Supplementary Information - Theoretical investigation of inorganic particulate matter: the case of water adsorption on a NaCl particle model studied using Grand Canonical Monte Carlo simulations

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List of the applied NaCl LJ parameters and point charges

Na^+: $R_{min}/2$ = 1.212 Å; ε = 0.3526418 kcal/mol; atomic charge = +1

Cl^-: $R_{min}/2$ = 2.711 Å; ε = 0.0127850 kcal/mol; atomic charge = -1

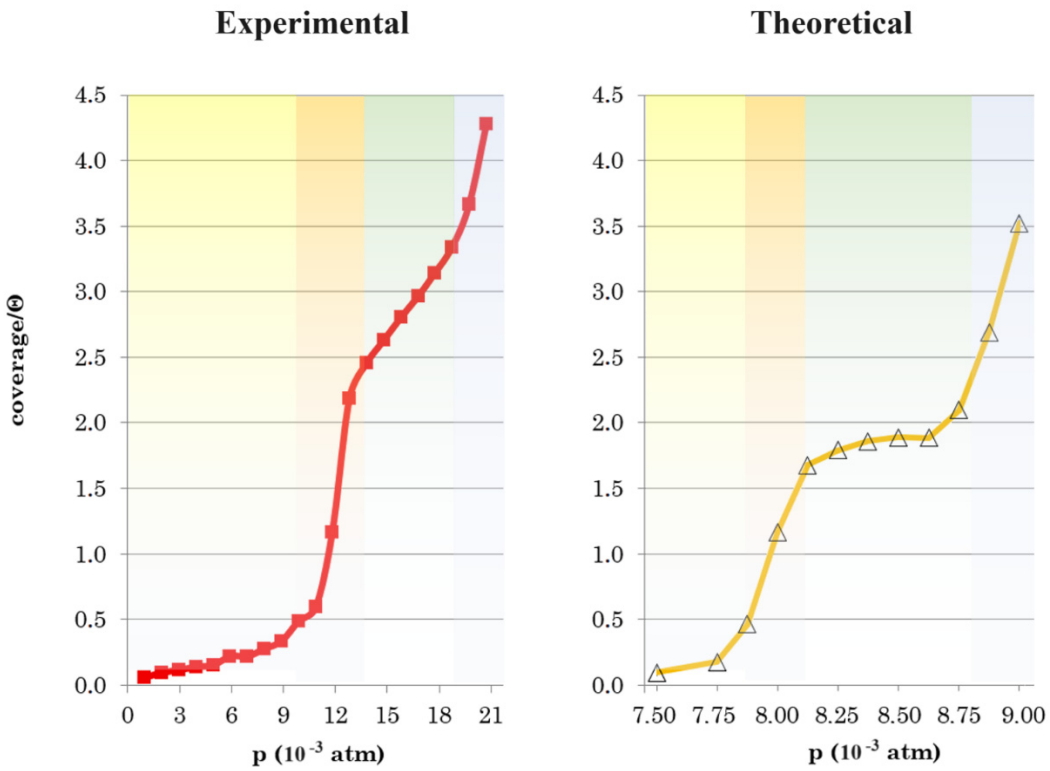

Figure S1: Experimental adsorption isotherm measured by Foster and Ewing [29] (left) and adsorption isotherm calculated by means of Monte Carlo simulations performed in the Grand Canonical ensemble, with focus on the pressure range between 7.5 and 9.0 matm (right). Yellow, orange, green and light blue areas evidence the low-coverage, transition, high-coverage and presolution regions of the isotherms, respectively.

