

General comments

Milsom et al., present results from an X-ray scattering study of oleic acid/sodium oleate and fructose coated capillaries as a proxy for organic material present in atmospheric aerosol. The authors use SAXS to explore the nanostructure of different mixtures of oleic acid and fructose, of increasing fructose concentration. They investigate the effect of humidity on the specific nanostructures that are formed and calculate hygroscopicity parameters for the different structures comparing these values to those calculated using Raoult's law. They also investigate the effect of different nanostructures on reactivity during ozonolysis of oleic acid under dry conditions using SAXS and Raman microscopy. The authors conclude that humidity impacts the nanostructure in mixtures of oleic acid/sodium oleate and fructose and further show that specific nanostructures impact the rate of reaction for oleic acid ozonolysis. They link these findings back to urban air quality and climate stating that aerosol containing nanostructures can affect the degradation of harmful species present in aerosol, and the ability of aerosols to act as CCN.

The paper presents novel ideas and data interpretation regarding nanostructure formation in organic aerosols and is suitable for publication in ACP after addressing the comments below. The authors should further discuss the limitations of their study in relation to the complexity of atmospheric aerosol, the atmospheric relevance of the high ozone concentrations and low humidity conditions used during their ozonolysis experiments, and comment on how a coated quartz capillary tube relates to a coating on an aqueous droplet. Furthermore, to aid understanding, the authors should clearly state the different nanostructure types early in the paper and use the same terminology throughout.

Specific comments

1. The authors should acknowledge the presence of other components in atmospheric aerosol, such as inorganics, which can undergo efflorescence, and discuss how this may impact their findings. This should be addressed in both the introduction and discussion sections to give a broader context to the relevance of their study.
2. Many of the film thicknesses given in Figure 5 are extremely thick considering the size range of atmospheric aerosols, and in particular CCN (~ 0.1 μm diameter). The authors should therefore comment on the atmospheric relevance of such film thicknesses and associated decay constants.
3. The authors acknowledge that the ozone concentration they use in their ozonolysis experiments is high (ppm), compared to atmospheric concentrations (ppb). If atmospherically relevant ozone concentrations were used on films of these thicknesses, would a reaction occur on atmospherically relevant timescales? Please discuss.
4. a) Please explain why ozonolysis was performed under **only** dry conditions ($<5\%$), not representative of the majority of atmospheric conditions, especially in a marine environment (source of coated aerosols) and discuss how humidity could affect reaction rates. The authors should further discuss how their findings on a dry coating in a quartz tube can be related to a coating on an aqueous aerosol.
b) In the discussion section on page 15, lines 506-508, the authors should directly mention that humidity influences specific nanostructures (as well as aerosol composition) and therefore also impacts the lifetime of a surfactant.

