# Anomalous wetting layer at the Au(111) surface.

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COMPARISON OF CLASSICAL MD AND AIMD SIMULATIONS

Summary of the AIMD results

In the following Figure S1 we report the water density profiles and the average number of hydrogen bonds per water molecules as obtained from our AIMD results to compare the classical MD results with. The figure also presents the error bars of the calculated values to evidence that the effects discussed in the paper are statistically significant.

(a)

(b)
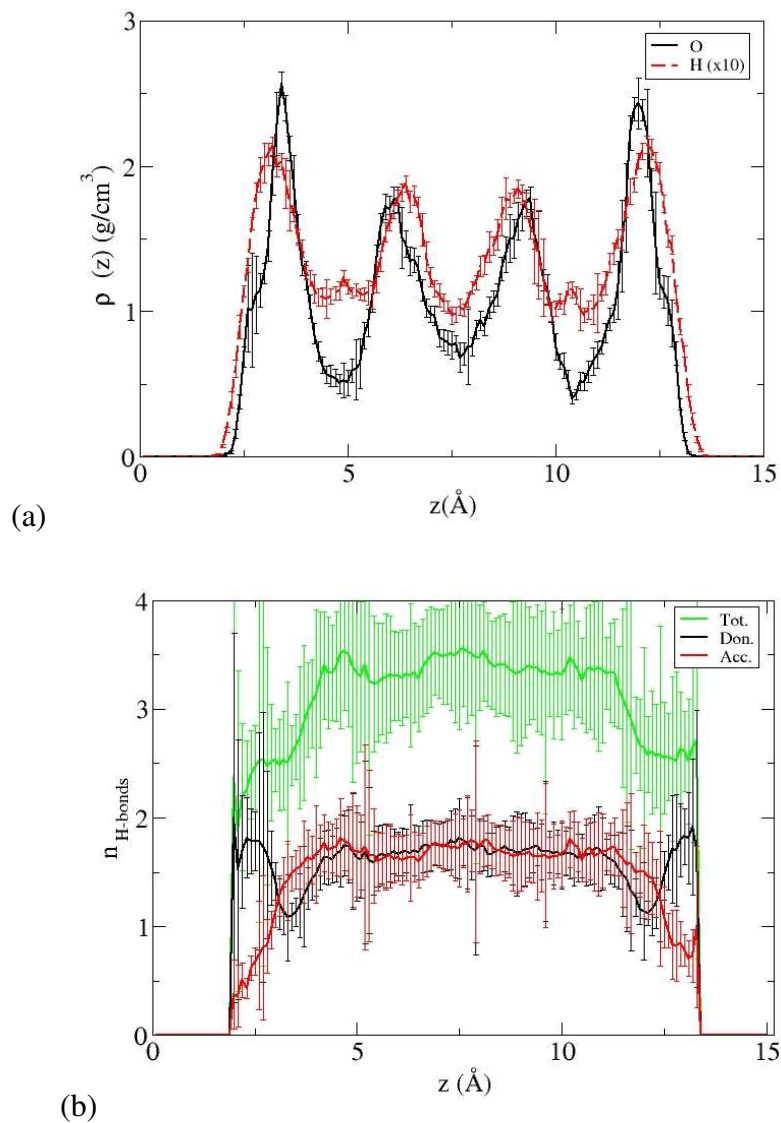
Figure S1: Water density profile (a) calculated with respect to the oxygen (black curve) and hydrogen (red curve) atoms. Average number of hydrogen bonds per water molecule (b); the green curve corresponds to the total number of H-bond, the black curve to the number of donors and the red curve to the number of acceptor. Error bars represent the standard deviation on the average density or number of hydrogen bonds per each point along the z direction (block average is used for estimating the standard deviation). Gold surfaces are at z=0 Å and z=15.2 Å (i.e., the edges of the graph). No symmetrization with respect to the center of the water slab is performed.

Gold Surface exposed to Water in the gas phase.

