Adsorption of ice on top of Pd⟨111⟩ surfaces: Neural Network mapping of the ab-initio Potential Energy Surface

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I. ABSTRACT

The understanding of the origin of the interactions between water and metal surfaces at the nanoscale is essential to characterize chemical processes where the metal/water interface is a key component such as corrosion, catalysis and electrochemical reactions[1–4]. While many classical force-fields exist for both water and metals, the treating of the two systems together requires the use of first-principle approaches, because the nature of the binding and interactions between both components is not well defined and both electronic and electrostatic interactions need to be described by a self-consistent ab-inito approach. This however imposes a limitation to the size of the systems studied, due to the very large computational loads (both in memory and time) involved in this calculations. We use Density Functional Theory calculations[7, 8] (DFT), including ab-initio molecular dynamics to study the adsorption of a monolayer of ice on top of a Pd⟨111⟩ surface. We are interested in the comparison between different Exchange and Correlation functionals [11–14] given that the description of the localized states of water together with the extended metallic states is a very delicate issue, at the limit of the approximations involved in DFT. According to ice rule and considering the smallest cell (1×1) (2 water molecules), there are only two different possible configurations for one layer of ice on top of our Pd⟨111⟩ surface. Clearly, as the cell increases, the number of possible configurations satisfying the ice rule increases dramatically. We counted for example that there are 2400 different configurations for a 2×2 unit cell (8 water molecules), (see fig : 1). It is impossible to calculate every configurations of these kind of systems using DFT. An idea to solve this problem is to use Neural Networks [5, 6] (NN). Based on the DFT energies of a few studied configurations, we then extrapolate the results to all the unknown wanted configurations. We show how this procedure is very powerful and present preliminary results for the NN extrapolated potential energy surface of all possible ice-1h monolayers grown on top of a

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Pd⟨111⟩ surface compatible with the periodic boundary conditions.

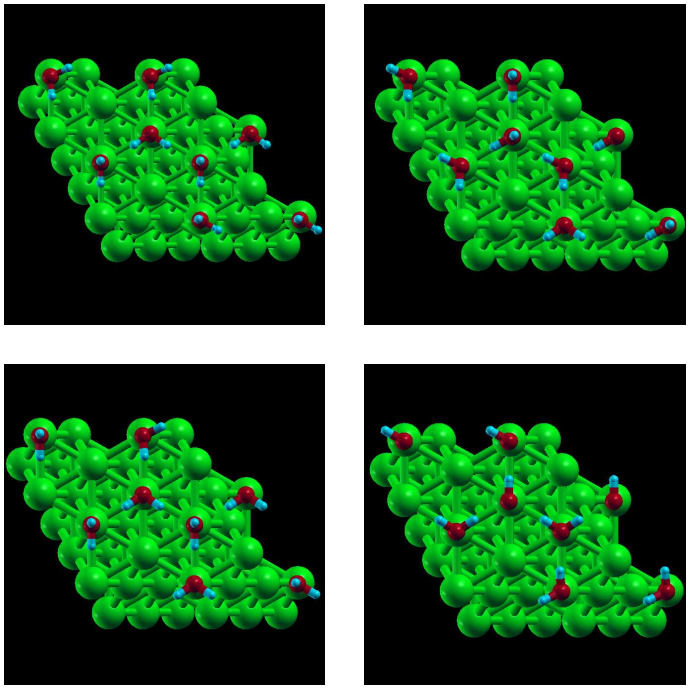

FIG. 1: *Here are represented 4 different possible configurations of one layer of ice on top of a Pd surface. For this unit cell size (8 water molecules), we counted 2400 different possible configurations saisfying the ice rule.*

All the DFT calculations are performed with the code SIESTA [9, 10]. The use of a Neural Network permits us to reduce by a factor of 15 the total number of DFT calculations, with an average 1% error on the rms of the energies.

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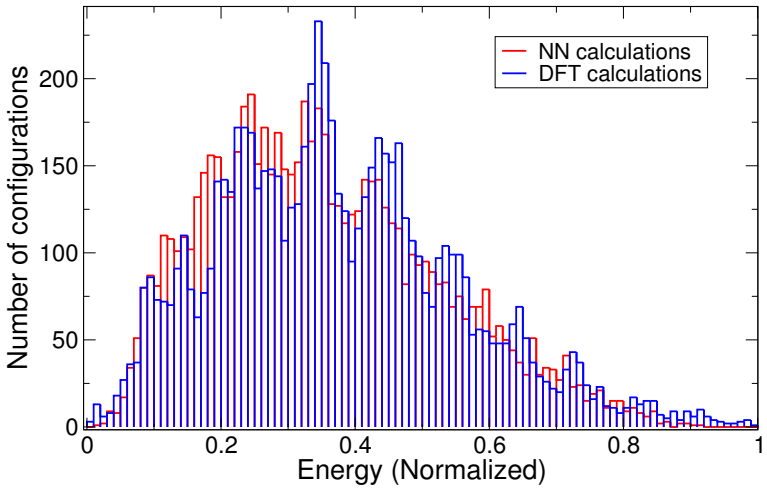

FIG. 2: *These plots are energy histograms of DFT (blue) and Neural Network calculations (red). Learning 500 patterns, the NN is able to give a good estimation of the 7200 other configurations.*

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