- c) Regarding the cloud formation potential of a surfactant containing aerosol discussed on page 15, lines 515 onwards, the authors should also acknowledge that the nanostructure will change at higher humidity (when cloud droplets form) and the associated surfactant lifetime will also change. Currently all reactivity information is based on ozonolysis under dry conditions (<5% RH).
5. a) Clearly label the nanostructures in Figure 1 and add an appropriate legend. It is very difficult to see the data points in Fig 1 a) to c) and their colours in relation to the data points in d) to f). Fd3m should be defined explicitly here, not later on Page 6, line 226. **It would be very useful to the reader to refer to a larger schematic clearly showing each nanostructure in detail** e.g. something like Fig 1 in Pfrang et al., 2017. This would also help with understanding when additional nanostructures are mentioned e.g. P6₃/mmc mentioned on page 6 and later regarding Figure 4.
- b) On page 5, line 185, the nanostructures should be clearly named at the start of the discussion.
- c) Related to the above, **please be consistent with naming of all nanostructures throughout the paper**. On page 5, line 199, it states that the nanostructures have different physical properties as outlined in the introduction, but the nanostructures discussed in Figure 1 and named in the introduction are somewhat different i.e. micellar compared to inverse micellar, hexagonal (cylindrical micellar) compared to inverse hexagonal etc. which can cause confusion for the reader. Sometimes ordered and disordered are mentioned and in other places these are omitted. The labels in the figures should be the same as the descriptions in the text e.g. page 11, Figure 5 and lines 381-382. Figure 5 shows inverse micellar and **ordered micellar** and the text discusses inverse micellar and **close-packed inverse micellar** which is the same as ordered micellar, as also stated in brackets on page 12, line 386. It would be much clearer for the reader if the same terms were used consistently throughout.
6. On page 5, line 190, it is stated that an **additional** effect is observed from the presence of fructose. Please clarify whether it is indeed an additional effect, meaning it acts as both as humectant and kosmotrope or it is actually a different effect? Later in the paper on page 7, line 254 it states fructose acts as a humectant and then on page 14, line 462, it states that fructose acts as a kosmotrope.
7. The decay constants reported in Figure 5 show results from the current study (light blue and green bars) and previous studies (other coloured bars). The previous studies were conducted on films in the absence of fructose, which, when present, the authors postulate could react with Criegee intermediates and impact the kinetics. The authors also saw a lamellar phase in the presence of 20 wt % fructose so why is this not compared here instead of a lamellar phase in the absence of fructose? Please discuss.
8. What humidity range was studied in the humidification experiments? Although shown on x axes in Figure 1, this is not explicitly stated anywhere. The information should be added to the 'Controlled humidification of coated films' section.
9. Page 8, lines 284-285 state that a detailed description of the calculation of κ is given in ESI but it is missing. There is only Table S2 stating the calculated values. Please add the description.

10. Please improve the presentation and description of the data in Figure 4 e.g. label specific peaks, e.g. ordered phase. There are several arrows present in the figure which are not mentioned in the figure caption, and it is difficult to follow the description of which peaks shift or appear in the text.
11. Please add a colour scale legend to Figure 6.
12. Why are no results shown in Figure 6 for the 50% wt Fructose concentration?
13. On page 14, lines 472-473 the sentence should make it clear that different nanostructures will cause different viscosities and therefore diffusivities. It initially reads as if there is something causing a change in viscosity (e.g. humidity) that effects the nanostructure but experiments were only conducted at < 5% RH so this is not the case.
14. The authors cite King et al., 2009 as a reference for material being left at the interface following oxidation of an oleic acid film at the air-water interface on page 13, line 443 and on page 15, lines 510-511. However, a more recent publication by King et al., PCCP, 2020 (The reaction of oleic acid monolayers with gas-phase ozone at the air water interface: the effect of sub-phase viscosity, and inert secondary components) showed this finding to be erroneous and due to impurities in the film material, concluding that when a pure oleic acid film is reacted, no material is left at the interface. Please correct or remove references.

Minor comments

Move the 'Controlled humidification of coated films' section on Page 4 before the 'Ozonolysis of coated films' section to mirror the order that the results are presented in.

Sentence on page 12, lines 393-394, specify that two orders of magnitude corresponds to the decay constant/reactivity as otherwise not clear.

The authors mention oleic acid and fructose can be found in the urban and marine environment in the introduction and go on to state that coatings are present on the surface of marine aerosols. Later in the discussion they refer to their proxy as relevant to the urban environment alone e.g. page 14, line 461. Please be consistent with the description.

Remove the word 'massively' from the conclusion on page 15, line 532. Experiments were conducted under a specific set of conditions and are not applicable to all scenarios, therefore the use of massively seems inappropriate.

Technical corrections

The first sentence in the abstract doesn't read well. Consider changing 'in determining **the** aerosol's fate' to 'in determining **an** aerosol's fate' or 'in determining **the fate of an** aerosol'

Page 2, line 82. Change ...in the urban environment **have** been... to ...in the urban environment **has** been...

Add the word 'section' to page 6, line 211 e.g. ...explored in the Hygroscopicity on observed nanostructures **section** and also to the end of line 257 on page 7, ...is presented in the Hygroscopicity on observed nanostructures **section**.

Page 13, line 420. Correct typo 'A new phase was formed **in the with** a peak...'