

Computational modelling of oleic acid at the air–water interface

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Fatty acids, which are present in many aerosols, partition at the air–water interface and hence form organic films on aerosols' surfaces. The fate of these films when reacting with ozone in the atmosphere is still not well understood, but their oxidation affects the growth of droplets and hence alters the properties of the aerosol.

The oleic acid/ozone reaction system has emerged as a benchmark for the study of atmospheric oxidation of organic materials. The main reaction products reported for this reaction are nonanal, azelaic acid, nonanoic acid and 9-oxononanoic acid (see *e.g.* Zahardis *et al.*, 2007). Studies have mainly focused on pure oleic acid droplets. Only a few studies are concerned with the ozonolysis of monolayer-thick oleic acid films at the air–water interface (see *e.g.* King *et al.*, 2009).

In this work, molecular dynamics simulations were employed to further both our understanding of film formation processes, as well as changes in films due to ozonolysis reactions within the atmosphere. A molecular level view of the monolayer was created, utilising the GROMACS simulation software in combination with the coarse-grained MARTINI force field, Marrink *et al.* (2007). The standard MARTINI model uses a 4-to-1 mapping, excluding hydrogen atoms. Measuring surface pressure of a surfactant monolayer, with respect to the surface area of water available per molecule, is a useful tool in determining the monolayer's properties, which is used here to validate the model. Our simulations include a compression run in the NPT ensemble to create starting structures, followed by a 200 ns equilibration and 800 ns production simulation for each starting structure, in the NVT ensemble. System set-ups are shown in Figure 1.

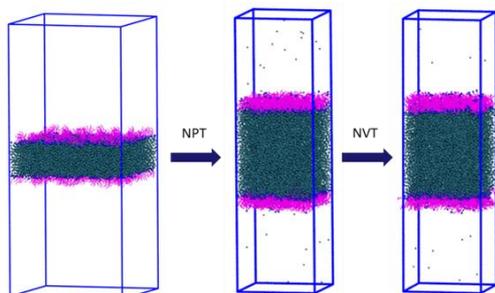


Figure 1. Compression run in the NPT ensemble, followed by a 1000 ns NVT ensemble simulation. Oleic acid chain (magenta), oleic acid headgroup (blue), water (teal).

The calculated pressure–area isotherms for oleic acid at the vacuum–water interface showed that the standard MARTINI force field parameters can be tuned to obtain a good agreement with experimental data. Both

the experimental isotherms, Pfrang *et al.* (2014), Voss *et al.* (2007), and simulated isotherm show equilibrium spreading pressures of approximately 30 mN m⁻¹ for oleic acid monolayers. When exceeding this equilibrium spreading pressure, the monolayers collapse. This approach was adapted to explore the properties and phase behaviour of the oleic acid ozonolysis products.

Insight into the molecular orientation within the monolayers was obtained from simulation data. As expected, the highest surface pressure corresponds to the lowest area per molecule.

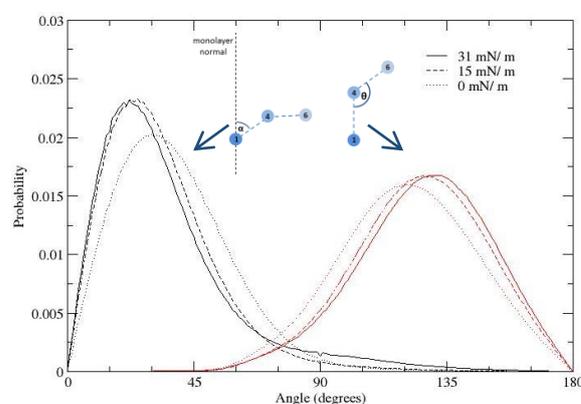


Figure 2. Angle Distributions of oleic acid's internal angles (α and θ) for three monolayers at varying surface pressures. Oleic acid sites: 1 = headgroup, 4 = double bond, 6 = terminal bead.

By reducing the area per molecule, the molecules become oriented in a way so as to increase their packing ability. Increasing the packing density of the molecules causes them to align straighter with respect to the monolayer normal (Fig. 2).

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