layer. Indeed, the peak around 0.98 is smaller for Ru4 than for Pd4 or Pt4. See also section S.I. 3.5.

Figure S.I. 15. Distribution of tetrahedrality separated by the layers defined by the original position of the molecules for Pd4 (upper panel), Pt4 (middle), and Ru4 (lower).