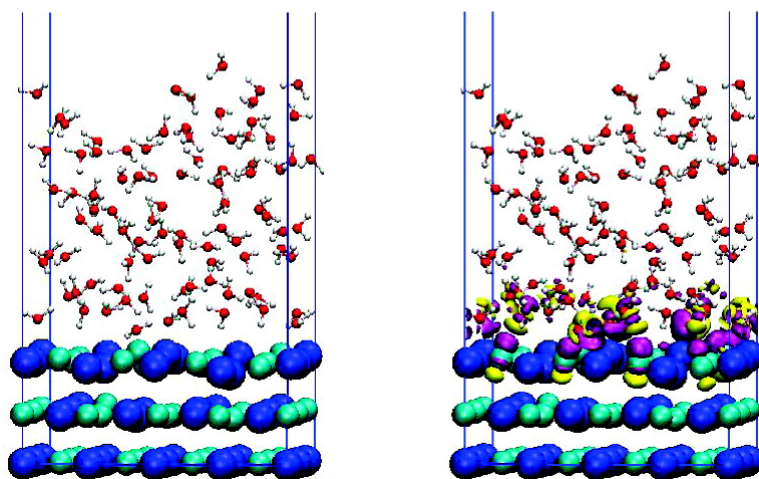


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Density Oscillations in a Nanoscale Water Film on Salt: Insight from Ab Initio Molecular Dynamics

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The salt–water interface is one of the most important and common on earth, playing a prominent role in disciplines such as atmospheric science and biology. Moreover, the interaction of salt with water has a particular resonance with chemists and nonchemists alike, being a piece of “science” exploited daily to, for example, inhibit the freezing or accelerate the boiling of water. Under ambient conditions, thin film water covers most surfaces and common salt—NaCl—is no exception.¹ At room temperature and at relative humidities below the deliquescence point of 75% NaCl, crystals are covered in a thin film of water believed to be about 1 nm thick or so.^{2,3} While much is known about the properties of the low energy NaCl(001) surface and water covered NaCl(001) under ultra high vacuum (UHV) conditions,^{4–6} the details of the ambient water/NaCl(001) interface and thus the essentially “native” state of NaCl crystals remains a mystery. Largely this is because probing the properties of ambient liquid water films remains a challenge for both experiment and first-principles electronic structure theory alike. The former generally struggle to obtain atomic-level understanding while out of UHV, and the latter are faced with the often computationally prohibitive twin demands of large system sizes and long time scales.⁷

Here, we use a predictive first-principles approach within the framework of density functional theory (DFT) as implemented in the CP2K/Quickstep⁸ package to explore the properties of the hitherto mysterious nanoscale water film that covers NaCl(001). From our ab initio molecular dynamics (MD) simulations, we find that the thin film water examined here differs significantly from that in the bulk. A pronounced layering is observed in the overlayer with a density maximum in the contact layer $\sim 40\%$ larger than that of bulk water. Furthermore, water molecules in the contact layer are involved in about 20% fewer hydrogen bonds with each other and carry considerably reduced dipole moments than they do in bulk liquid water.

The model for the salt/water interface examined here is composed of a three-layer NaCl(001) slab covered in 89 D₂O molecules (Figure S1). An initial structure was obtained from an equilibrated simulation performed with empirical potentials. This simulation was followed by a 35 ps ab initio MD simulation, of which the last 20 ps were used for data collection and analysis. The Perdew, Burke, and Ernzerhof (PBE)⁹ exchange–correlation functional was employed, and in line with previous studies which show that room temperature PBE liquid water diffuses too slowly compared to experiment, a temperature of 330 K was adopted.^{7,10}

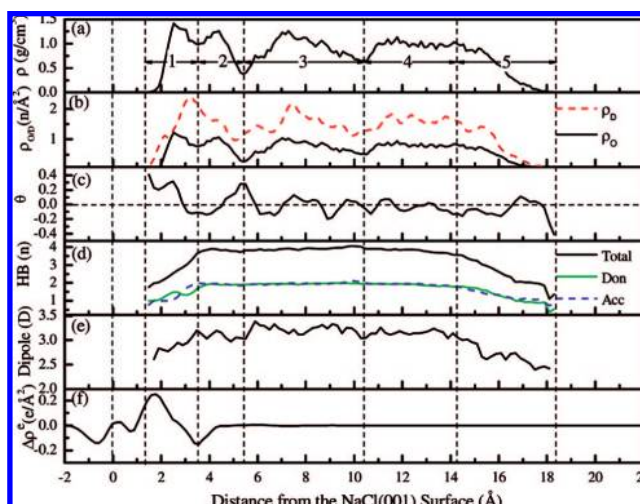


Figure 1. Structural and electronic properties of a water film on NaCl(001), displayed along the distance perpendicular to the (average) location of the NaCl(001) surface: (a) density of water molecules; (b) density of O and D atoms; (c) orientational order parameter, θ ; (d) total number of HBs and number of donor and acceptor HBs per molecule; (e) distribution of dipole moments per molecule; (f) electronic charge density difference between the water and NaCl. The dashed vertical lines and numbers in (a) specify the layers into which the film is divided for analysis purposes.