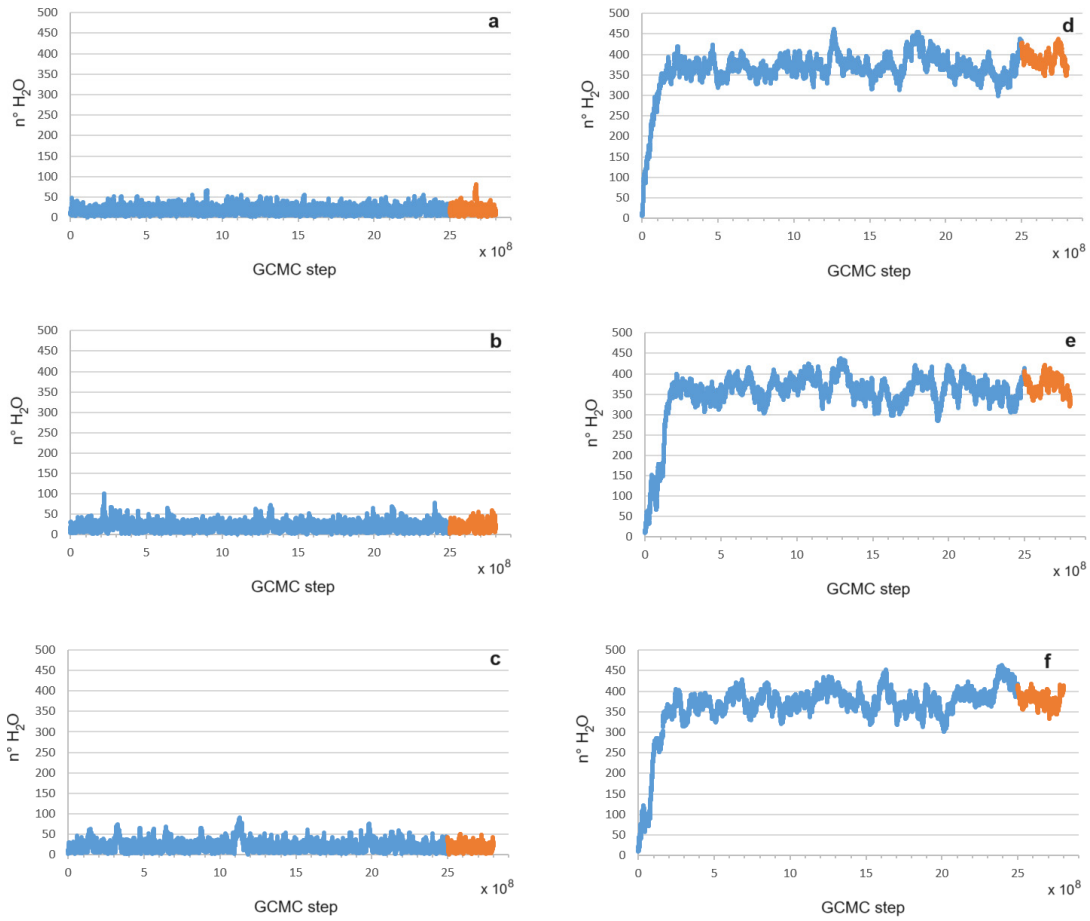

Figure S2: Graphs of the number of water molecules in the system as a function of GCMC steps: panels a, b and c: $p = 7.5 \times 10^{-3}$ atm, replica 1, 2 and 3, respectively; panels d, e and f: $p = 8.5 \times 10^{-3}$ atm, replica 1, 2 and 3, respectively. Productive part of the simulations is highlighted in orange.