To verify if the enhancement of the interaction between water molecules and gold surface atoms and the corresponding reduction of the Au···O distance is determined by the oscillations of the gold surface atoms and the molecular vibrations, we performed an ab initio molecular dynamics (AIMD) simulation in which gold is exposed to a single layer of water molecules at 400 K. The AIMD trajectory reveals that the features of the interaction between gold and water are similar to the one observed for the liquid water/gold interface. Indeed, although most of the molecules tend to evaporate, some of them clearly interact with the gold atoms through their lone pair. The distance of the oxygen atoms of the water molecules from the Au atoms at surface attains a value of 2.4 Å which is smaller than that obtained from the calculation of the interaction of a single water molecule at 0 K.
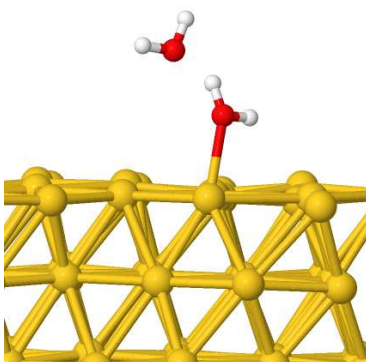
Figure S2: Representative snapshot (side view) along the MD simulation run for Au(111) surface exposed to 1 ML of water molecules. One water molecule interact through its lone pair with a surface gold atom (Au···O = 2.5 Å) and at the same time it is involved in a hydrogen bond interaction with a water molecule in the gas phase (O···O = 2.6 Å). The other water molecules have been removed for a clearer rendering.

Computational details of the classical potential calculations.

Classical molecular dynamics simulations have been done by using the same water layer thickness as in the AIMD simulation. The in-plane cell size (2.0304 nm x 2.0529 nm) and the thickness of the gold slab (5 layers) are larger to allow a meaningful value for the cutoff distance of non-bond interactions in the classical MD (in AIMD, the in-plane cell size is 1.5239 nm x 1.4663 nm and 4 gold layers are used). For consistency, the same number of water molecules per surface area used in AIMD is used in the classical MD. Simulations have been run for 150 ps. Different force fields (ff) to describe water-gold interaction have been tested, with the aim of comparing with the structural results of interfacial water obtained by AIMD. The various combinations of force fields that have been used are summarized in the following table:

|	ff water-water	ff water-gold	ff gold-gold	Notes
a	SPC	GolP[a]	-	-
b	SPC	modified GolP (to reproduce PW91 adsorption energy and including a LJ term between water H and Au with ε_{AuH}=0.01 kJ/mol; σ_{AuH}=0.34 nm)	-	-
c	SPC	CVFF-METAL[b]	CVFF-METAL.[b]	mobile Au

[a] Ref. 1
[b] Ref. 2

Table S1 Summary of the force fields (ff) employed in the classical molecular dynamics simulations.

GolP is a force field developed to study proteins on Au(111) surfaces in water and includes gold polarizability, while CVFF-METAL was developed to describe metal surfaces and their interaction with physisorbed molecules and water. These force fields were not specifically tailored to reproduce structural properties of the water-Au(111)

interface. They were instead built to provide a balanced description of Au-water and Au-adsorbate (specifically Au-peptides for GolP) interactions preserving at the same time the computational efficiency of classical force fields for biomolecules. Still, they are representative of some force fields used in the past to describe water-metal interfaces based on Lennard Jones (LJ) Au-water potentials.[3]

All the calculations have been performed with GROMACS 3.2.1[4], by employing PME for electrostatics (with default parameters), cutting-off the Lennard-Jones (LJ) interaction at 10 Å (unless otherwise stated) and using a time-step of 2 fs, with rigid water molecules. A Nosé-Hoover thermostat (T=300K) has been used, simulations have been performed at constant volume. For one of the test case a temperature of 400 K has been set, similarly to the AIMD simulations.

Results for Classical MD with force field (*a*): SPC water and GolP

(a)   (b)
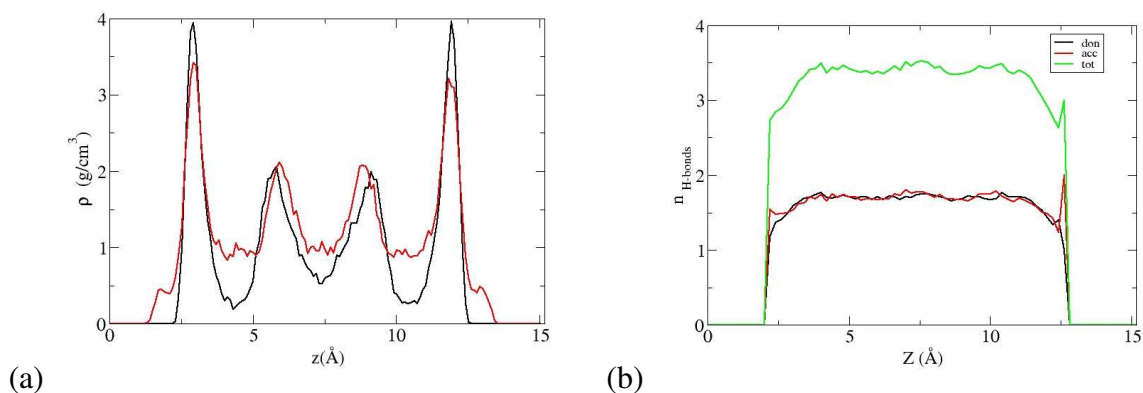
Figure S3: Water density (a) and H-bond (b) profiles calculated from the classical MD trajectory obtained for case a reported in Table S1. Color code as in Fig. S1.

