Response to Reviewer 1 (Reviewer comments in black text):

This manuscript investigates liquid-liquid phase separation in particles containing ammonium sulphate, water and dicarboxylic acids. These particles are used as proxies for atmospheric particles containing inorganic salts, organics, and water. Since the number of studies on liquid-liquid phase separation of atmospherically relevant particles is rather limited, these studies are timely and important. Previous work on the subject mainly focused on particles containing one organic species. This study improves on these previous studies by investigating particles containing three organic species. Included in this manuscript is information on the relative humidities at which liquid-liquid phase separation occurs, information on the mechanism of phase separation, and information on particle morphology after phase separation. The authors have also included thermodynamic calculations to better understand the studied phase transitions.
In short, the manuscript is rich with new information and insight, and I strongly recommend it for publication. Listed below are several comments that should be addressed adequately before publication.

We thank Reviewer 1 for the careful reading of the manuscript and the helpful suggestions and comments. Below are detailed answers to the reviewer comments with the locations of the incorporated changes in the revised manuscript.

1. Page 29146, line 5-12. Here I think the authors are implying (likely inadvertently) that crystallization of the organic substance may have occurred in previous studies. This is a minor comment, but I would not criticize some of the previous studies since often care was taken to pick systems where the organics didn't crystallize (for example Ciobanu et al. 2009). I would argue things differently. Studies on more complex organic mixtures are needed since atmospheric aerosols are more complex.
We have reformulated the paragraph.

2. Page 29150, line 15 to 20. At this point it was not clear why calculations were necessary on both 5-component systems and 3-component systems. It may be useful to the reader to add this information at this point in the manuscript.
We have added the following sentences to the text at page 29150, line 22: "Such comparisons of the 5-component with 3-component systems allow an evaluation of the influence of using a mixture of three structural isomers for the organic fraction versus only one corresponding organic compound in AIOMFAC group-contribution model calculations. Furthermore, the ternary systems are of

use as they allow a mathematically simpler computation of metastable and unstable regions of the phase diagram employing the algorithm of Zuend et al.(2010), as detailed in Section 3.5."

3. Page 29157, line 25-30; Page 29158, line 1-5; and Figure 5. The authors suggest that the needles are composed of crystalline ammonium sulphate. These needles appear to grow out of the organic rich phase. Is it possible that the needles consist of crystalline organic material? Also, in these experiments, did nucleation start in an aqueous AS inclusion?

Pure C6 organic particles do not effloresce without AS even down to 0 %RH meaning that AS is the trigger for the crystallization of the C6/AS/H_2O particle. In Fig. 5, the efflorescence started from the rim of the particle at 35 %RH and then the needles grew. The needles mostly consist of AS because they deliquesce at the DRH of AS. Some solid material remains above DRH of AS indicating that also a part of the organic material has effloresced. We discuss this now in more detail in the manuscript.

4. Page 29158, line 24-26. In the experiments where LLPS was not observed, is it possible that LLPS occurred, but the phase separation was not detected with the optical technique? For example, could AS inclusions spread out at the bottom of the droplet and not be detected?

It could be possible that LLPS occurred but the phase separation was not detected with the optical technique if the AS spreads out at the bottom of the droplet. However, in this case the AS inclusions should have become visible when AS effloresced. In the other AS dry mass fraction ranges we saw the AS inclusions even though they were small (see example Fig. 5). From the point of view of interfacial tensions, we do not expect that AS spreads out on the hydrophobically coated substrate.

5. Page 29160, line 29. Would it be clearer and still accurate to say that spinodal curves were calculated for 3-component particles rather than 5-component particles due to the computation expense of calculating spinodal curves for 5-component particles.

Computations of spinodal curves are simpler for 3-component as compared to 5-component mixtures because of simpler mathematical expressions describing the conditions of instability. The computational demands are not a concern here. The sentence in the manuscript has been changed to reflect this: "On the basis of a mathematically much simpler computation of phase stabilities in case of only three thermodynamically independent components, the limit of stability between metastable and unstable one-phase states, the spinodal curves, were calculated only in case of the ternary systems using the method described by Zuend et al. (2010)."

6. Page 29162, line 15. Smaller than what?

The sentence has been changed to read as follows: “These differences are considerably smaller than in the case of the C5/AS/H_2O system. Regarding the group-contribution concept used within AIOMFAC to represent organic molecules and their interactions with other species/functional groups, it is not surprising that there are some differences between model predictions and measurements.”

7. Page 29163, line 14-25. I don’t completely understand this section. The authors state “we do not have a regular LLPS in this composition range but a more structured phase with a fixed stoichiometry”. Later on they state “leading to a different mixture composition and a LLPS in a relatively narrow AS mass fraction range, partly overlapping with the coexistence curve at higher AS mass fractions”. The two statements above sound inconsistent. Are they referring to a crystalline phase? It would be good to add some references to show that this type of behaviour has been observed before.

We tried to find literature that would give us a good explanation for the complex phase behavior of the C6/AS/H_2O system but we were not successful. What we offer on page 29163 is rather a discussion than an explanation of this behavior. We have reformulated this section to avoid the alleged inconsistency of the two sentences. We exclude the presence of a crystalline phase because the inclusions are spherical and seem to be liquid.

8. Page 29165, line 29. I assume “wt %” should be “wt % AS”?

It is wt% (C6+AS) in water as weighted in during solution preparation. We have added this information to the text.

9. Page 29167, line 25-27. “Figure 11 gives the position of the organic components of alcohol and polyol/AS/water and carboxylic and dicarboxylic acid/AS/water system from literature (see table 2).” Table 2 also includes ethers, esters and aromatics. Does Figure 11 include data for these functional groups as well, or have they been excluded from the figure?

Figure 11 includes all data from Table 2. We have made this clear now by changing the figure accordingly.

10. Page 29169, line 24-26 (as well as other places in the manuscript). The authors conclude from their studies that a core-shell structure and partially engulfed configuration might very likely be present in the troposphere. Can the authors rule out that the hydrophobic surface doesn’t affect/change the morphology

of the particles in their experiments? In other words, if someone repeated these studies with suspended particles, would the authors expect the same result? This should be discussed in the manuscript.
This is a good point that we will address in the revised manuscript in the conclusion.

11. Page 29159, line 26. "... spinodal decomposition occurs barrier-free at the border to the unstable region." Do the authors mean that when spinodal decomposition occurs at the border to the unstable region, it occurs without a kinetic barrier? Maybe rewrite this sentence to improve clarity.
We have revised the sentence.