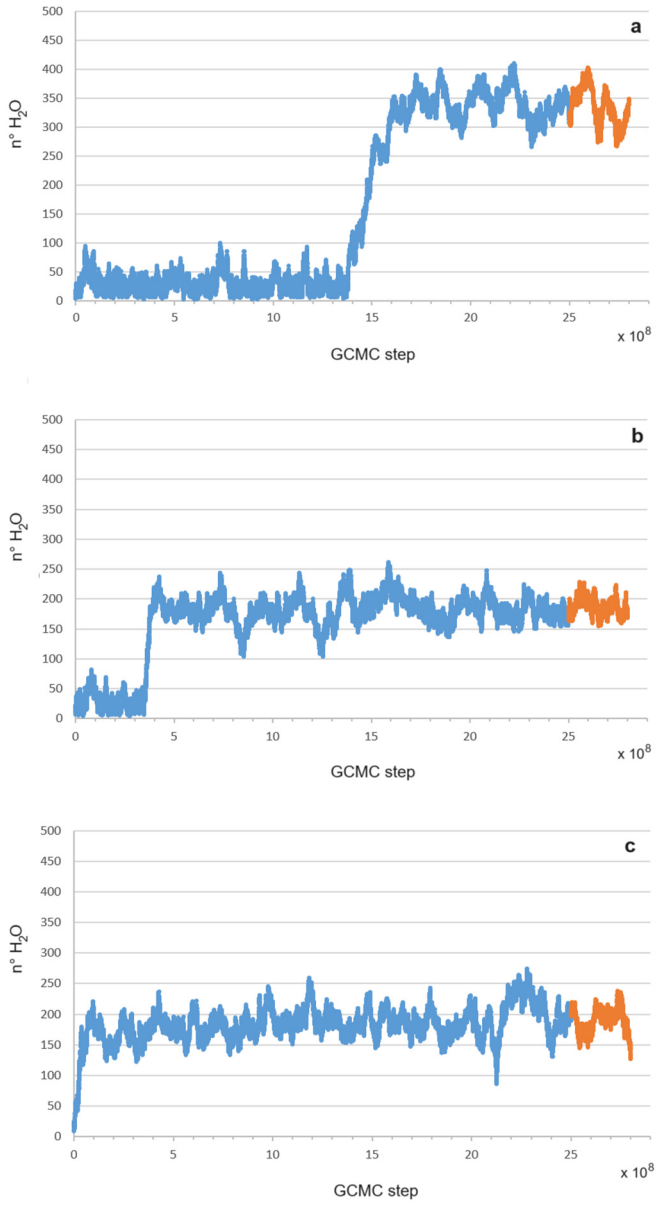

Figure S3. Graphs of the number of water molecules in the system as a function of GCMC steps: panels a, b and c: p = 8.0 x 10^{-3} atm, replica 1, 2 and 3, respectively. Productive part of the simulations is highlighted in orange.

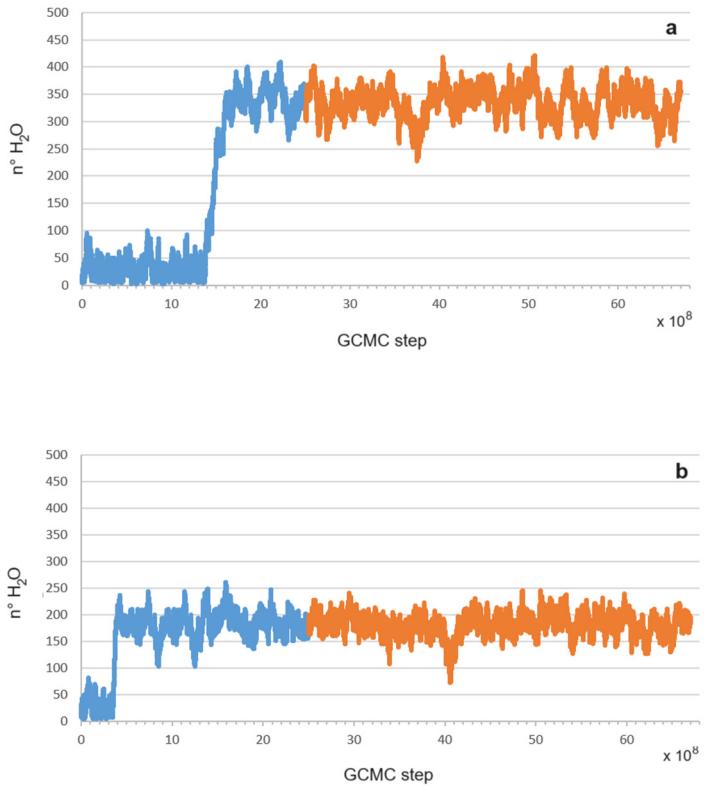

Figure S4 Graphs of the number of water molecules in the system as a function of GCMC steps: panels a and b: p = 8.0 x 10^{-3} atm, replica 1 and 2, respectively. Productive part of the simulations is highlighted in orange.