From the comparison of the density profiles and average number of hydrogen bonds reported in Fig. S1 for AIMD results and the one reported in Fig. S3 for this combination of classical potentials the following differences can be noted:

1. In the O density, the peaks of the water layers close to the surface are higher and narrower in the classical calculations than in the AIMD. There is no shoulder at d=2.6 Å in the classical results. However, if the surface area of water O in the first layer is calculated, one gets $\bullet_{area}$=3.06 g Å/cm^3 for the classical results and $\bullet_{area}$= 3.12 g Å/cm^3 for the AIMD simulations, which are quite similar.

2. In the H density, small peaks are visible at ~2.0 Å from gold. No such peak is seen in AIMD. Similarly to O, the classical peaks are narrower than AIMD ones.

3. While the AIMD results show that at the interface water molecules are more often H-bond donors than H-bond acceptors, the classical results give the same number of donors and acceptors (within statistical uncertainties). The variation of total number of H-bonds per molecules at the interface with respect to the bulk is similar for both classical and AIMD simulations (within statistical errors).

Water H has no LJ interactions in SPC classical force fields. This is to better represent H-bonds. Since H has no LJ interaction with gold, there is nothing preventing them to get close to the Au atoms in the classical simulation. This is the origin of the H density peak at 2.0 Å from the surface that corresponds to molecules oriented as in Fig. S3. On the basis of peaks area, the number of water molecule with this orientation in the first layer is about 10% of the total.

Figure S4: Snapshot representing the preferential orientation of water molecules at the gold surface as obtained with the classical potential indicated with (a) in Table S1.

The molecule found in this orientation can accept 2 H-bonds and can donate only 1 H-bonds. By assuming this conformation, the balance between H-bond donors and acceptors can be restored at the interface as well, which explains why Fig. S3b is different from Fig. S1b. Interestingly, when the H density profile is calculated from AIMD excluding the water molecule of the layer at 2.6 Å, small peaks similar to those in Fig. S3 are recovered (Figure S5). This indicates that in AIMD the first "normal" water layer contains water molecules oriented as in Figure S4, similarly to classical MD. The main difference between the classical and the ab initio calculations is therefore confirmed to be the lacking of the water layer that corresponds to the shoulder in the density profile of Fig. S1(a)
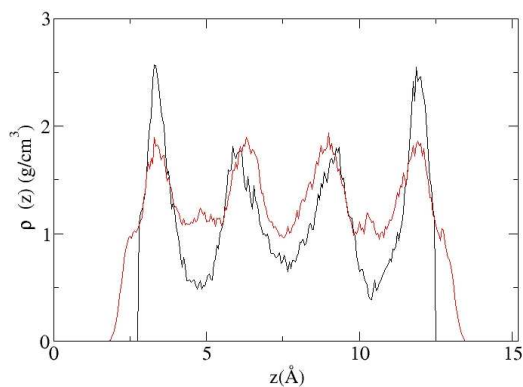
Figure S5: Water density calculated from the AIMD trajectory by excluding the water molecules with Oxygen atoms closer than 2.6 Å to the gold surface. Color code as in Fig. S1.

Simulations performed at a different temperature (T=400K, as in AIMD), with a different water model (TIP3P instead of SPC) or with Au-O LJ parameters derived to reproduce the DFT (PW91) adsorption energy of a single water molecule[1] provided the same picture described here in this paragraph.