The first feature of the system revealed by our ab initio MD simulations is the density profile through the adsorbed water film. From Figure 1a, it can be seen that the density oscillates strongly along the surface normal, exhibiting a pronounced layering. For discussion purposes, we define five layers within the water film with the first being at the water/NaCl interface and the fifth at the water/vacuum interface. Interestingly, we find that the density maximum in the contact layer is at $\sim 1.4 \text{ g/cm}^3$, about 40% higher than that of bulk liquid water. Likewise, the density maximum in the second layer is about 25% greater than bulk water. Outside the second layer, there is a depletion zone, where the density drops to 0.3 g/cm^3 . Beyond this, the oscillations become less pronounced, and at about 10 Å from the surface, the bulk liquid water density of 1 g/cm^3 is recovered (layer 4).¹¹ Outside the fourth layer, the density drops to zero at the water/vacuum interface, in a similar manner to the other reported ab initio MD density profile of the water/vacuum interface.¹²

Examination of the density associated with the O and D atoms (rather than the water molecules) provides insight into the orientation of the molecules within the film. Specifically, at the water/vacuum interface, the density associated with the D atoms extends $\sim 0.5 \text{ Å}$ beyond that of the O atoms, indicating that a large

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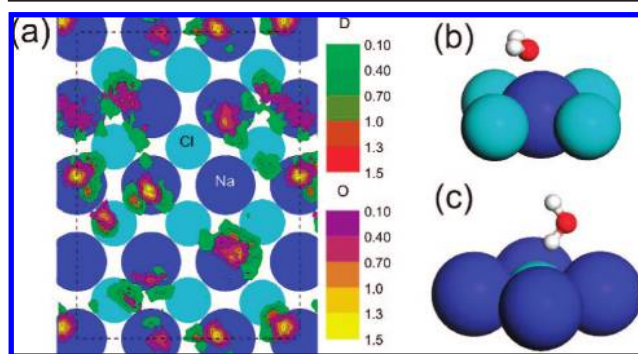


Figure 2. Spatial probability distribution of O and D atoms within layer 1, projected onto the NaCl(001) surface (a). (b, c) Two common adsorption geometries within layer 1: water above a Na ion; and (b) water above a Cl ion (c).

proportion (76%) of the water molecules at this interface has at least one OD group, which dangles into the vacuum. When we examine in detail the nature of the water molecules in the first layer, we find that there is a considerable degree of structure. This can be seen in Figure 2a, where the spatial probability distributions of O and D atoms in layer 1 are displayed, revealing that just two specific configurations predominate. In one, the O atoms of the water molecules are located above Na sites (Figure 2b), and in the other, a single OD bond of an upright water interacts with Cl ions (Figure 2c). We note that the adsorption structure at the Na site resembles the 1 ML UHV structure of water on NaCl(001) as determined by helium atom scattering.¹³ A further measure of the orientational order of the water molecules in the film can be obtained from an orientational order parameter, θ , which is defined as the average of the cosine of the angle between the water dipole and the surface normal. In the interior of the film (layers 3 and 4), θ fluctuates around zero, indicating an almost isotropic water distribution. However, at the two interfaces and the boundary between layers 2 and 3, it deviates noticeably from zero, being positive (0.3–0.4) at the water/NaCl interface and in the region between layers 2 and 3 and being negative (–0.3 to –0.4) at the water–vacuum interface.

It is interesting to consider the network of hydrogen bonds (HBs) in the water film and consider how this may differ from bulk liquid water. To facilitate this, we adopt a common geometric definition of the HB,¹⁴ which predicts a value in bulk PBE water of 3.84/water. The distribution of the number of HBs the water molecules within the film are involved in is shown in Figure 1d. It can be seen that within layers 2–4 the number of HBs per molecule is close to the bulk value. However, in the immediate vicinity of the water/NaCl and water/vacuum interfaces (layers 1 and 5), the molecules in the film possess a significant fraction of broken HBs, dropping to as few as 2/water at each interface. At the water/NaCl contact layer, this is true despite the density in this region rising to 1.4 times the bulk value. We also explored the number of HB donors and acceptors within the water film. While the number of donors and acceptors tended to be the same, slight disparities are apparent in layers 1 and 5. Specifically, in the immediate vicinity of the water/NaCl interface, there is a slight predominance of HB donors, whereas at the water/vacuum interface there is a slight predominance of acceptors.

As can be seen from Figure 1e, the water molecules at the water/NaCl and water/vacuum interfaces possess reduced dipole moments (2–2.5 D) compared to the interior of the film, which matches the

computed dipole moment of bulk water (~ 3.1 D). The reduction in the dipole moments of the molecules directly at the two interfaces is related to the greater number of broken HBs. Indeed, upon inspection of the dipole moments of individual water molecules throughout the entire trajectory of our simulation, a linear correlation between the number of HBs a water molecule is involved in and its dipole moment is observed. Furthermore, as can be seen from Figure 1d,e, the dipole moment per HB is moderately (~ 0.2 D) larger at the water/NaCl interface than at the water/vacuum interface. A consideration of how the electron density rearranges upon bringing the water film into contact with the NaCl surface (Figure 1f and Figure S1) reveals that this is because the molecules in the immediate vicinity of NaCl are polarized through their interaction with the substrate. This can be seen in the planar averaged electron density difference profile displayed in Figure 1f by the accumulation of electron density just above the top layer of NaCl.

In conclusion, an ab initio MD simulation of the water/salt interface has revealed a pronounced layering in the water film. The water density exhibits a damped oscillatory behavior in the direction of the surface normal, rising to a maximum of 1.4 g/cm^3 and not behaving as bulk water does until about 10 \AA from the substrate. Other properties of the water film, such as the number of HBs and the dipole moments of the water molecules in the film, have been explored and shown to differ noticeably from bulk water. Likewise, water molecules in the contact layer are polarized through their interaction with the substrate and tend to adopt one of two configurations. It will be interesting to explore what the implications of the dense contact layer predicted here are for the solvation of ions and dissolution of the salt crystal.

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Supporting Information Available: Further simulation and analysis details are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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