Ab Initio Molecular Dynamics study of the AlOOH boehmite/water interface: role of steps in interfacial Grotthus proton transfers

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Supplementary Information

S1: Water organization in between the two slabs (periodic boundary conditions)

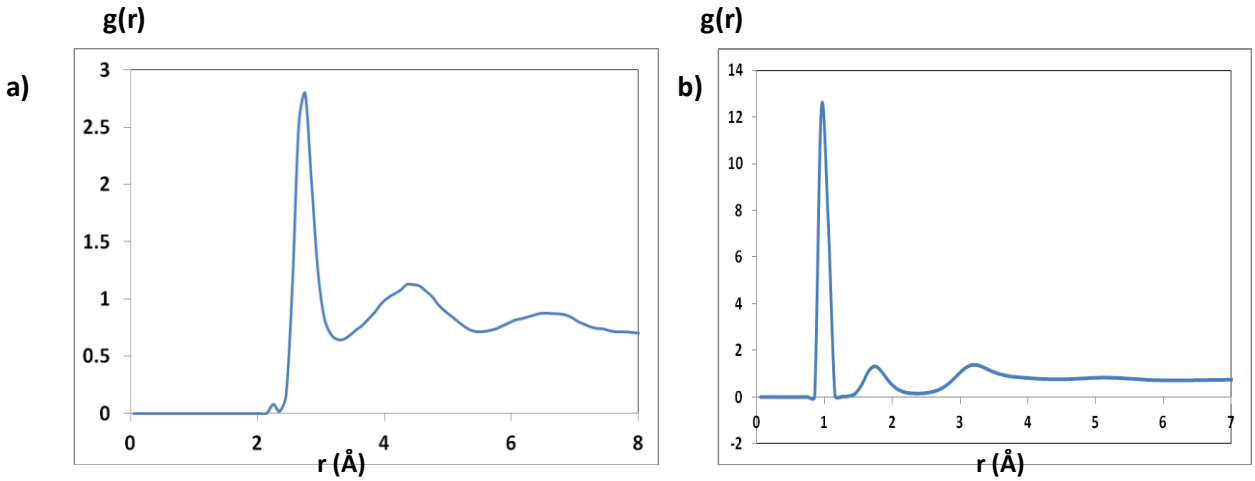
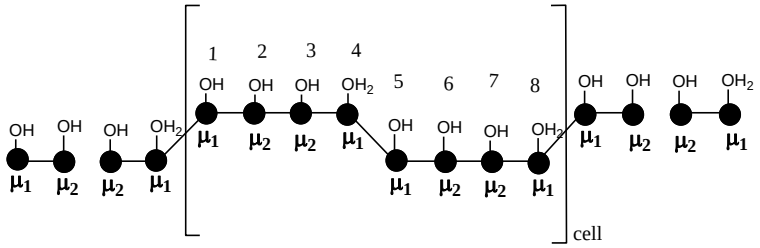


Figure S1 : Normalized radial distribution functions (rdf) of water oxygen-oxygen (Ow-Ow) and oxygen-hydrogen (Ow-Hw) pairs in the water slab in-between the two surfaces (which geometry is shown in Figure 1 of the article).

These curves are representative of liquid water.[i-ii] The hydrogen bond between water molecules is 1.7 Å long on average. The integrated rdf function indicates that each O has 4.07 water molecules as first neighbours (d < 3.25 Å). This confirms that the "confined" water inbetween the two slabs (Periodic Boundary Conditions applied in our simulations) behaves as liquid water.

S2 : Stastistical Analysis of the surface hydroxyls O-H populations.

Tables S2-I and II report the results of the statistical analyses on the nature of the hydroxyls at the surface of the boehmite surface, in terms of μ_1-O (Table S2-I) and μ_2-O (Table S2-II) sites. The cut-off value applied for considering a covalent bond between O and H is the O-H distance lower than 1.25 Å, a value taken from the rdf analysis. The nomenclature chosen for the O atoms is shown in Scheme 1 (also shown in the main text).



Scheme 1 : Repartition of the different OH species on the surface.

Table S2-I	Position 1		Position 4		Position 5		Position 8	
nature	$\mu1$-OH_2	$\mu1$-OH	$\mu1$-OH_2	$\mu1$-OH	$\mu1$-OH_2	$\mu1$-OH	$\mu1$-OH_2	$\mu1$-OH
%	4.5	95.5	90.9	9.1	30.8	69.2	78.6	21.4

Table S2-II	Position 2		Position 3		Position 6		Position 7	
nature	$\mu2$-OH_2	$\mu2$-OH	$\mu2$-OH_2	$\mu2$-OH	$\mu2$-OH_2	$\mu2$-OH	$\mu2$-OH_2	$\mu2$-OH
%	2.5	97.5	7.7	92.3	3.2	96.8	1.1	98.9