Results for Classical MD with force fiels (*b*): SPC water including LJ between gold and water and modified GolP potential to reproduce DFT (PW91) results
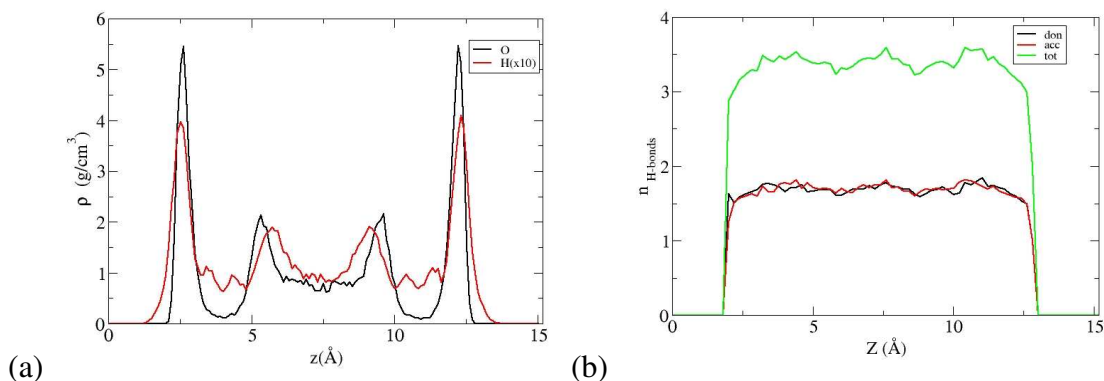

(a)

(b)

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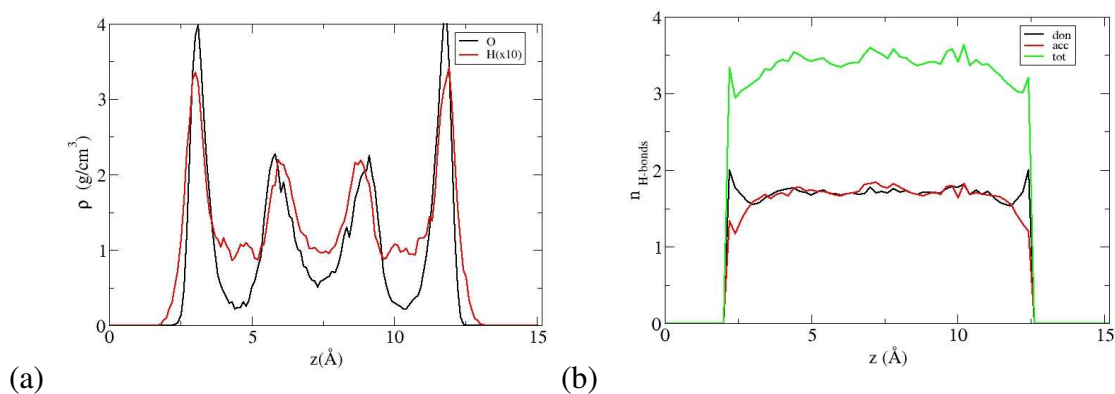
Figure S6: Water density (a) and H-bond (b) profiles calculated from the classical MD trajectory obtained for case b reported in Table S1. Color code as in Fig. S1.

As discussed with reference to Fig. S3, some discrepancies between the AIMD and the classical calculations are related to the absence of a LJ interaction between water H and gold in the classical force fields. To partially correct the classical results, a small LJ term has been added between H and gold. The depth of the LJ potential is very small (0.01 kJ/mol), and does not modify the adsorption energy of the single water molecule. The addition of this LJ improves the qualitative agreement with AIMD: the two small peaks close to gold in the density of H disappear, and the molecules close to the surface acts more as H-bond donors than as H-bond acceptors. However, quantitative discrepancies remain.

Results for Classical MD with force fiels (c): SPC water and CVFF-METAL force field for gold water interaction (mobile gold atoms)

(a) (b)

Figure S7: Water density (a) and H-bond (b) profiles calculated from the classical MD trajectory obtained for case c reported in Table S1. Color code as in Fig. S1.

9

In this test case, we have employed a force field that has been recently proposed by Heinz et al.[2] This potential involves LJ interactions among water molecules and gold atoms, no image charge is considered and it allows using mobile gold surface. Results reported in Fig. S7a are in agreement with water density profile previously obtained with the same force field. With respect to the AIMD and the GolP simulations, higher maximum densities are obtained, although the surface density is very similar (ρ_{area}=3.12 g Å/cm^3). Even if the gold atoms are mobile, the water density peaks are much narrower than in AIMD, moreover the position of O density maximum is much closer to surface gold atoms if compared to the AIMD results of Fig. S1 (2.6 Å instead of 3.3 Å). Although the peaks in the H density are not present, this force field does not describe the H-bond of molecule at surfaces (Fig.S7b). This is consistent with the absence also in this force field of H-Au LJ interactions.

Finally, we point out that this force field gives preferential water adsorption in the hollow sites, while GolP in the on-top site (see Fig. S8), as the AIMD simulation.

