Molecular level study of Palmitic acid substrate on NaCl(100): physical phenomena of atmospheric interest

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Aerosol and gases present in the atmosphere have implications on health, air quality and climate, affecting both political decisions and economic activities around the world (Boucher et al, 2013). The radiative forcing induced by aerosols, especially Secondary Organic Aerosols (SOA), is characterized by a large uncertainty (Boucher et al, 2013), indicating that the aerosol chemistry is still not fully understood.

Sea Spray Aerosols (SSA) are among the most abundant aerosols in the troposphere (10^9T/year) (R. Lewis, and S. E. Schwartz, 2004). Sampling campains have shown a significant coating of these particles by Fatty Acids (FA), palmitic acid being the most abundant (Mochida et al 2002). As the coating alters the interface between the aerosol and its environment, the importance of the interactions between SSA, FAs and incoming gases has inspired laboratory studies (Sobanska et al., 2015), in order to deepen the knowledge on this heterogeneous chemistry.

Complementary to experiments, computational modelling at the molecular level provides valuable insights on the elementary chemical and physical mechanisms responsible for particle growth, ageing or reactivity.

Our theoretical work consists thus in modelling a NaCl(100) surface coated with palmitic acid (PA) molecules with varying the PA coverage and the humidity at two different temperatures.

The first step consists in describing, by means of classical molecular dynamics, the molecular interactions in the fatty acid/salt crystal system. The structural organization depends strongly on the humidity with formation of organized islands of PA (Lovric et al.), on NaCl surface, as observed experimentally (Sobanska et al., 2015).

In a second step, we study the influence of this heterogeneous PA coating on the uptake and reactivity of incoming gaseous species, namely NO_2 and O_3.
Focus is made on a reaction proposed by the group of S. Sobanska (Sobanska et al., 2015) to explain the uptake of NO_2 by the NaCl surface: $NaCl(s) + 2NO_2 \rightarrow NaNO_3(s) + NOCl(g)$. Classical molecular dynamics is used to sample the favourable configurations and identify the stable configurations for the incoming molecules. Then, to describe to eventual reactivity, a hybrid Quantum Mechanical (QM)/Molecular Mechanics (MM) approach is employed with selecting the interesting sites to be treated quantum-mechanically by the QM/MM method.

This study proposes a model to study aerosol aggregation mainly by terms of classical molecular dynamics, then heterogeneous reactivity and accommodation of incoming particles, for example NO_2 and O_3 with a QM/MM approach.

Classical molecular dynamics simulations were carried out with using the GROMACS (D. van der Spoel et al, 2015) package and CP2K (CP2K, 2016) was used for the QM/MM study.

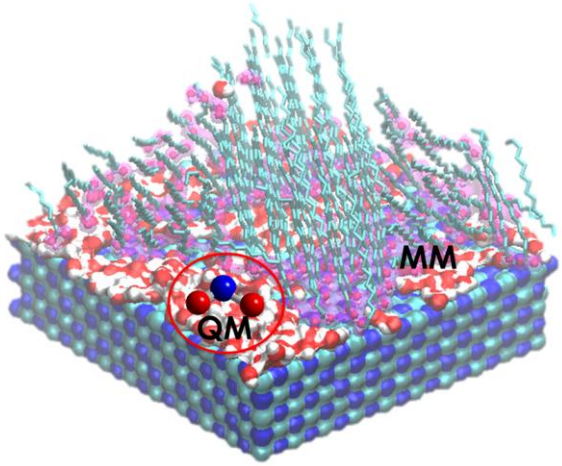

Figure 1. Snapshot taken from the QM/MM simulation of NO_2 interacting with the NaCl surface coated with PA and water. Only a reduced part of the system is treated quantum mechanically.

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