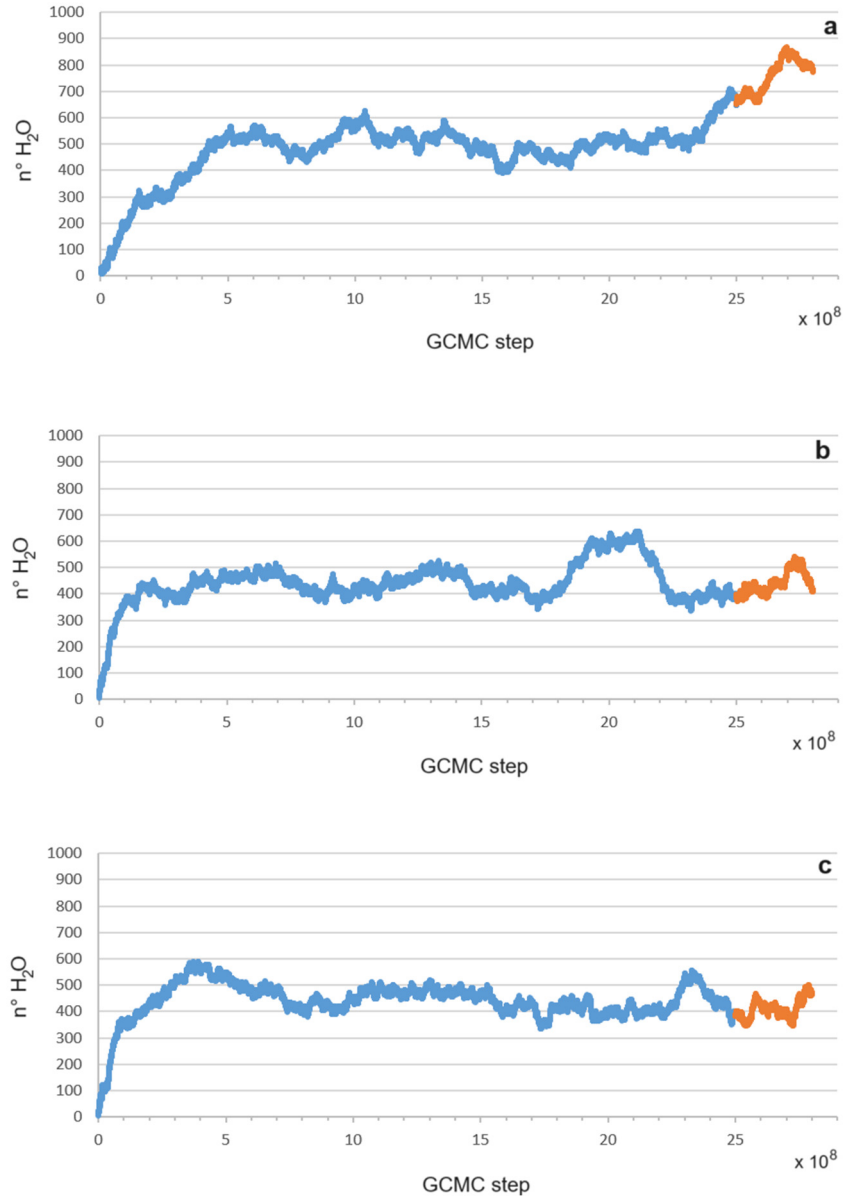

Figure S5. Graphs of the number of water molecules in the system as a function of GCMC steps: panels a, b and c: p = 8.875 x 10^{-3} atm, replica 1, 2 and 3, respectively. Productive part of the simulations is highlighted in orange.

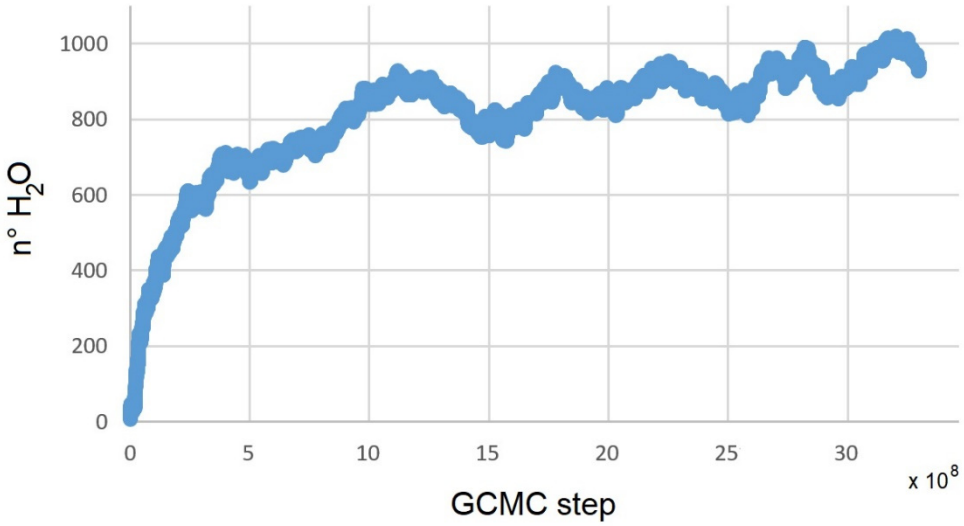

Figure S6. Graph of the number of water molecules in the system as a function of GCMC steps, $p = 9.100 \times 10^{-3}$ atm