S3 : Radial distribution functions (rdf) and hydrogen bond networks

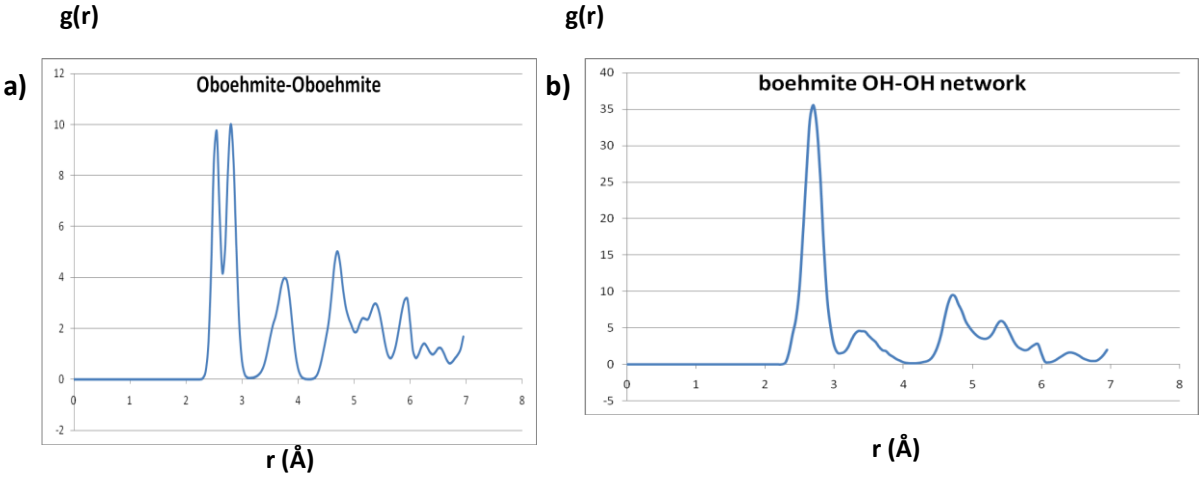


Figure S3-1 : O-O rdf between the oxygen atoms in boehmite: a) in the bulk and b) at the surface of boehmite, i.e. between hydroxyls oxygens.

In **Figure S3-1**a, the crystalline network is clearly identified by the net minima indicating the first, second and third neighbors of each O atom. We also notice (**Figure S3-1**b) the ordering for the surface groups, which reflects the underlying crystalline order.

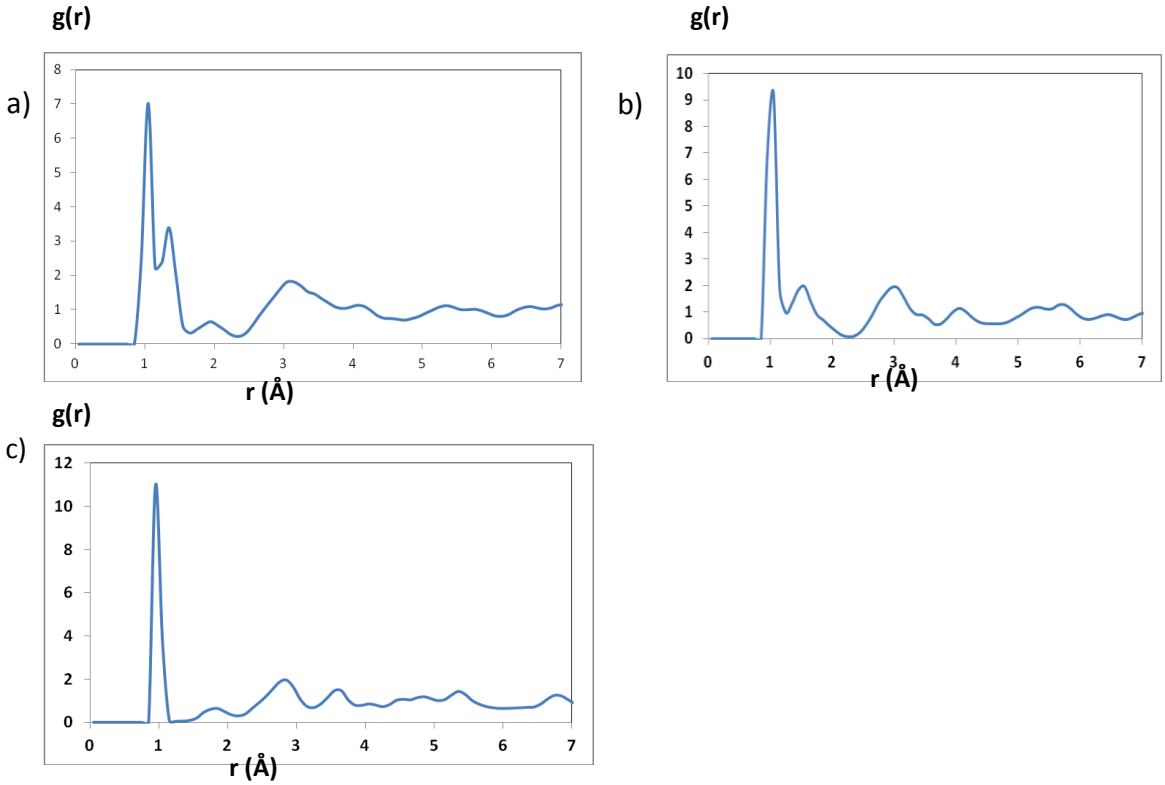


Figure S3-2 : O-H rdf functions between Oxygens belonging to the hydroxyls at the boehmite surface (in positions 1 to 8) and hydrogens belonging to water and to hydroxyls. a) case of μ1-OH groups, top edge, positions 1 and 4, b) Case of μ1-OH groups, low step, position 5 and 8 and c) Case of μ2-OH groups, low terrace, position 2, 3, 6 and 7.

[i] J. M. Sorenson, G. Hura, R. M. Glaeser, and T. Head-Gordon, J. Chem. Phys. **113**, 9149.
[ii] A. K. Soper, Chem. Phys. **258**, 121 s2000.