We thank the reviewer for the comments on this revised manuscript. We note that points **1, 2, 3, 5, 6, 8 and 9** were all raised and specifically addressed in the previous review round, so we have left those responses unchanged from our previous author response. Point **4** and **7** are addressed specifically here and we have amended the Supporting Information accordingly.

1) In the Methodology, please provide a little more information on the experimental set up. Where was the ozone concentration measured and using what instrument/ports? For the POM analysis, how long were the samples allowed to equilibrate?

The ozoniser was calibrated offline by UV-Vis spectroscopy as described in the manuscript. We did not make this as clear as possible and have now addressed this point, adding to section 2.3:

[*The ozone concentration was kept constant at 51.9 ± 0.5 ppm and was calibrated* ***offline*** *by UV/Vis spectroscopy* ***at the outlet of the ozoniser*** *using a* ***PerkinElmer Lambda 465 Spectrophotometer*** *and the ozone absorption band at 254 nm and the absorption cross-section for ozone at this wavelength* (1.137 ± 0.070 x10^{-17} cm^{2})]

The POM experiments are described in more detail in the Supporting Information (not originally accessible to reviewer 2). We have now included an additional description of the equilibration times in the main text in any case:

[*Samples* ***for humidity experiments were*** *deposited on microscope slides* ***and allowed to equilibrate at ~ 50 % RH over 6 days. Samples were then*** *humidified by suspending the slides above distilled water inside a small, sealed, container. This provided a saturated environment for the samples to equilibrate with* ***for 7 days****.* ***Samples for temperature experiments were prepared in the same way but without any humidification.***]

2) ***For Figure 1, what was the RH value for each of the time points (g-l)?***

The experiment involved a step increase from ~38 to 90 % RH, with the target humidity being reached within 3 – 4 min. For the humidification plots (Fig. 1 (g) - (i)) only the first plot (g) was at 38 % RH. The rest were at 90 % RH. For the dehumidification plots (Fig. 1 (j) – (l)) again, the first plot was at 90 % RH and the rest at ~38 % RH (room RH). This is not clear in the caption and has been amended accordingly:

[*Figure 1. ((a) and (b)) 1-D SAXS and WAXS patterns obtained from a dry levitated particle of the acid–soap complex – 1st, 2nd and 3rd lamellar peaks are labelled and a cartoon of the lamellar phase is presented (a). ((c) and (d)) experimental fraction of maximum water content as a function of distance from particle centre and time humidifying/dehumidifying. ((e) and (f)) modelled fraction of maximum water content – best fits to experimental data for humidification and dehumidification. 3–D surface plots of 1–D SAXS patterns plotted against distance from the particle centre for the same particle humidifying ((g) – (i)) and dehumidifying ((j) – (l)) 180 with time humidifying/dehumidifying presented at the top right of each plot (particle size: ~ 150 µm (vertical radius) x 500 µm (horizontal radius); humidification experiment: ~ 38 % (room RH)* ***((g))*** *to 90 %* ***((h) and (i))*** *RH, dehumidification experiment: 90 %* ***(j)*** *to ~ 38 % (room RH)* ***((k) and (l))*** *RH).*]

3) Page 13, Figure 7 is mentioned but there is no Figure 7 in the manuscript.

We thank the reviewer for spotting this error. The figure referred to was Fig. 2(i). This has been amended.

4) Images in Figure S9 were collected after the chemicals were deposited onto glass slides. What role does the substrate play in the observed structures in Figure S9? Can you provide scale bars to show the size of the crystals? Would these be relevant for aerosol particles?

We believe that the substrate did not affect the structure formed on the glass slides. The Raman spectrum of the acid-soap complex exhibits the same strong peak at ~ 2887 cm^{-1} as demonstrated in the characterisation section (sect. S1) and in levitated particles of the same mixture (Fig. S4). The formation of the inverse hexagonal phase at high humidity is consistent with a bulk mixture of this organic composition with excess water (see sect. S9), where the sample vial would not have affected the resulting nanostructure. The non-birefringent phase observed after the humidification-dehumidification experiment is likely the inverse micellar phase, observed in levitated particles after humidity changes (see Fig. 1(l) in the main text and Fig. S4(c)). As we are confident that the glass substrate does not affect the observed structures, one can reasonably assume that this is the case for this non-birefringent phase.