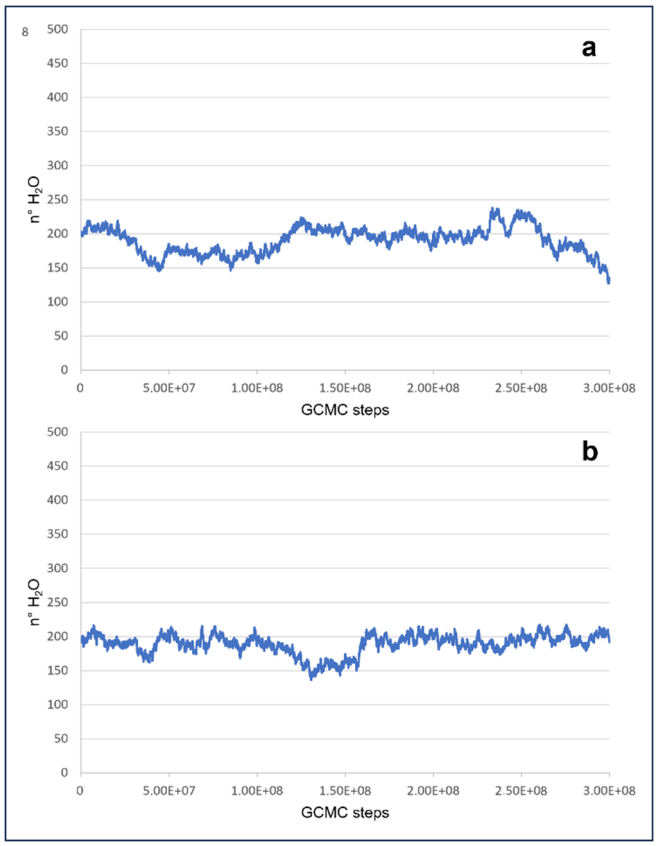

Figure S7. Comparison between productive runs of GCMC simulation at 8.000×10^{-3} atm (replica 3), carried out either with a box shrunk to 35 Å length along z axis (panel b) or with the box of the standard size along z axis (50 Å length).

Table S1. Average number of water molecules on the outermost layers of NaCl slab: lower layer (LL) and uperr layer (UL).

Low coverage region		**7.500 matm**	**7.750 matm**
Replica 1	**LL**	9.7	109.0
	UL	10.5	11.2
Replica 2	**LL**	11.4	11.9
	UL	8.6	12.5
Replica 3	**LL**	8.8	11.6
	UL	9.4	12.4

Transition region		**7.875 matm**	**8.000 matm**	**8.125 matm**
Replica 1	**LL**	35.1	-	179.4
	UL	13.4	-	175.9
Replica 2	**LL**	12.3	-	142.5
	UL	12.3	-	186.6
Replica 3	**LL**	12.7	24.1	173.8
	UL	151.8	175.6	152.3

High coverage region		**8.250 matm**	**8.375 matm**	**8.500 matm**	**8.625 matm**	**8.750 matm**
Replica 1	**LL**	176.5	189.1	191.7	184.5	232.1
	UL	184.3	191.0	181.3	192.3	198.9
Replica 2	**LL**	174.0	176.7	182.5	185.8	235.9
	UL	174.1	193.4	179.8	190.2	196.2
Replica 3	**LL**	202.7	185.8	183.9	201.4	198.8
	UL	171.3	195.3	208.8	185.6	222.8

LL

Pre-deliquescence region		**8.875 matm**	**9.000 matm**			
Replica 1	**LL**	371.0	352.7			
	UL	294.5	422.1			
Replica 2	**LL**	210.5	363.5			
	UL	214.9	410.0			
Replica 3	**LL**	204.7	244.8			
	UL	227.4	292.4			

Table S2. First replica: results of clustering and classification.

