Review of Milsom et al., “The impact of molecular self-organisation on the atmospheric fate of a cooking aerosol proxy”

Overview:

Milsom et al. describe a modelling experiment to complement previous and current laboratory work on the oleic acid/sodium oleate system, which exhibits intriguing self-organisation behaviour of interest to the atmospheric chemistry community. They demonstrate that a multi-layer kinetic model agrees well with observations of reactant loss for the oleic/oleate system and “liquid” oleic acid. They conclude that the formation of organised structures and viscous products near the film surface reduces ozone diffusion and hence significantly extends the lifetime of the double bonds in these atmospheric proxies.

Intuitively, this makes sense and is an interesting conclusion. It is qualitatively supported by the literature. I support publication in ACP but have two main concerns: Firstly, the paper dives deep quickly which limits its readability and relevance to a general ACP audience. Secondly, and more of a problem: the model treats diffusion in significant detail but I am not sure the observations they use, of oleic loss, are a sufficient constraint. How quantitatively useful the model results are is unclear. More explanation as to the limitations of the work and requirements for future observations are required.

General comments:

1. Self-organisation: Can the authors describe for the general reader the structure they think their oleic/oleate films have? How should “lamellar phase” be understood – crystalline vs amorphous, domains…? Is there anything special happening at the surface? Do the films show an “orientation”? Does “liquid” oleic acid exhibit any organisation? Many of these details are discussed in the authors’ previous publications but it would be a good framing for the ACP community.

2. Overview of results: It would be good to see a simple discussion of the observations before the modelling discussion begins. From the first two figures, the following is apparent without modelling: the lifetime of double bonds in “liquid” oleic acid is shorter than any of the self-organised films; and the lifetime is longer for thicker films. The authors could tabulate the lifetimes (experimental fits) to make this explicit, which in turn can positively motivate the idea of diffusion limitation in general and self-organisation in particular being important. They should also discuss whether other possible explanations (e.g. differences in ozone solubility or accommodation coefficient) can be ruled out.

3. Chemical mechanism: I think the only chemical species observed/compared with here is oleic itself. If so, is the measurement-model agreement shown in Fig 1/2 sensitive to the mechanism except indirectly via diffusivity changes? The authors used a fixed chemical scheme, but how sensitive would the results be to e.g. different branching ratios?

In terms of products, I did not see diffusivity of the classic “monomer” C_9 products mentioned anywhere in the main manuscript or SI. This must be rectified – how are they represented? These are the major products in previous studies (e.g. ~90% yield in the Hosny et al. study used by the authors) and would generally be expected to show an increased diffusivity compared to oleic acid or oligomers.

Finally, the authors' mechanism is based on a study of liquid oleic acid but self-organisation could drive the chemistry down a very specific route? For example, Zhou et al. (2019) observed a single secondary ozonide product in triolein ozonolysis, likely because the initial CI and carbonyl products are "caged" in a viscous matrix and so preferentially react together.

4. Diffusivity in the lamellar phase: The authors have been honest about their model performance, which is to be commended. However, some of the ranges in diffusivity shown in Table 1 are very wide, and it is not clear why. The widest range (Dx,lam, factor of 70000) corresponds to a critical parameter for oleic loss (Figure 5b). As the authors point out there are also orders of magnitude discrepancies in this parameter compared with experimental bilayer studies. This makes the quantitative value and appropriateness of the modelling hard to assess. I would like to see the authors address these wide ranges: especially, are they derived from experiment uncertainty and/or a lack of constraint on certain parameters? Further, are factor of 3 (Line 158) or 10% (Line 173) differences for diffusivities between the lamellar/dimer/trimer phases significant in this context?

This may be a motivation for future work: it suggests to me that different observations, especially of diffusivity/phase separation, are really needed. Can the viscosity of fully oxidised particles in Hosny et al. (2016) be used as a constraint? Finally, perhaps the lamellar phase needs to somehow be described differently in future, e.g. with anisotropy?

Specific comments:

Figure 1: Is it a coincidence that the modelled loss rate is higher than measured for thin films and lower than measured for thicker films?

Table 1: Please choose either "ozone" or "O_3" for the descriptions.

Line 148: Why might the agreement be good for two of the films and less good for the other two? Do the authors have repeats for the experimental data or a measure of experiment uncertainty?

References:

Hosny et al., Chem. Sci., 1357-1367, 2016.

Zhou et al., Environ. Sci. Technol., 12467-12475, 2019.