This paragraph has been added to the Supporting Information sect. S7:

[We believe that the glass substrate did not affect the structure formed on the glass slides. The Raman spectrum of the acid-soap complex exhibits the same strong peak at ~ 2887 cm^{-1} as demonstrated in the characterisation section (sect. S1) and in levitated particles of the same mixture (Fig. S4). The formation of the inverse hexagonal phase at high humidity is consistent with a bulk mixture of this organic composition with excess water (see sect. S9), where the sample vial would not have affected the resulting nanostructure. The non-birefringent phase observed after the humidification-dehumidification experiment is likely the inverse micellar phase, observed in levitated particles after humidity changes (see Fig. 1(l) in the main text and Fig. S4(c)). As we are confident that the glass substrate does not affect the observed structures, one can reasonably assume that this is the case for this non-birefringent phase.]

Unfortunately, we are unable to provide scale bars for these microscope images. The purpose of these microscope slide experiments was to qualitatively observe nano-structural changes over a much longer time period than is practicable for a beamtime experiment. It is unlikely that large crystallites would form in real aerosol particles. See the response to reviewer 1 (point **2**) in the previous review round where we discuss where acid-soap complexes could exist. Also see the additional discussion added to sect. 4 of the manuscript.

5) In Section 3.3 a discussion is made about the ozonolysis experiments. However, no discussion of the role of ozonolysis products is included. Is it known if the particles loss mass? Is the levitator a closed system, or could semi-volatile products evaporate out of the particle? What effect might this have on the observed rates? The raw data for the C=C peak are not provided, please include these as a supplemental figure.

We thank the reviewer for this comment. A brief description of the ozonolysis was provided at the beginning of section 3.3, however we understand the reviewer's point about not discussing the role of reaction products. Our response is summarised in an extra paragraph at the beginning of section 3.3:

[***Of the reaction products, only nonanal is known to be volatile enough to evaporate appreciably (Vesna et al., 2009). The rest of the ozonolysis products are assumed to remain in the particle phase. There is evidence that particles of oleic acid lose a small proportion of mass during ozonolysis (~ 6 % mass loss after 20 h at 2 ppm), probably due to nonanal loss (Lee et al., 2012). If this is the case, a size change in these particles is likely to be smaller than can be resolved by the X-ray beam in these experiments (~ 15 µm in diameter). Being in an open system with a constant flow of oxygen and ozone, we cannot rule out any mass loss occurring during these experiments. Compared with the effect of particle phase state, we do not expect nonanal loss to impact significantly on the reaction rate.***]

We assume that the reviewer refers to the Raman spectra for the levitated particles. The Raman spectrum before and after ozonolysis is included in the Supporting Information file.

6) In section 3.3.3 it is stated that the weak shoulder at ~2854 cm-1 becomes more defined during oxidation and that this indicates the oleic acid left is not involved in the acid-soap structure. Please include what this shoulder corresponds to, how does the increase in definition show this?

The shoulder at ~2854 cm^{-1} corresponds to the –CH_2 symmetric stretching band in the free oleic acid, as opposed to the asymmetric stretching band of the ordered alkyl chains (~2887 cm^{-1}) (Tandon et al., 2001). There is a molar excess of oleic acid in the mixture, so this is to be expected. As ozonolysis proceeds this shoulder becomes a more defined peak. This area of the Raman spectrum now resembles that of liquid oleic acid. This spectrum is presented in the Supporting Information file along with a comparison with the other components of the mixture. We have amended the text accordingly to define these two bands more clearly.

[*Three key changes in the Raman spectrum are observed during ozonolysis. First, there is a clear shift of the strong acid–soap peak from ~ 2887 cm^{-1}* ***(-CH_2 asymmetric stretching band)*** *to ~ 2897 cm^{-1} accompanied by some broadening.*]

And:

[*Secondly, the weak shoulder at ~ 2854 cm^{-1}* ***(-CH_2 symmetric stretch)*** *becomes a more defined* **peak** *during oxidation.****This region of the Raman spectrum resembles that of oleic acid (Fig. S1(c))****. This is further evidence, in combination with SAXS observations (Fig. 2(j)), that the oleic acid left in the system is not involved in an acid–soap structure after ozonolysis.*]

7) Is there data for the evolution of the Raman spectra during ozonolysis? I could not find this in the supplemental and it would be nice to include, especially given that changes in peaks are discussed.

We thank the reviewer for this comment and we have now included the raw Raman spectra data for ozonolysis of the acid-soap complex in the .zip file accompanying the Supporting Information document. These data backup Fig. 2(j) in the main text and Fig. S6 in the Supporting Information, which show the evolution of the Raman spectrum during ozonolysis.

8) Page 17 discusses inverse micellar vs. micellar. Please provide a little more information on why inverse micelles are expected for this system, even at the highest RH values.