Partial pressure of H_2O (matm)	$\underline{n}$° of islands per *frame*	$S_{\underline{X}}$	$\underline{n}$° of H_2O per island	$S_{\underline{X}}$	$\underline{n}$° of fully covered surfaces	$S_{\underline{X}}$	$\underline{n}$° di H_2O for entirely covered surface	$S_{\underline{X}}$
7.500	1.60	0.02	6.78	0.11	0.00	0.00	0.00	0.00
7.750	1.60	0.02	9.66	0.17	0.31	0.01	129.18	1.14
7.875	1.89	0.02	10.98	0.16	0.29	0.01	147.04	1.12
8.125	0.00	0.00	3.00	0.00	2.00	0.00	178.48	0.20
8.250	0.00	0.00	3.00	0.00	2.00	0.00	180.12	0.22
8.375	0.00	0.00	0.00	0.00	2.00	0.00	193.98	0.26
8.500	0.00	0.00	0.00	0.00	2.00	0.00	194.38	0.22
8.625	0.00	0.00	0.00	0.00	2.00	0.00	186.76	0.18
8.750	0.00	0.00	0.00	0.00	2.00	0.00	203.95	0.22
8.875	0.00	0.00	0.00	0.00	2.00	0.00	379.85	1.07
9.000	0.00	0.00	0.00	0.00	2.00	0.00	399.38	0.54

Table S3. Second replica: results of clustering and classification.

Partial pressure of H_2O (matm)	$\underline{n}$° of islands per *frame*	$S_{\underline{X}}$	$\underline{n}$° of H_2O per island	$S_{\underline{X}}$	$\underline{n}$° of fully covered surfaces	$S_{\underline{X}}$	$\underline{n}$° di H_2O for entirely covered surface	$S_{\underline{X}}$
7.500	1.60	0.02	7.30	0.09	0.00	0.00	0.00	0.00
7.750	2.01	0.02	6.78	0.07	0.00	0.00	0.00	0.00
7.875	2.05	0.02	8.50	0.10	0.00	0.00	0.00	0.00
8.125	0.00	0.00	4.00	0.00	2.00	0.00	182.94	0.23
8.250	0.00	0.00	3.25	0.22	2.00	0.00	175.56	0.17
8.375	0.00	0.00	3.22	0.21	2.00	0.00	183.87	0.23
8.500	0.00	0.00	0.00	0.00	2.00	0.00	185.72	0.18

8.625	0.00	0.00	3.50	0.31	2.00	0.00	189.13	0.24
8.750	0.00	0.00	0.00	0.00	2.00	0.00	212.15	0.27
8.875	0.00	0.00	0.00	0.00	2.00	0.00	226.34	0.28
9.000	0.00	0.00	0.00	0.00	2.00	0.00	384.67	0.36

Table S4. Third replica: results of clustering and classification.

Partial pressure of H_2O (matm)	$\underline{n}$° of islands per *frame*	$S_{\underline{X}}$	$\underline{n}$° of H_2O per island	$S_{\underline{X}}$	$\underline{n}$° of fully covered surfaces	$S_{\underline{X}}$	$\underline{n}$° di H_2O for entirely covered surface	$S_{\underline{X}}$
7.500	1.57	0.02	6.21	0.07	0.00	0.00	0.00	0.00
7.750	1.73	0.02	6.95	0.08	0.00	0.00	0.00	0.00
7.875	0.78	0.02	5.88	0.09	1.00	0.00	173.75	0.24
8.000	1.05	0.02	7.24	0.12	1.00	0.00	177.96	0.32
8.125	0.00	0.00	4.50	0.35	2.00	0.00	181.53	0.19
8.250	0.00	0.00	3.25	0.22	2.00	0.00	176.49	0.24
8.375	0.00	0.00	3.00	0.00	2.00	0.00	182.98	0.22
8.500	0.00	0.00	0.00	0.00	2.00	0.00	189.64	0.20
8.625	0.00	0.00	3.00	0.00	2.00	0.00	193.07	0.33
8.750	0.00	0.00	3.00	0.00	2.00	0.00	216.87	0.44
8.875	0.00	0.00	0.00	0.00	2.00	0.00	204.99	0.29
9.000	0.00	0.00	0.00	0.00	2.00	0.00	278.07	0.72

