In this study Milsom et al. investigate fatty acid/sugar mixtures using SAXS and Raman microscopy. In particular, films that are mixtures of oleic acid/sodium oleate and fructose are studied as proxies of atmospheric aerosols. The authors explore the different types of nanostructures formed within such internal mixtures as a function of fructose mass fraction and as a function of relative humidity. They also derive hygroscopicity values for the different nanostructures and investigate the reactivity of oleic acid with ozone within these. They find both hygroscopicity and reactivity to be impacted by the nanostructure of the mixtures.

Overall, I feel that the data presented here provides new insights into the physical chemical properties of atmospheric aerosols, a topic that is of interest for the readership of ACP. However, I would like the authors to address the points below, before publication in ACP.

General comments:

G1: Introduction, L91-112: Please elaborate on your introduction and discussion of the possible three-dimensional nanostructures. It would be good to introduce the nanostructures relevant to this study already here along with e.g. a schematic (as you have them already as very small insets in your Fig. 1). This would greatly help the reader to visualize and distinguish the various nanostructures discussed throughout the text. I also encourage the authors to add clear labels and terms to each of the nanostructures and use the same terminology throughout the text, to make it easier for a reader to follow.

G2: Ozonolysis of coated films, L148: The ozone concentrations used herein are not atmospherically relevant, as acknowledged by the authors. It would be good to reiterate this when discussing Fig. 4 and the timescales therein. Given typical tropospheric ozone concentrations are much lower, what would be the typical atmospheric timescales at which the changes in SAXS pattern take place? In this regard, it would be helpful to consider discussing timescales of ozone exposure, to take the ozone concentration into account.

G3: The authors studied three different mixtures of oleic acid: sodium oleate:fructose, different in their mixing ratios, or simpler fructose fractions. I am missing some information whether these ratios were chosen to cover typical mixing ratio ranges found in the atmosphere, or for any specific other reasons? Furthermore, the authors note on L198 that “a set of fructose content-dependent nanostructures are possible”. Neglecting the RH-dependency of (irreversible; L212) phase changes, can the authors comment on the range of fructose fractions for which they expect each of the three nanostructure types depicted in Fig. 1 (Fd3m phases, hexagonal phases, lamellar phases) to be present? I.e. is the Fd3m structure always expected in such mixtures if the fructose mass fraction is larger than 50% wt?

G4: Deriving hygroscopocity values for the different nanostructures is an interesting approach. The κ-values derived are extremely low, indicating a low water uptake capacity of theses nanostructures. For inorganic materials κ-values are often between 0.5 to 1.4, i.e. significantly higher than those observed here. The authors should comment on whether subtle differences in hygroscopicity as observed here (Fig. 3) would still be resolvable in aerosols that are internal mixtures of organic and inorganic material, as is often the case for atmospheric particles? Related, for the potential of a particle to act as a CCN, the inorganic fraction is probably considerably more relevant than the nanostructure of the organic fraction. I encourage the authors to include a discussion on this in their Section “Hygroscopicity of observed nanostructures” and when discussing the impact of nanostructure on hygroscopicity (L466-467) and cloud formation (e.g. L534-535) and climate.

Specific comments:

L75: Please add: DOI: 10.1039/c9cp03731d

L116: Add punctuation: “in Milsom et al. (2021a).”

L117-119: Can you comment if and to what degree esterification of the oleic acid and the methanol can take place during sample preparation, and how this could impact your results?

L120: “oleic acid: sodium oleate:fructose)”

Fig. 1a-c: The meaning of the background colormap is unclear; not specified. Also, consider using non-filled, open markers for “inverse micellar” structures in panel d-f, to allow for easier visual distinction.

L188: add “(water-absorbing substance)” or “(moisture attracting agent)” or similar to clarify the meaning of humectant.

L189: The relation between “more hydrated” and “lower water-surfactant interactant interfacial curvature” warrants some more detailed explanation considering the discussion following in this paragraph.

L212-214: Is the statement of the irreversibility of the phase change generally true, or could this be dependent on the drying rate, when going from high back to low RH?

L220-222: I might be missing something here, but I do not see the coexistence of pink and blue hexagons between 40-60 min in Fig. 1e that you seem to refer to here in the text.

L227: Your Fig. 1d shows red squares (i.e. Fd3m structures) for ~175-200 min, i.e. at RH < 90%, please clarify.

L236: This inverse micellar phase does only seem to appear after around 50 min in Fig. 1e, despite the RH being constant for the previous ~20 min. Why is that?

L297: Add: “The *hygroscopicity of the* disordered…”

Fig. 4: Figure 4 and the discussion of it (L344 onwards) warrant some improvements. I interpret the solid black arrows in Fig. 4 as indicators of general trends, which peaks disappear and appear, but a clear explanation is missing. Consider adding some specific labels to the individual peaks. Also, the same-colored line corresponds to different times during ozonolysis across the different panels, which is a bit misleading. Having a consistent color code (map) throughout the panels could help with that.

L382: I am unclear why you specify “(dry) lamellar” here, since your ozonolysis was only performed under dry conditions (L344). Related, would you expect the stated trend to be different at different RH conditions?

Fig. 6: a-d: An explanation of the color map(s) is missing and should be added. Also, adding horizontal lines to highlight the peaks at 1650 cm^{-1} and 1442 cm^{-1} in panels a and b could help to guide the eye.

L475-480: This is a very interesting finding in my eyes. Is there a way to highlight this aspect already in the abstract of the manuscript? Right now, it is only mentioned here and on L426.

L532: “… with significant impacts on air quality and climate”: I suggest toning this down a little bit here, as your work shows the fundamental effects of nanostructure on water uptake and reactivity. These parameters in turn affect the particles´ impacts on air quality and climate, but an assessment of these effects is not done here.