We thank the reviewer for this comment and understand the need for extra clarity on this point. We have added the following to the paragraph discussing this in section 4:

[…~~It is therefore likely that the micellar phase observed in this system has an inverse rather than the normal topology suggested in the preceding atmospheric literature (see Fig. 3 for a cartoon representation).~~ ***The larger hydrophobic tail region of the oleic acid molecule compared with its hydrophilic head drives interface curvature towards water, and therefore the formation of inverse phases, even in excess water. Inverted micellar and other inverted topology phases have been observed for oleic acid – sodium oleate mixtures in excess water (Seddon et al., 1990). Normal topology micelles (polar head groups at the micelle surface) form in systems with larger / charged headgroups, and are only observed within the sodium oleate – oleic acid system at high sodium oleate content (> 80 wt %) (Seddon et al., 1990). It is therefore likely that the micellar phase observed in this system has an inverse rather than normal topology suggested in the preceding atmospheric literature (see Fig. 3 for a cartoon representation).***]

9) The data provided in the figures in the manuscript look like data for a single experiment. Were replicate experiments run for these samples? If so, which ones and how many replicates?

The ozonolysis and humidity experiments were carried out in different particles. The vertical and horizontal radii are quoted in the figure captions for Fig. 1 and 2. We recognise that in the methods section 2.3 the final paragraph makes reference to the size of the particles but does not state the number studied. One particle was studied for the humidity experiment and three for the ozonolysis experiments (including the oleic acid particle) – see Fig. 2(i) in the main text.

The methods section 2.3 has been updated:

[*The levitated particles were analysed on the I22 beamline at the Diamond Light Source (UK). Solid samples, crystallised from ethanolic solutions, were placed into a node of the acoustic levitator. The particles had vertical radii of ~ 90–150 µm and horizontal radii of ~ 500 µm (determined using the attenuation of the X-ray beam).* ***One particle of proxy mixture was levitated subjected to the humidity change experiment. Two particles of the proxy mixture and one pure oleic acid particle were levitated and subjected to ozonolysis experiments.]***

The figure caption for Fig. 2 has also been updated for extra clarity:

[*Figure 2. Vertical scans through the particle showing the effect of ozonolysis on self-assembly. Each row of plots ((a) and (b), (c) and (d), (e) and (f), (g) and (h)) shows simultaneous 1–D SAXS and WAXS scattering patterns vs. distance from the particle centre (measured in µm from what was deemed the particle centre from attenuation data) at* *increasing time exposed to ozone (labelled at the top-right of every WAXS plot). The particle moved and possibly changed shape during the experiment, vertical movement is apparent from the SAXS and WAXS patterns. (i) Comparison of a levitated pure oleic acid droplet vs. a levitated acid–soap complex particle undergoing ozonolysis, measured by Raman microscopy - A longer ozonolysis experiment on a different levitated acid–soap complex particle is also presented,* ***totalling two ozonolysis experiments on this proxy****. (j) Evolution of the Raman spectra between 2750 and 3050 cm^{-1} of a levitated acid–soap complex during ozonolysis. (Particle size: ~ 85 µm (vertical radius) x ~ 500 µm (horizontal radius); [O3] = 51.9 ± 0.5 ppm).*]

An extra sentence has been added to the conclusion which clarifies that the acid-soap complex was also observed on microscope slide deposits:

[*The oleic acid/sodium oleate acid–soap complex has been identified in an unsaturated fatty acid aerosol proxy. Raman and IR spectroscopy, along with SAXS/WAXS, were used to confirm the formation of the acid–soap complex in acoustically levitated particles.* ***The acid–soap complex was also identified by Raman microscopy on microscope slide deposits.*****]**

Additional change:

We noticed a typo on line 300 referring to a “Fig. 6”. We have amended this to read “**Fig. 1(d) and (f)**”.

References

Lee, J. W. L., Carrascón, V., Gallimore, P. J., Fuller, S. J., Björkegren, A., Spring, D. R., Pope, F. D. and Kalberer, M.: The effect of humidity on the ozonolysis of unsaturated compounds in aerosol particles, Phys. Chem. Chem. Phys., 14(22), 8023–8031, doi:10.1039/c2cp24094g, 2012.

Seddon, J. M., Bartle, E. A. and Mingins, J.: Inverse cubic liquid-crystalline phases of phospholipids and related lyotropic systems, J. Phys. Condens. Matter, 2, SA285–SA290, doi:10.1088/0953-8984/2/S/043, 1990.

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