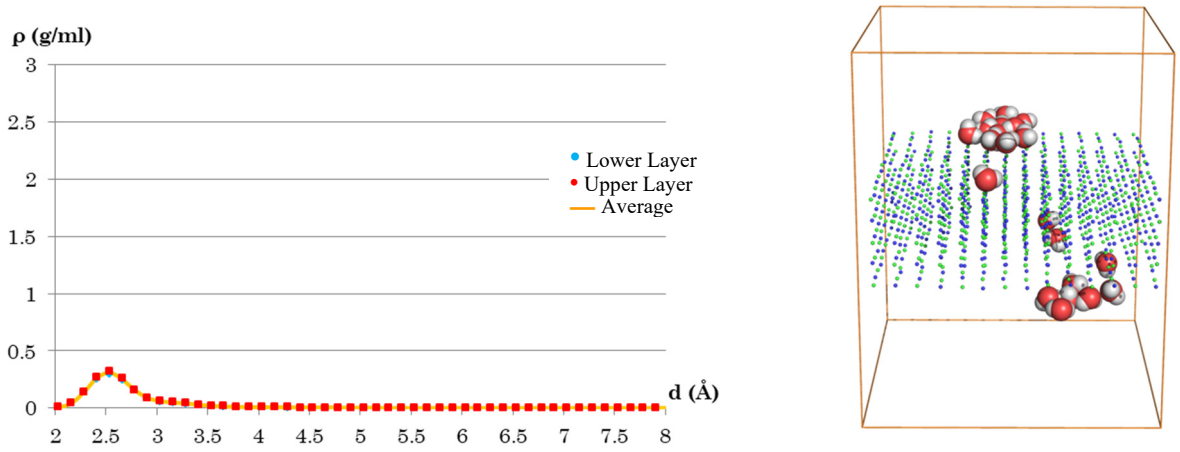

Figure S8. Low coverage ($\theta < 0.4$), simulation at 7.500 matm (replica 1). Water density as a function of the distance from the NaCl surface and a representative frame from the simulation: lower layer (cyano), upper layer (red), average with respect both layers (yellow line).

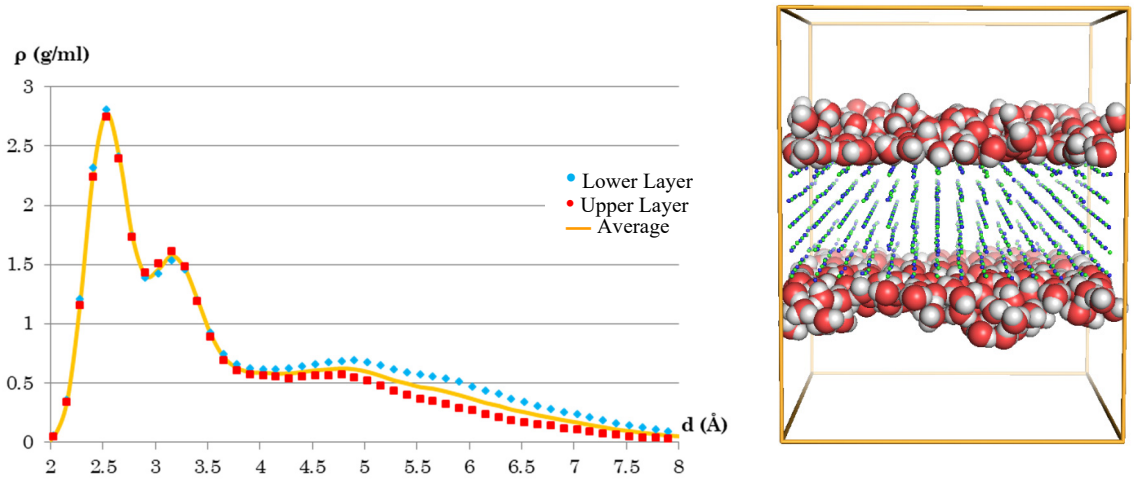

Figure S9. High coverage ($1.7 < \theta < 2.5$), simulation at 8.750 matm (replica 1). Water density as a function of the distance from the NaCl surface and a representative frame from the simulation: lower layer (cyano), upper layer (red), average with respect both layers (yellow line).