(a) (b)

(c) (d)
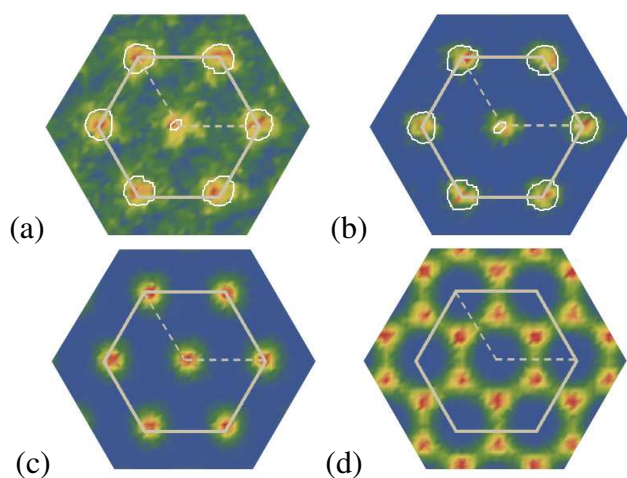
Figure S8: Two-dimensional O-Au in plane distribution function for water molecules in the layer "in contact" with the metal surface for (a) the AIMD simulation (the entire first layer is used); (b) the AIMD simulation (only molecules closer to gold than 2.6 Å are considered); (c) calculations performed using GolP and (d) using the CVFF-METAL force field[2]

PBE-D calculations

The influence of the London dispersion forces on the interaction between a water molecule and the Au(111) surface has been evaluated by applying a London dispersion correction following the DFT-D approach proposed and parameterized in Ref. [10-11]. Upon structural relaxation the water molecule remains at an on-top site and the distance between the oxygen atom of the water molecule and the gold atom at the surface decreases from 2.81 Å (at PBE level) to 2.54 Å (at PBE-D level) corresponding to strengthening of the interaction. We also notice that the inclusion of dispersion forces does not alter the electronic features characterizing water/gold interaction and, in particular, it does not affect the charge transfer contribution to the binding. This is shown both by the values of the Löwdin charges reported in Table S2 and by the Density of States (DOS) of Fig. S9. In particular the shift al lower energies of the DOS induced by London dispersion inclusion is another indication of the strengthening of the interaction between water and gold, further supporting the conclusion of our paper on gold surface hydrophilicity.
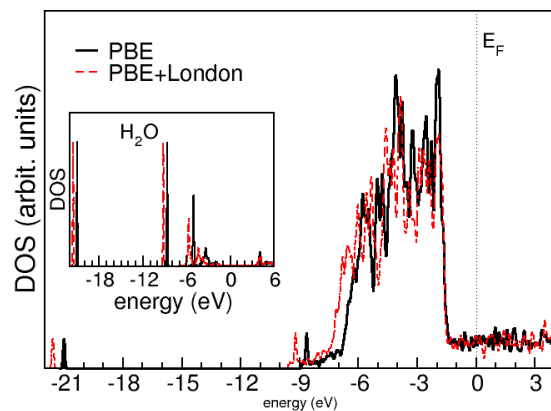
Figure S9 Density of States (DOS) for a water molecule interacting with Au(111) surface in the minimum energy configuration calculated at PBE level with (red dashed line) and without (black line) the inclusion of the London dispersion contribution.

	PBE	PBE-D
O (isolated mol)	6.731	6.731
O (interface)	6.617	6.586
Au (top)	10.993	10.987

Table S2 Löwdin Charges for the oxygen atom and gold atom involved in the interaction calculated at PBE and PBE-D level.

Conclusions

In conclusion, the molecular dynamics tests here presented evidence that the structural features of the interfacial water at the gold surface cannot be entirely captured with these simple classical force fields. In particular the tested classical potentials do not predict the existence of a shoulder towards the surface in the first density peak, ascribed to water

molecules interacting with gold atoms through their lone pair. The hydrogen bonding features of interfacial water molecules are also not completely described by classical potentials (although a simple correction such as adding Au-H LJ terms improves the situation) since, as discussed in the main text, such features appear to be determined by electronic effects. We remark that the tested potentials were not specifically designed to reproduce the structural features of the water-Au interface, but to provide a balanced treatment of Au-water and Au-peptides interactions. For peptide-Au simulations in water, they indeed yield results consistent with experimental evidences collected so far.[5,6] On the contrary, further potential developments, likely including the use of more complex potential terms than just Lennard-Jones and polarization interactions,[3,7-9] are needed to properly reproduce the characteristics of interfacial water at the gold surface disclosed here by AIMD simulations.

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