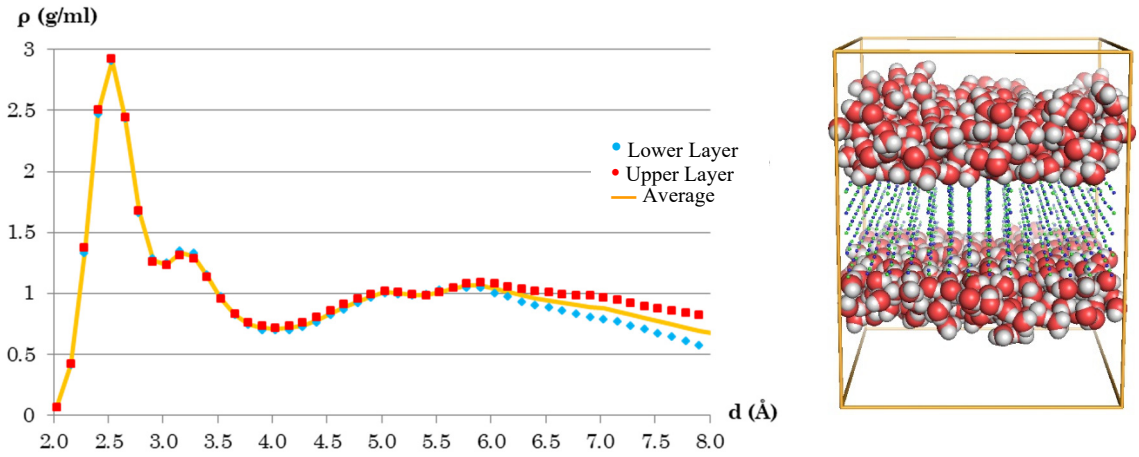

Figure S10. Predeliquescence region, simulation at 9.000 matm (replica 1). Water density as a function of the distance from the NaCl surface and a representative frame from the simulation: lower layer (cyano), upper layer (red), average with respect both layers (yellow line).

Based on the data of Table S1 and Figures S8-S10, the following findings can be derived:

-) at low coverage ($\theta < 0.4$), on average, there are about 10 water molecules (Table S1) over each surface of the model. The density profile (at 7.500 matm) presents a unique peak at 2.5 Å (Figure S8) from the surface ($\rho < 0.3$ mg ml^{-1}), thus supporting the presence of islands on the two surfaces, as highlighted also in Figure S8 where a frame of the simulation is reported.

-) in the transition region ($0.4 < \theta < 1.4$), one (at 7.875 matm) or both surfaces (at 8.000 and 8.125 matm) present about 180 water molecules per side (Table S1). In the latter case, the density profiles present a first peak at 2.5 Å ($\rho \approx 2.5$ mg mL^{-1}), and a second peak ($\rho \approx 1.5$ mg mL^{-1}) around 3.3 Å. These peaks correspond to a different disposition of the Oxygen atoms of the water molecules with respect to the surface. The first peak corresponds to water molecules with the Oxygen atoms pointing to the surface, the second peak corresponds to water molecules in the same layer which feature the Hydrogen atoms towards the surface;

-) at high coverage ($1.7 < \theta < 2.5$) (at 8.750 matm) about 200 water molecules per side are present (Table S1); the density profiles (Figure S3) present a first peak at 2.5 Å ($\rho \approx 2.5$ mg mL^{-1}), and a second peak ($\rho \approx 1.5$ mg mL^{-1}) around 3.3 Å; a third smooth maximum ($\rho \approx 0.5$ mg mL^{-1}) at around 4.7 Å highlights the beginning of the formation of a successive water layer. As in the case of the transition region, the two peaks (at 2.5 and 3.2 Å) correspond to the two possible arrangement of the water molecules in the mono-layer with respect to the surface. Figure S9 reports a frame of the simulation.

-) in the predeliquescence region (9.000 matm) 300-400 water molecules per side are present; the density profiles present a first peak at 2.5 Å ($\rho \approx 2.5$ mg mL^{-1}), a second peak ($\rho \approx 1.5$ mg

mL^{-1}) around 3.3 Å and a two large and smooth peak around 5.0 and 6.0 Å ($\rho \approx 1.0$ mg mL^{-1}). The first two peaks refer to the first water monolayer and the second two peaks to upper layers.

All these findings prompt us to define water molecule clusters that present on one surface less than 70 water molecules as islands; clusters that present on one surface more than 70 water molecules were classified as fully covered surfaces, monolayer structured (about 150 water molecules), bilayer structured (about 300 water molecules) or multilayer structured (more than 450 water molecules).